Activation of C–O and C–N Bonds in Allylic Alcohols and Amines by Palladium Complexes Promoted by CO_2. Synthetic Applications to Allylation of Nucleophiles, Carbonylation, and Allylamine Disproportionation

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The direct activation of the C–O bonds in allylic alcohols catalyzed by palladium complexes has been accelerated by carrying out the reactions under CO_2. On reaction with diethylamine, allyl alcohol can be converted into *N,N*-diethylallylamine in the presence of palladium complexes at room temperature under normal pressure of carbon dioxide. Allylation of various carbon nucleophiles such as β-keto esters and β-diketones can be achieved by using allylic alcohols directly in the presence of palladium complexes and CO_2. Direct carbonylation of allylic alcohols into unsaturated carboxylic acids can be catalyzed by palladium complexes under the pressure of CO and CO_2. Disproportionation of diallylamine into triallylamine and allylamine is also catalyzed by palladium complexes in the presence of CO_2. On the basis of studies on the behavior of η^3-allylpalladium hydrogencarbonate complexes with the nucleophiles, mechanisms are proposed to account for the palladium-catalyzed allylation processes influenced by CO_2.

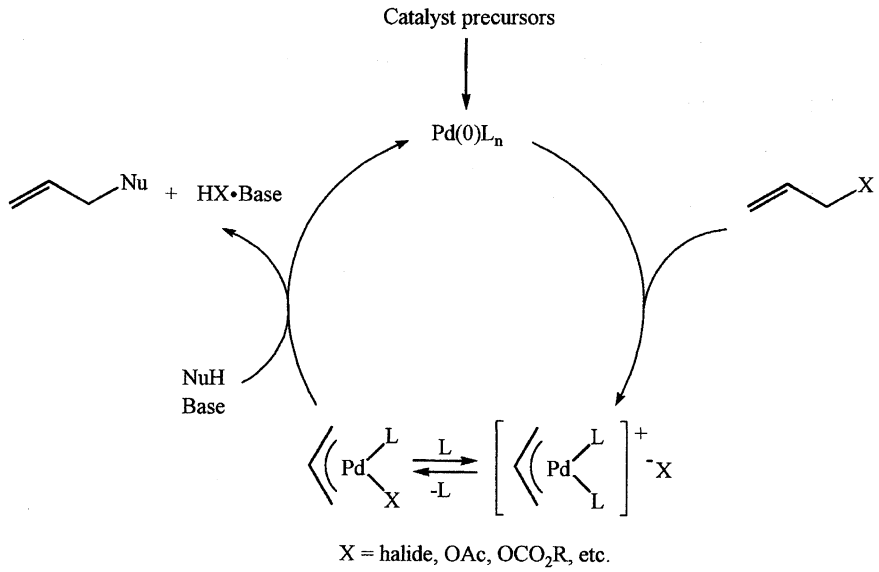
Allylation of carbon-, nitrogen-, and oxygen-nucleophiles catalyzed by palladium complexes has been widely applied to organic synthesis.[1] The processes have been established to proceed by attack of nucleophiles on intermediate η^3-allylpalladium(II) complexes generated by oxidative addition of allylic compounds including allylic halides, acetates, and carbonates to a Pd(0) complex (Scheme 1). Although oxidative addition of allylic halides to Pd(0) complexes involving allyl-halide bond cleavage is a facile process, the halide eventually should be removed as a salt. Thus, from an environmental point of view, realization of a halide-free process is very desirable. Palladium-catalyzed processes involving C–O bond cleavage in allylic compounds have been developed, notably by Tsuji, Trost and their co-workers. Particularly the processes utilizing allylic carbonates as the substrates provide considerable advantages over the process utilizing allylic acetate in achieving the catalytic reactions under mild conditions in the absence of strong bases.[2] However, allylic carbonates have to be first prepared using allylic alcohols and chloroformates. Thus, the processes starting from the allylic carbonates are not really halide-free. For achieving the Pd-catalyzed C–O bond cleavage of allylic alcohols, various other processes to facilitate the bond cleavage have been examined.[3] These processes include conversion of allylic alcohols into esters of As_2O_3,[4] of B_2O_3,[5] or employment of a Lewis acid such as $BF_3 \cdot Et_2O$,[6] or use of other reagents such as $SnCl_2$,[7] or BuLi–BPh_3,[8] or PPh_3–DEAD.[9]

However, there have been only limited and sporadic reports dealing with the direct cleavage of the C–O bond in allylic alcohols on interaction with a transition metal complex.[10] Precedents of successful applications of a process using allylic alcohols directly to catalytic processes are even more limited.

This paper reports our attempts and some successful applications of a process involving the C–O bond cleavage with direct use of allylic alcohols catalyzed by palladium complexes. The direct C–O bond cleavage is applicable to allylation of secondary amines, allylation of carbon-nucleophiles, and carbonylation of allylic alcohols into unsaturated carboxylic acids. In these catalytic reactions, we found pronounced effects of carbon dioxide to accelerate the catalytic processes.[11] The effect of addition of carbon dioxide to promote the palladium-catalyzed allyl–OH bond cleavage revealed in the present study may have potential applications to provide methodologies for using allylic alcohols directly in organic syntheses. The acceleration effect of CO_2 in the presence of a palladium catalyst was also found in activation of the C–N bond in diallylamine to cause catalytic disproportionation reactions of diallylamine to triallylamine and allylamine.

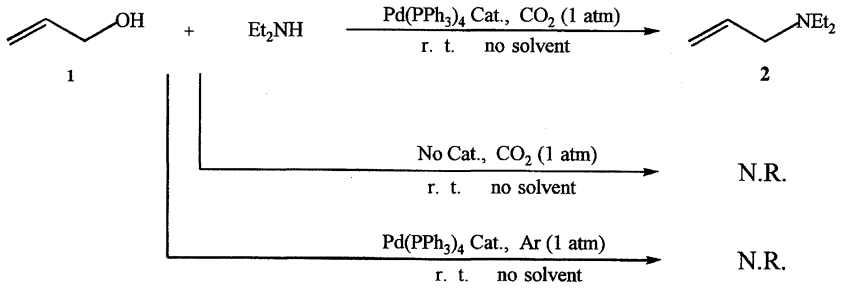
Results

1. Allylation of Secondary Amines with Allylic Alcohols. We have first observed a pronounced acceleration effect of CO_2 in allylation of secondary amines with allyl alcohol. As shown in Scheme 2, treatment of allyl alcohol **1** with diethylamine in the presence of a catalytic amount of $Pd(PPh_3)_4$ (0.58 mol%/allyl alcohol) under an atmosphere of CO_2 (with a rubber balloon) at room temperature gave *N,N*-diethylallylamine **2** in 70—80% yields without solvent and over 96% yield in acetone. The process is very simple and conditions are very mild when the reaction is carried



X = halide, OAc, OCO_2R, etc.

Scheme 1.



Scheme 2.

out in acetone at room temperature. In previous examples reporting the palladium- or nickel-catalyzed direct allylation of amines using allylic alcohols without carbon dioxide, a much higher temperature was necessary to achieve the allylation reactions.[12] No allyl diethylcarbamate was produced in the reaction.[13] Use of molecular sieves did not affect the product yield. The reaction of allyl alcohol with diethylamine without the palladium catalyst under CO_2 atmosphere at room temperature afforded no *N*,*N*-diethylallylamine. The reaction between allyl alcohol and *N*,*N*-diethylamine with the same catalyst carried out at room temperature under argon atmosphere instead of carbon dioxide afforded no diethylallylamine either. The catalytic reaction is slow, but turnover numbers (TON) over 100 can be readily achieved when the reaction is carried out in appropriate solvents (acetone or CH_2Cl_2). Proper choice of the solvent is very important for achieving the high turnovers and the solubility of the catalyst in the solvent seems to play an important role in determining the reaction rate.

The reaction is not restricted to the simple allyl alcohol; other allylic alcohols substituted with an alkyl group at 2- or 3-position of 2-propen-1-ol can be converted into allylic diethylamines in low to modest yields (see Experimental). For an allylic alcohol such as 3-methyl-2-buten-1-ol (prenol) containing two methyl groups attached at the olefinic moiety, the reaction is severely hindered. The hindrance of the reaction was also observed for 2-isopropyl-2-propen-1-ol, where the olefinic carbon is substituted at the 2-position with a bulky isopropyl group. Other amines than diethylamine such as morpholine can also be used to produce allylic amines.

Various combinations of the palladium complexes with tertiary phosphines were examined, as shown in Table 1. The presence of a tertiary phosphine is essential for the catalytic allylation reaction to proceed. $Pd(acac)_2$ is considered to be reduced in the system to a catalytically active Pd(0) species, whereas $PdCl_2(PPh_3)_2$ proved to be inactive. Among the tertiary phosphines examined, triphenylphosphine was found most suitable for the reaction when four equivalents of the phosphine per palladium were used in combination with a complex, $Pd(acac)_2$ or $Pd(dba)_2$. The zerovalent complex $Pd(PPh_3)_4$ also gave the allylation product in a good yield. This may not necessarily mean that active species is coordinated with four phosphine ligands, since it is known that $Pd(PPh_3)_4$ is dissociated in solution with liberation of one to two triphenylphosphine ligands. A bidentate phosphine such as 1,2-bis(diphenylphosphino)ethane (DPPE) can be also used, but addition of two equivalents of DPPE hindered the reaction.

2. Allylation of Carbon Nucleophiles with Allylic Alcohols. After we found a simple method of allylating amines with allylic alcohols in the presence of a palladium catalyst and CO_2, we examined if the process can be applied

Table 1. Reaction of Allyl Alcohol with Diethylamine under CO_2 under Various Conditions[a)]

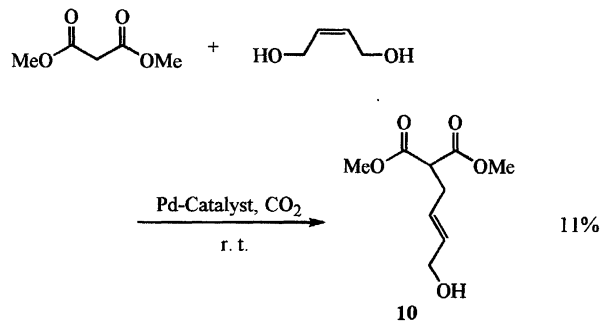
Entry	Pd-catalyst[b)]	Phosphine[c)]	Equiv[d)]	Yield/%[e)]
1	$Pd(acac)_2$	—		0
2		PPh_3	1.0	Trace
3		PPh_3	2.0	9
4		PPh_3	4.0	78
5		PPh_2Me	4.0	60
6		$PPhMe_2$	4.0	24
7		PMe_3	4.0	2
8	$Pd(dba)_2$	—		0
9		PPh_3	1.0	0
10		PPh_3	2.0	3
11		PPh_3	4.0	23
12		DPPE	1.0	26
13		DPPE	2.0	4
14	$PdCl_2(PPh_3)_2$	—		0
15	$Pd(PPh_3)_4$	—		88

a) Pd-catalyst, 0.58 mol%; solvent, CH_2Cl_2; temperature, room temp; P_{CO_2} = 1 atm; Time > 17 h. b) acac = acetylacetonato; dba = dibenzylideneacetone. c) DPPE = 1,2-bis(diphenylphosphino)ethane; d) Equivalent to Pd. e) Determined by GLC.

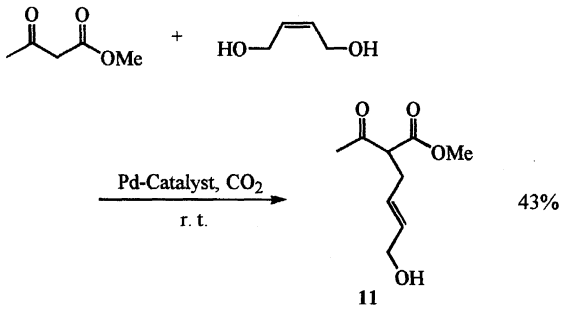
to reactions with carbon nucleophiles such as β-diketones and β-keto esters having active hydrogens. Tsuji and others have extensively explored the utility of the allylic carbonates that are susceptible to cleavage at the allylic-oxygen bond to afford η^3-allylpalladium intermediates with a carbonate anion.[2)] Since the carbonate moiety is readily decarboxylated to liberate a potent alkoxide ion that abstracts a hydrogen atom from active hydrogen compounds, the process proved to be very useful for carrying out the allylation reactions without using a strong base.

Table 2 summarizes the results of allylation of active methylene compounds (**3**–**5**) with allylic alcohols carried out at room temperature with or without solvent. No allylation proceeded without $Pd(PPh_3)_4$ (Entry 7) or without CO_2 (Entries 8 and 11). The yield of the allylated product was low at normal pressure of carbon dioxide (Entries 1 and 10), while performing the reaction under 20 to 30 atm of CO_2 pressure improved the yields considerably (Entries 2, 6, and 9). Employment of higher temperature (ca. 70 °C) under CO_2 did not improve the yields. While substitution of the allylic moiety with a methyl group at the 2-position of allyl alcohol does not seriously hinder the reaction (Entry 3), substitution with two methyl groups at the 3-position in the allyl alcohol (Entry 4) or the substitution with the bulky isopropyl group at the 2-position of allyl alcohol (Entry 5) severely hinders the reaction. It should be noted here that by using greater amounts of the palladium catalysts and by performing the reaction at higher temperature, allylation was reported to have been achieved without CO_2.[14)]

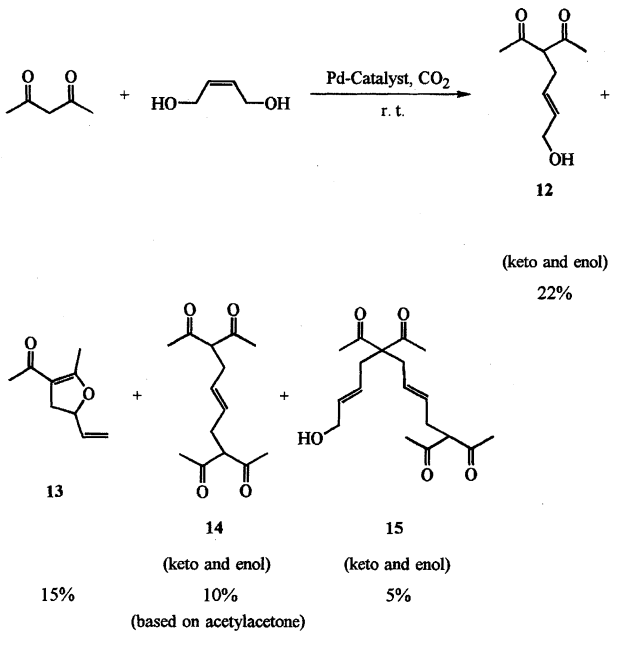
As extension of the newly found CO_2-promoted direct allylation with allylic alcohols, we examined if a bifunctional allylic alcohol, *cis*-2-butene-1,4-diol, will undergo the similar allylation on treatment with active methylene compounds in the presence of a palladium catalyst ($Pd(PPh_3)_4$, 1.0 mol%) under CO_2 atmosphere (Eqs. 1, 2, and 3).



(1)



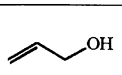
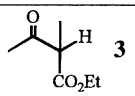
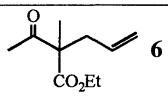
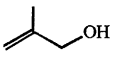
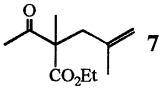
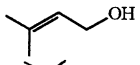
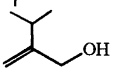
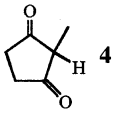
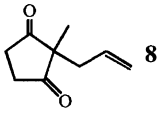
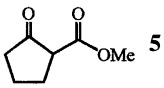
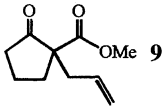
(2)



(3)

Reactions of dimethyl malonate and methyl acetoacetate with *cis*-2-butene-1,4-diol gave the allylation products **10** and **11** where the diol reacted at the one terminal. The allylation yield to give **11** was higher for methyl acetoacetate than for dimethyl malonate, suggesting that the more acidic β-keto ester is more susceptible to the allylation than the less acidic methyl malonate. On the other hand, acetylacetone having the two acidic hydrogens of higher acidity underwent further allylations to afford a complicated product mixture, as shown

Table 2. Pd-Catalyzed Reactions of Allylic Alcohols with Active Methylene Compounds under CO_2[a)]

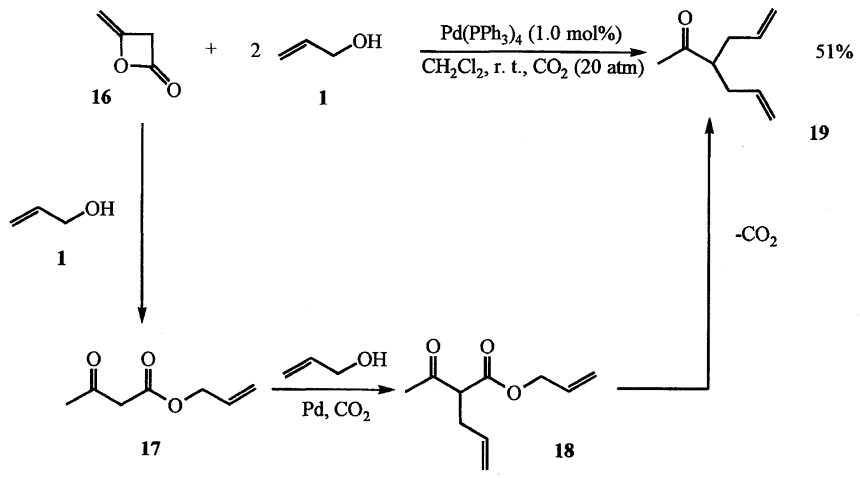
Entry	Allylic alcohol	Active methylene compound	Solvent	CO_2 atm	$Pd(PPh_3)_4$ mol%	Time h	Product	Yield %
1	 **1**	 **3**	None	1	0.58	45	 **6**	22[c)]
2	**1**	**3**	None	30	0.58	24	**6**	77
3		**3**	None	30	1.0	25	 **7**	57
4		**3**	None	30	1.0	18	—	0[c)]
5		**3**	None	30	1.0	49	—	0[c)]
6	**1**	 **4**	CH_2Cl_2	20	2.0	24	 **8**	65
7	**1**	**4**	CH_2Cl_2	20	—	36	—	0[c)]
8	**1**	**4**	CH_2Cl_2	0[b)]	2.0	36	—	0[c)]
9	**1**	 **5**	None	20	1.0	18	 **9**	66
10	**1**	**5**	None	1	1.0	20	**9**	13[c)]
11	**1**	**5**	None	0[b)]	1.0	19	—	0[c)]

a) All the reactions were conducted at room temperature. b) Performed under atmosphere of argon. c) The starting materials were recovered.

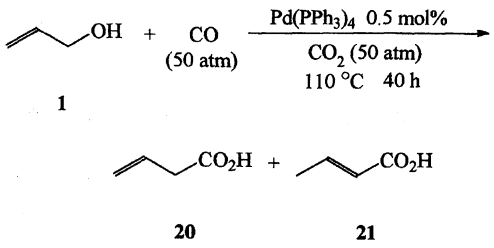
in Eq. 3.

For exploring the applicability of the present process, the reaction of allyl alcohol with diketene **16** (precursor for an ester of acetoacetic acid) was examined. Diallylation product **19** was isolated by carrying out the reaction at room temperature under 40 atm of CO_2 with $Pd(PPh_3)_4$ as the catalyst (Scheme 3). The reaction can take place without adding CO_2 (diketene itself is known to react with a Ni(0) complex to afford CO_2[15)]) but the yield of the allylation product was low (10%). Scheme 3 shows a likely reaction course involving the formation of an intermediate **17** by cleavage of the C–O bond in **16** and the subsequent allylation of the ester at the active methylene group with allyl alcohol to give **18**, followed by decarboxylation to give **19**.[16)]

3. Palladium-Catalyzed Carbonylation of Allylic Alcohols in the Presence of CO_2. Over three decades ago, Tsuji and co-workers reported palladium-catalyzed carbonylation of allylic compounds including allylic halides, allylic acetate, and allylic alcohols.[17)] He has further explored the palladium-catalyzed carbonylation of allyl carbonates and succeeded in obtaining esters of 3-butenoic acid.[18)] We have now found that allyl alcohol can be carbonylated directly to give butenoic acids **20** and **21** when the reaction is performed in the presence of carbon dioxide (Eq. 4).[19)]



Scheme 3.



(4)

Table 3 shows the results with a variety of catalyst systems and solvents. The yields of the butenoic acids were influenced by the nature of the solvents and also by the kind and quantities of the tertiary phosphines employed. The highest yield was obtained in dioxane with $Pd(PPh_3)_4$ as a catalyst. Use of four equivalents of PPh_3 with $Pd(dba)_2$ gave better yields of butenoic acids compared with cases where less amounts of PPh_3 were used. Other bidentate tertiary phosphines can be used with somewhat less effectiveness than triphenylphosphine. 2-Butenoic acid proved to be the main product in most cases, while 3-butenoic acid was produced predominantly when the conversion was low.

Figure 1 shows the time-conversion curves in the reactions of allyl alcohol with CO performed in the presence and absence of CO_2. The reaction is slow when 0.5 mol% of $Pd(PPh_3)_4$ was used, but fast conversion of allyl alcohol into butenoic acids can be achieved when a higher concentration of the catalyst $Pd(PPh_3)_4$ (5.0 mol%) was used in the presence of CO_2. As shown in Table 3, the promotion

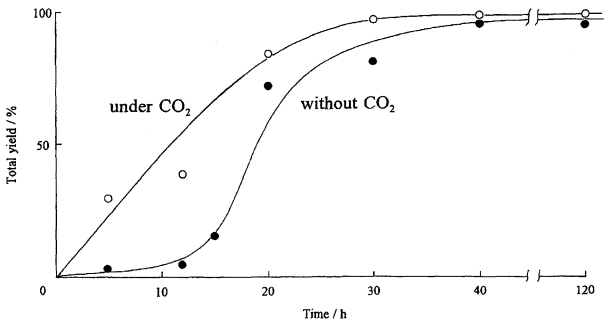
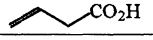
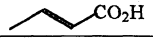


Fig. 1. Time-conversion curves of the reactions of allyl alcohol with CO under CO_2 (○) and without CO_2 (●) to butenoic acids (Eq. 4). Reaction conditions are as follows: allyl alcohol, 20.0 mmol; palladium- catalyst, $Pd(PPh_3)_4$ (0.5 mol%); temperature, 110 °C; P_{CO_2}=50 atm; P_{CO}=50 atm; solvent, dioxane.

effect of CO_2 on conversion of allyl alcohol can be clearly seen in DMF. In the presence of CO_2, a 94% total yield of 2- and 3-butenoic acids can be achieved in DMF (Entry 6 in Table 3), whereas only traces of butenoic acids were formed when the reaction was carried out under 80 atm of CO without CO_2 (Entry 7). However, Fig. 1 shows that, after a prolonged treatment of the reaction mixture at 110 °C under CO, the carbonylation took place even without CO_2. In this case we observed a marked increase in the yield after an induction period of 12 h. A possible reason for the later rate enhancement is the acceleration effect by butenoic acids

Table 3. Reactions of Allyl Alcohol with CO under CO_2 under Various Conditions[a)]

Entry	Pd-catalyst	Phosphine (Equiv to Pd)	Solvent	Ratio			Total yield
					:		%
1	$Pd(PPh_3)_4$	—	Toluene	7	:	93	20
2		—	*o*-xylene	10	:	90	67
3		—	Dioxane	8	:	92	99
4		—	DMI	21	:	79	41
5		—	NMP	7	:	93	31
6		—	DMF	5	:	95	94
7		—	DMF	—	:	—	Trace[b)]
8	$Pd(dba)_2$	—	Dioxane	—	:	—	Trace
9		PPh_3(4)	Dioxane	7	:	93	63
10		DPPM(2)[c)]	Dioxane	94	:	6	8
11		DPPE(2)	Dioxane	14	:	86	44
12		DPPP(2)[d)]	Dioxane	12	:	88	14
13		DPPB(2)[e)]	Dioxane	10	:	90	53
14	$Pd(acac)_2$	—	Dioxane	—	:	—	Trace
15		PPh_3(2)	Dioxane	91	:	9	8
16		PPh_3(4)	Dioxane	5	:	95	55
17	$Pd(OAc)_2$	—	Dioxane	—	:	—	Trace
18		PPh_3(4)	Dioxane	9	:	91	65
19	$PdCl_2(PPh_3)_2$	—	Dioxane	91	:	9	24
20	$PdCl_2(PMePh_2)_2$	—	Dioxane	—	:	—	N.R.

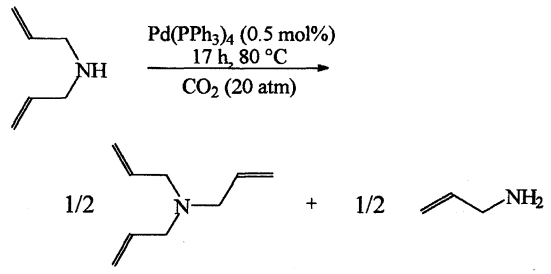
a) Allyl alcohol, 10 mmol; solvent, 10 mL; Pd-catalyst, 0.5 mol%; P_{CO}=50 atm; P_{CO_2}=50 atm; temperature, 110 °C; time, 40 h. b) P_{CO_2}=0 atm, P_{CO}=80 atm. c) 1,2-Bis(diphenylphosphino)methane. d) 1,3-Bis(diphenylphosphino)propane. e) 1,4-Bis(diphenylphosphino)butane.

formed. The acids may interact with allyl alcohol and the interaction may facilitate the allyl–O bond cleavage by the palladium catalyst. In fact, addition of acetic acid (0.4 mM) to the system caused disappearance of the induction period. However, the yields of butenoic acids did not increase as in the reaction performed in the presence of CO_2 and did not exceed 60%. Use of *p*-toluenesulfonic acid deactivated the catalyst system giving palladium black. Suspecting that the possible cause of the acceleration effect of CO_2 may be due to a hydrogencarbonate ion formed, we examined reaction systems containing carbonates such as $NaHCO_3$, Na_2CO_3, and $KHCO_3$ under biphasic conditions with a solvent mixture of dioxane–water to find that the yields did not exceed 50%.

In Table 4 are shown the results of carbonylation with a variety of allylic alcohols having substituents at 1-, 2-, or 3-positions.

Introduction of a methyl group at the 1- or 3-position in allyl alcohol causes lowering in the conversion, whereas substitution of the methyl, isopropyl, or phenyl group at the 2-position does not seriously hinder the reaction. The results imply the operation of an S_N2' mechanism in the oxidative addition of allylic alcohols with a Pd(0) species in the catalytic process. The fact that an almost identical *E*/*Z* isomer ratio of 3-pentenoic acid **22** was obtained in reactions of both 1- and 3-methyl-substituted 2-propen-1-ols with CO (Entries 2 and 3 in Table 4) is consistent with a mechanism proceeding through the η^3-allylpalladium intermediates.

4. Disproportionation of Diallylamine to Triallylamine and Allylamine. On finding the catalytic cleavage of the C–O bond in allylic alcohols promoted by CO_2 we have further examined if a similar cleavage might be observed with the corresponding compounds having the C–N bonds in diallylamine. In fact, the palladium-catalyzed disproportionation reaction of diallylamine to triallylamine and allylamine was found to proceed at 80 °C (Eq. 5).



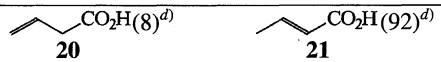
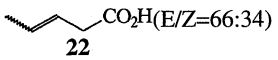
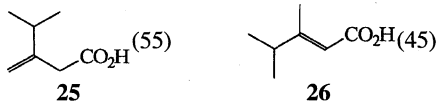
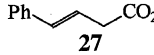
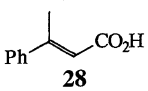
(5)

Again the pronounced effect of CO_2 on the reaction is evident (Fig. 2). Although the reaction is slow, about 80% of diallylamine was converted into triallylamine and allylamine in 15 h when the reaction is performed under the pressure of 20 atm of CO_2. The yields of the disproportionation products in the reaction of diallylamine with $Pd(PPh_3)_4$ under argon after the same intervals were negligible (Fig. 2).

Figure 3 shows the effect of the CO_2 pressure on the yield of triallylamine. Application of pressure is favorable for the reaction up to 20 atm, beyond which higher pressure showed no effect to increase the product yield.

Figure 4 shows the effect of temperature on the yield of triallylamine. When the reaction was carried out under CO_2, a pronounced effect of temperature on the product yield was observed. The yield increased sharply by heating the system under CO_2 over 60 °C, while under argon acceleration of the

Table 4. Reactions of Allylic Alcohols with CO[a)]

Entry	Allylic alcohol	Products(Ratio)[b)]	Total Yield/%[c)]
1		 **20** **21**	99[d)]
2		 **22**	60
3		**22**(E/Z=68:32)	20[e)]
4		 **23** **24**	72
5		—	—[e)]
6		 **25** **26**	69
7		 **27**	33[e)]
8[f)]		 **28**	73

a) Allylic alcohol, 20.0 mmol; catalyst, $Pd(PPh_3)_4$ (0.5 mol%); solvent, dioxane; temperature, 110 °C; P_{CO_2}/P_{CO}=50/50 (atm/atm); time, 40 h. b) Determined by NMR. c) Isolated yield unless otherwise noted. d) Determined by GLC. e) The starting material was recovered. The yield was determined by NMR. f) The allylic alcohol, 1.03 mmol; Catalyst, $Pd(PPh_3)_4$ (4.9 mol%).

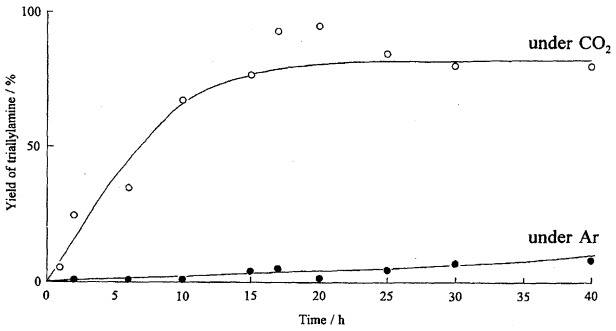


Fig. 2. Effect of CO_2 on the disproportionation reactions of diallylamine under CO_2 (○) and under argon (●). Reaction conditions are as follows: diallylamine=20.0 mmol, Pd-$(PPh_3)_4$=0.5 mol%, temperature=80 °C, CO_2=20 atm (or Ar=1 atm).

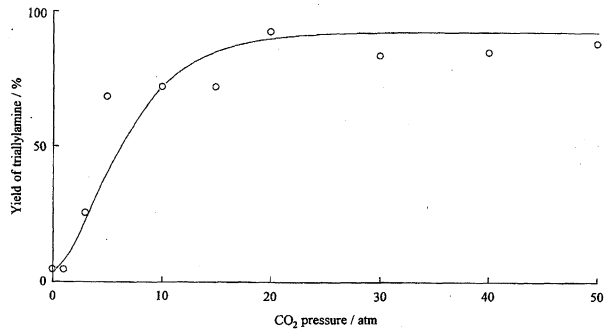


Fig. 3. Effect of CO_2 pressure on the yield of triallylamine formed in disproportionation reactions of diallylamine. Reaction conditions are as follows: diallylamine, 20.0 mmol; palladium-catalyst, $Pd(PPh_3)_4$ (0.5 mol%); temperature, 80 °C; time, 17 h.

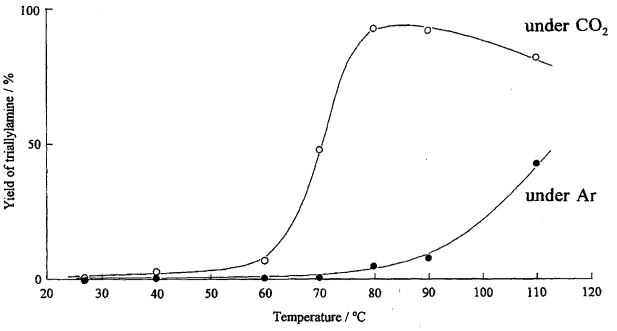


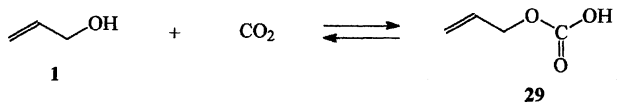
Fig. 4. Effect of temperature on the yield of triallylamine formed in disproportionation reactions of diallylamine under CO_2 (○) and under argon (●). Reaction conditions are as follows: diallylamine, 20.0 mmol; palladium-catalyst, $Pd(PPh_3)_4$ (0.10 mmol); P_{CO_2}=20 atm (or P_{Ar}=1 atm); time, 17 h.

reaction was observed only by heating the system over 100 °C.

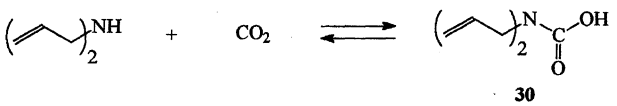
There are some precedents of the C–N bond cleavage in allylic amines catalyzed by palladium complexes.[20] However, no mention has been made on the effect of CO_2 on the C–N bond cleavage.

Discussion

Mechanisms of the Palladium-Catalyzed C–O and C–N Bond Cleavage in Allylic Alcohols and Amines Promoted by CO_2. The previously reported fundamental studies on the reactions of allylic compounds with palladium complexes[3] make it probable that the present reactions proceed through the common η^3-allylpalladium(II) intermediates and their subsequent reactions. A probable cause for the promotion effect of CO_2 on the C–O bond cleavage in allyl alcohol is the formation of allyl hydrogencarbonate **29** on interaction of allyl alcohol with CO_2 (Eq. 6).



1 **29** (6)



30 (7)

Our attempts to prove the formation of allyl hydrogencarbonate **29** on interaction of allyl alcohol with CO_2 by means of proton NMR were unsuccessful, even under a pressure of 10 atm. Nevertheless, formation of a minor amount of the allyl hydrogencarbonate **29** which may escape the identification by NMR in the reaction system can not be excluded. The allyl hydrogencarbonate may have a considerably different character from that of the allyl alcohol to make the allyl–O bond more susceptible to cleavage on interaction with a Pd(0) species by an S_N2' mechanism. The acceleration effect of CO_2 on the disproportionation of diallylamine may be likewise accounted for by assuming the formation of diallylcarbamic acid **30** by interaction of diallylamine with CO_2 (Eq. 7). The diallylcarbamic acid may further form its salt on interaction with diallylamine. The effects of solvents on the catalytic reactions may be related with the shift of the equilibria in Eqs. 6 and 7.

In our previous studies on the reactions of dimethylpalladium complexes having tertiary phosphine ligands, we have observed that the dimethylpalladium complexes react with alcohols and amines *only* in the presence of CO_2 to give methylpalladium alkyl carbonate and alkyl carbamate complexes.[21] We have ascribed the reason for the requirement of CO_2 to the formation of reactive alkyl hydrogencarbonates and carbamic acids produced by interaction of the alcohols and amines with CO_2. It is reasonable to assume the similar formation of allyl hydrogencarbonates and of diallylcarbamic acid and that the reactivities of theses acids differ from those of the starting allylic alcohols and diallylamine.

We have previously observed that the tertiary phosphine-coordinated Pd(0) complexes, derived from diethylpalladium(II) complexes on thermolysis, react with allyl alkyl carbonates to afford the cationic η^3-allylpalladium(II) complexes having the alkyl carbonate counter anion.[22] The

ionic complex with the alkyl carbonate counter anion proved to be very moisture-sensitive and the alkyl carbonate is readily hydrolyzed, affording cationic η^3-allylpalladium complex **31** having a hydrogen carbonate anion (Scheme 4). Treatment of these cationic η^3-allylpalladium(II) complexes with active methylene compounds liberated the allylated products of these nucleophiles.

To confirm the reactivity of the cationic η^3-allylpalladium-(II) complexes with nucleophiles, we have prepared the η^3-allylpalladium complexes with the hydrogencarbonate as the counteranion (**31a** and **31b**) and examined their reactions with active methylene compounds and diethylamine (Eq. 8 and Table 5).

Table 5 shows that the cationic η^3-allylpalladium complexes **31** readily react with carbon nucleophiles to liberate the allylated products of the nucleophiles in good yields. No base had to be added to afford the allylated nucleophiles.

The yield of the reaction product of the η^3-allylpalladium complex **31b** with diethylamine was not so high as with the carbon nucleophiles but formation of allylamine was also established (Entry 3, Table 5). These results support the assumed reaction course involving the oxidative addition of allyl hydrogencarbonate to a Pd(0) complex to form a η^3-allylpalladium complex having the hydrogencarbonate anion and the subsequent attack of nucleophiles on the η^3-allyl ligand to liberate the allylated nucleophiles (Scheme 5).

In the actual catalytic systems, the hydrogencarbonate anion and OH anion derived by decarboxylation thereof may be

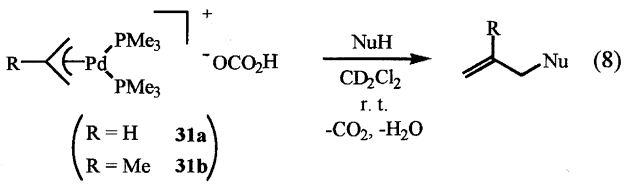


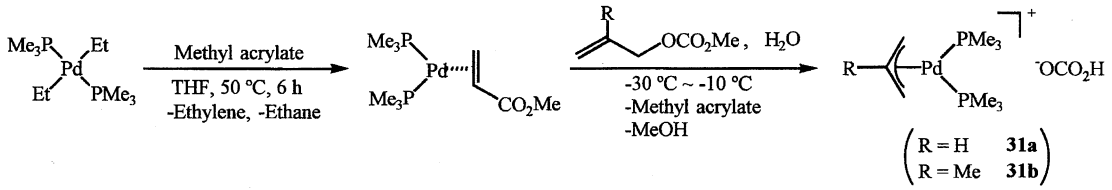
Table 5. Reactions of $[Pd\{\eta^3\text{-}CH_2C(R)CH_2\}(PMe_3)_2](OCO_2H)$ with Various Nucleophiles

Entry	R	Nucleophile[a)]	Yield/%[b)]
1	H	**3**	95
2	Me	**3**	85
3	Me	Et_2NH	21
4	H	**5**	96
5	Me	**5**	92

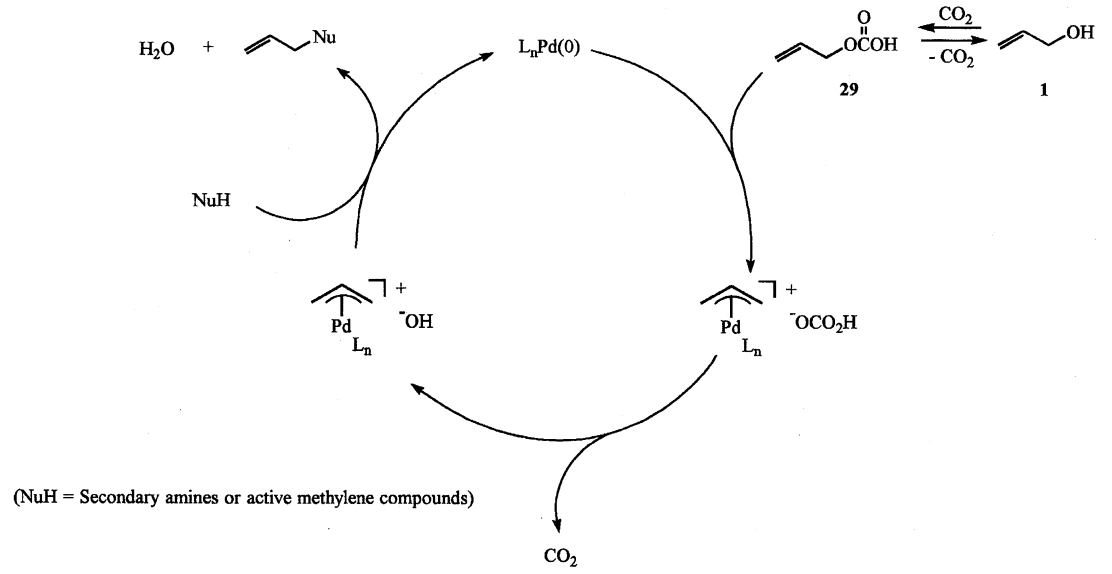
a) For compounds **3** and **5**, see Table 2. b) Yield of allylated nucleophiles determined by NMR.

in outer or inner coordination sphere of palladium depending on the solvent used and the reaction conditions. When the hydrogencarbonate anion is decarboxylated, it may release the OH anion as a strong base that is capable to abstract a proton from the amine or from active methylene compounds to liberate a nucleophile attacking the allyl ligand.

For the catalytic carbonylation of allylic alcohols in the presence of CO_2, formation of η^3-allylpalladium hydrogencarbonates from a Pd(0) complex, allylic alcohol and CO_2 may be similarly explained as for the catalytic allyl-



Scheme 4.

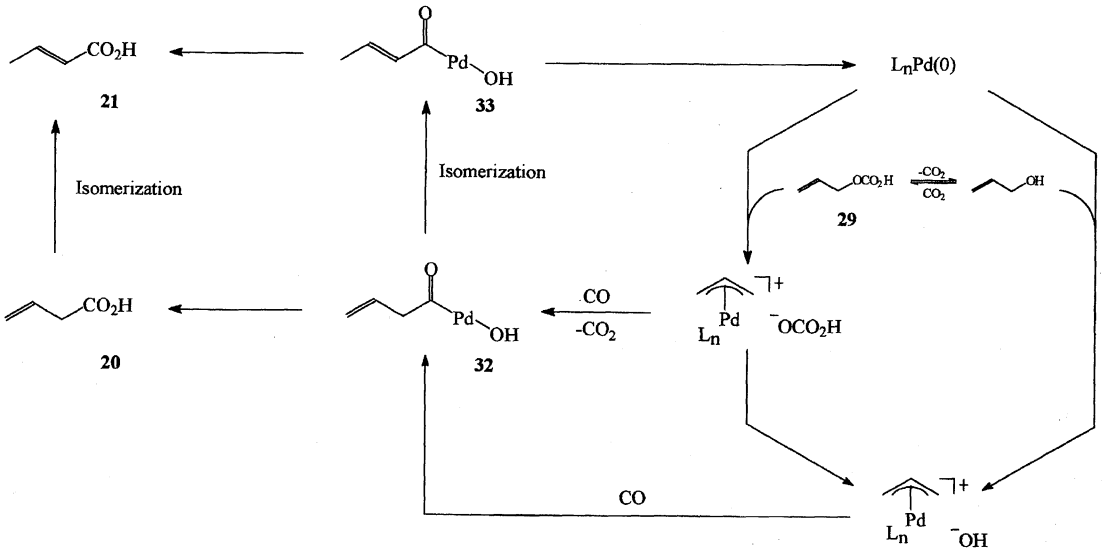


Scheme 5.

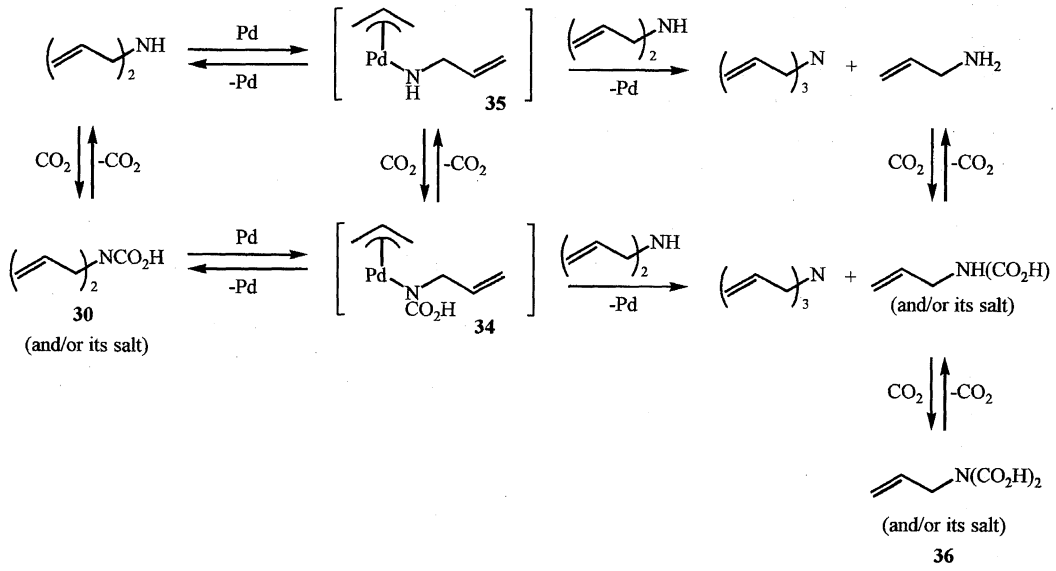
ation of nucleophiles. The η^3-allylpalladium(II) intermediate may undergo the CO insertion to give the acylpalladium intermediate as we have previously confirmed.[23] The acyl ligand in **32** may then combine with the OH group to be reductively eliminated to produce butenoic acid **20**, as shown in Scheme 6. The double bond isomerization may take place in the acyl ligand (**32** to **33**) or in the produced butenoic acid (**20** to **21**). An alternative possibility to the process shown in Scheme 6 is the CO coordination to the cationic palladium(II) center to be attacked by OH anion affording carboxy ligand, which is reductively eliminated on combination with the allyl ligand to liberate butenoic acid.

For disproportionation of diallylamine to triallylamine and allylamine, a mechanism shown in Scheme 7 is proposed. Diallylamine may form diallylcarbamic acid **30** (and/or its salt) on interaction with CO_2. The allyl–N bond in **30** may be cleaved on interaction with a Pd(0) species to afford a η^3-allylpalladium(II) intermediate **34**. The subsequent attack of diallylamine on the η^3-allylpalladium complex **34** will liberate the triallylamine and allylcarbamic acid, which on decarboxylation releases allylamine, as confirmed by gas chromatography. The disproportionation reaction proceeds, albeit slowly, in the absence of CO_2, as shown in Fig. 2. Scheme 7 includes the possible route involving the direct allyl–N bond cleavage in diallylamine on interaction with a Pd(0) species to give another type of η^3-allylpalladium species **35**. Attack of diallylamine on the allyl ligand in **35** liberates triallylamine and allylamine. The fact that the disproportionation of diallylamine proceeds only very slowly in the absence of CO_2 may due to the difficulty for direct cleavage of the allyl–N bond in diallylamine.[24]

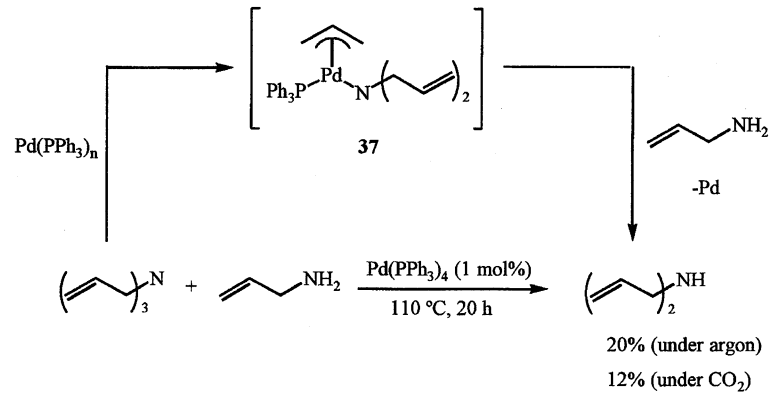
The disproportionation of diallylamine is a reversible process. Heating the 1 : 1 mixture of triallylamine and allylamine at 110 °C for 20 h in the presence of 1 mol% of $Pd(PPh_3)_4$



Scheme 6.



Scheme 7.



Scheme 8.

produced 20% of diallylamine (Scheme 8). In this case, addition of CO_2 to the same system rather hindered the reaction giving 12% of diallylamine.

The conproportionation of triallylamine and allylamine to diallylamine may be initiated by the allyl–N bond cleavage of triallylamine on interaction with a Pd(0) species, as shown in the upper part of Scheme 8. Treatment of allylamine with the same amount of $Pd(PPh_3)_4$ at 110 °C for 20 h under argon produced only a trace amount of diallylamine, whereas no diallylamine was produced when the reaction was performed under CO_2 under otherwise similar conditions. Therefore, it is likely that the interaction of the Pd(0) species with triallylamine leads to cleavage of the allyl–N bond to produce a η^3-allylpalladium species **37**. The subsequent attack of allylamine on the η^3-allyl ligand in **37** will lead to formation of diallylamine.

The hindrance effect of CO_2 on the allyl–N bond cleavage of allylamine may be due to the formation of allylcarbamic acid and its salt with allylamine, which are less soluble in the system and tend to separate out of the liquid phase. In fact, mixing allylamine with CO_2 gave an insoluble white solid.

Conclusion

The overall reaction patterns of allylic compounds on interaction with palladium complexes in the presence of CO_2 can be accounted for in a consistent manner by assuming the intermediate formation of allyl hydrogencarbonates and allylcarbamic acids and the resulting enhancement of the reactivity for their oxidative addition processes to Pd(0) species. The behavior of the presumed intermediate η^3-allylpalladium(II) complexes is consistent with that observed for the model η^3-allylpalladium(II) complexes independently prepared and examined, supporting the feasibility of the proposed mechanisms.

Experimental

General Procedures. All reactions and manipulations were performed under argon or CO_2 atmosphere except where otherwise stated, by using Schlenk techniques. Solvents were dried, distilled, and stored under argon. $[PdCl_2(PPh_3)_2]$ and $[PdCl_2(PMePh_2)_2]$ were synthesized by reactions of $[PdCl_2(PhCN)_2]$[25] with 2 equivalents of PPh_3 and $PMePh_2$, respectively. $Pd(acac)_2$ was prepared by treating $Na_2[PdCl_4]$ with acetylacetone and NaOH (aq). $Pd(dba)_2$[26,27] and $Pd(PPh_3)_4$[28] were prepared by reported procedures. Trimethylphosphine was synthesized according to the procedure[29] modified in our laboratory. Triphenylphosphine used was recrystallized from hot hexane. All the other tertiary phosphines were used as received from commercial suppliers. Allyl alcohol, 2-isopropyl-2-propen-1-ol, and diethylamine were distilled and stored under argon. 2-Phenyl-2-propen-1-ol was obtained by treating α-methylstyrene with SeO_2 followed by purification. All the other reagents were used without further purification. GLC analyses were carried out with a Hitachi 263-30 or a 263-50 instrument equipped with a Silicone SE-30 (5% on Uniport HP, 60—80 mesh, 3 mm×3 m), or a Gaskuropack 54 (80—100 mesh, 3 mm×2 m) column, using He or N_2 as carrier gas, respectively. ^1H (referenced via residual solvent protons), $^{13}C\{^1H\}$ (referenced to the solvent resonance, $^{31}P\{^1H\}$ (referenced to 85% H_3PO_4) NMR were recorded on a JEOL EX-270 or a GSX-400 spectrometer. Coupling constants (J values) are given in hertz (Hz), and spin multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), and m (multiplet). Infrared spectra were recorded on a Hitachi I-3000 or on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. Peak positions are given in reciprocal centimeters (cm^{-1}) and are listed as very strong (vs), strong (s), medium (m), weak (w), broad (br), and shoulder (sh). Mass spectra were obtained on a JEOL JMS-SX102A double-focusing high-resolution spectrometer and on a Hitachi QP-1000. Thin-layer chromatography (TLC) was performed on Merck TLC aluminum sheets silica gel $60F_{254}$ with the compounds being identified in one or more of the following ways: UV (254 nm), iodine, H_2SO_4/*p*-anisaldehyde charring. Column chromatography was performed on 70—230 mm silica gel (C-200 or C-300) purchased from Wako Chemical Industries, Ltd.

Typical Procedure for the Reaction of Allyl Alcohol with Diethylamine under CO_2. To a 50-mL round-bottom flask equipped with a magnetic stirring bar and a rubber balloon containing CO_2 were added $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.58 mol%), acetone (10 mL), allyl alcohol (1.17 mL, 17.2 mmol), and Et_2NH (1.80 mL, 17.2 mmol). The heterogeneous mixture was stirred at room temperature under CO_2 for 21 h. During the reaction, the yellow heterogeneous system changed gradually to a yellowish homogeneous solution. GLC analysis of the solution showed the formation of *N*,*N*-diethylallylamine **2** (> 96%) with the remainder being the starting materials (2—4%). For isolation of **2**, the reaction was performed without solvent. Work up of the system by treatment with NaOH, washing with a brine, and drying over $MgSO_4$ followed by distillation (110 °C/760 mmHg, 1 mmHg=133.322 Pa) gave analytically pure **2**. All the spectroscopic data of **2** were consistent

with those of a commercially available authentic sample. HRMS. Found: *m/z* 113.1193. Calcd for $C_7H_{15}N$: M, 113.1206.

Other tertiary amines were obtained similarly under the reaction conditions stated below.

***N,N*-Diethyl-2-methyl-2-propenylamine:** A mixture of 2-methyl-2-propen-1-ol (7.2 mL, 100 mmol), Et_2NH (7.3 mL, 100 mmol), and $Pd(PPh_3)_4$ (231 mg, 0.2 mmol) in CH_2Cl_2 (30 mL) under CO_2 (1 atm) stirred at room temperature for 17 h gave 16% yield (NMR) of the product. Turnover number (TON) was 51.

***N,N*-Diethyl-2-butenylamine:** A mixture of 2-buten-1-ol (*trans/cis*=13/2) (1.46 mL, 17.2 mmol), Et_2NH (1.80 mL, 17.2 mmol), and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) under CO_2 (1 atm) at room temperature stirred for 21 h gave 16% (*trans/cis*=13/3) yield (NMR) of the product. TON was 27.

***N*-Allylmorpholine:** A mixture of allyl alcohol **1** (6.80 mL, 100 mmol), morpholine (8.70 mL, 100 mmol), and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) in CH_2Cl_2 (30 mL) under CO_2 (1 atm) at room temperature for 38 h gave 58% yield (isolated) of the product. TON was 578. HRMS. Found: *m/z* 127.0991. Calcd for $C_7H_{13}NO$: M, 127.0998.

General Procedures for Reactions of Allylic Alcohols with Active Methylene Compounds. Into a 100-mL stainless steel autoclave filled with argon were charged an allylic alcohol, an active methylene compound, solvent, and $Pd(PPh_3)_4$. After the system was pressurized with CO_2, the mixture was stirred at room temperature for several hours. Then the pressure was released and the solution was filtered through Celite or filter paper, and the filtrate was concentrated by means of a rotary evaporator. The residue was purified by using silica gel chromatography to give corresponding C-allylated products. Conditions for the reactions performed are shown below together with spectroscopic data.

Ethyl 2-Allyl-2-methylacetoacetate (6) (Table 2, Entry 2): A mixture of allyl alcohol **1** (293 μL, 4.31 mmol), ethyl 2-methylacetoacetate **3** (621 μL, 4.31 mmol), and $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol) were stirred without solvent under CO_2 (30 atm) at room temperature for 24 h. The yield of **6** isolated as clear oil was 77%. ^{1}H NMR (C_6D_6) δ=5.59—5.74 (m, 1H), 4.96 (br s, 1H), 4.92 (br s, 1H), 3.85 (q, *J*=7.0 Hz, 2H), 2.68 (dd, *J*=13.9, 7.0 Hz, 1H), 2.47 (dd, *J*=13.9, 7.3 Hz, 1H), 1.83 (s, 3H), 1.24 (s, 3H), 0.83 (t, *J*=7.0 Hz, 3H); ^{13}C{^{1}H} NMR (C_6D_6) δ=203.3, 172.3, 133.4, 118.7, 61.0, 59.5, 39.7, 25.7, 19.0, 13.9; IR (neat) 1742 (sh), 1714 (s) cm^{-1}; HRMS. Found: *m/z* 184.1072. Calcd for $C_{10}H_{16}O_3$: M, 184.1100.

Ethyl 2-(2-Methy-2-propenyl)-2-methylacetoacetate (7) (Table 2, Entry 3): A mixture of 2-methyl-2-propen-1-ol (841 μL, 10.00 mmol), ethyl 2-methylacetoacetate **3** (1.44 mL, 10.00 mmol), and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) were stirred without solvent under CO_2 (30 atm) at room temperature for 25 h. The yield of **27** isolated as yellowish oil was 57%. ^{1}H NMR ($CDCl_3$) δ=4.82 (s, 1H), 4.66 (s, 1H), 4.16 (q, *J*=7.0 Hz, 2H), 2.70 (d, *J*=14.0 Hz, 1H), 2.51 (d, *J*=14.0 Hz, 1H), 2.14 (s, 3H), 1.62 (s, 3H), 1.31 (s, 3H), 1.24 (t, *J*=7.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ=205.2, 172.9, 140.9, 115.3, 61.3, 59.2, 42.2, 26.0, 23.5, 18.8, 13.9; IR (neat) 1742 (sh), 1714 (s) cm^{-1}; HRMS. Found: *m/z* 198.1233. Calcd for $C_{11}H_{18}O_3$: M, 198.1256.

2-Allyl-2-methyl-1,3-cyclopentanedione (8) (Table 2, Entry 6): A mixture of allyl alcohol **1** (170 μL, 2.50 mmol), 2-methyl-1,3-cyclopentanedione **4** (280 mg, 2.50 mmol), and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) was stirred in CH_2Cl_2 (5 mL) under CO_2 (20 atm) at room temperature for 24 h. **8** was isolated as colorless oil in the yield of 65%. ^{1}H NMR ($CDCl_3$) δ=5.64—5.48 (m, 1H), 5.06 (s, 1H), 5.01 (d, *J*=5.5 Hz, 1H), 2.79—2.58 (AA′BB′ m, 4H), 2.31 (d, *J*=7.3 Hz, 2H), 1.08 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ=216.1, 131.4, 119.7, 56.6, 40.0, 35.3, 18.7; IR (neat) 1728 (s) cm^{-1}; HRMS. Found: *m/z* 152.0870. Calcd for $C_9H_{12}O_2$: M, 152.0838.

Methyl 1-Allyl-2-oxocyclopentanecarboxylate (9) (Table 2, Entry 9): Allyl alcohol **1** (681 μL, 10.00 mmol), methyl 2-oxocyclopentanecarboxylate **5** (1.24 mL, 10.00 mmol), and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) were reacted without solvent under CO_2 (20 atm) at room temperature for 18 h to give **9** as colorless oil in the isolation yield of 66%. ^{1}H NMR ($CDCl_3$) δ=5.74—5.58 (m, 1H), 5.10 (d, *J*=3.7 Hz, 1H), 5.05 (s, 1H), 2.65 (dd, *J*=13.9, 7.0 Hz, 1H), 2.44—1.89 (overlapping m, 7H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ=214.4, 171.3, 132.9, 119.0, 59.9, 52.5, 38.0, 37.9, 32.0, 19.4; IR (neat) 1754 (s), 1728 (s) cm^{-1}; HRMS. Found: *m/z* 182.0930. Calcd for $C_{10}H_{14}O_3$: M, 182.0943.

Dimethyl 2-(4-Hydroxy-2-butenyl)malonate (10): *cis*-2-Butene-1,4-diol (2.04 mL, 25.0 mmol), dimethyl malonate (2.87 mL, 25.0 mmol), and $Pd(PPh_3)_4$ (289 mg, 0.25 mmol) in CH_2Cl_2, (10 mL) were treated with CO_2 (30 atm) at room temperature for 26 h to give **10** as slightly yellow oil in 11% yield (isolated). From the reaction mixture 82% of dimethyl malonate and 87% of *cis*-2-butene-1,4-diol were recovered. **10**: ^{1}H NMR ($CDCl_3$) δ=5.74—5.58 (overlapping m, 2H), 4.04 (d, *J*=5.1 Hz, 2H), 3.71 (s, 6H), 3.42 (t, *J*=7.3 Hz, 1H) 2.61 (dd, *J*=7.3, 6.0 Hz, 2H), 2.23 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ=169.2, 132.4, 127.2, 63.0, 52.5, 51.4, 31.3; IR (neat) 3432 (br), 1740 (s) cm^{-1}; HRMS. Found: *m/z* 184.0721 M−H_2O. Calcd for $C_9H_{14}O_5$: M−H_2O, 184.0736.

Methyl 2-(4-Hydroxy-2-butenyl)acetoacetate (11): *cis*-2-Butene-1,4-diol (2.04 mL, 25.0 mmol), methyl acetoacetate (2.69 mL, 25.0 mmol), and $Pd(PPh_3)_4$ (289 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) were treated with CO_2 (30 atm) at room temperature for 13.7 h. **11** was isolated in 43% yield as slightly yellow oil. From the reaction mixture 51% of methyl acetoacetate and 55% of *cis*-2-butene-1,4-diol were recovered. **11**: ^{1}H NMR ($CDCl_3$) δ=5.71—5.52 (overlapping m, 2H), 4.00 (d, *J*=4.8 Hz, 2H), 3.69 (s, 3H), 3.49 (t, *J*=7.3 Hz, 1H), 2.61 (shoulder br, 1H), 2.53 (dd, *J*=7.3, 6.4 Hz, 2H), 2.19 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ=202.5, 169.6, 132.1, 127.3, 62.8, 59.0, 52.4, 30.6, 29.1; IR (neat) 3408 (br), 1742 (s), 1716 (s) cm^{-1}; Mass: Found: *m/z* 186 M, 168 M−H_2O.

Reaction of Acetylacetone with *cis*-2-Butene-1,4-diol. *cis*-2-Butene-1,4-diol **7** (2.04 mL, 25.0 mmol) was mixed with acetylacetone (2.57 mL, 25.0 mmol), and $Pd(PPh_3)_4$ (289 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) under CO_2 (30 atm) at room temperature for 44 h. 3-(4-Hydroxy-2-butenyl)-2,4-pentanedione **12** was obtained in 22% yield together with 4-acetyl-5-methyl-2-vinyl-2,3-dihydrofuran **13** (15%), 3,8-diacetyl-5-decene-2,9-dione **14** in 10% yield based on acetylacetone and 3,8-diacetyl-3-(4-hydroxy-2-butenyl)-5-decene-2,9-dione **15** in 5% yield. From the reaction mixture 47% of *cis*-2-butene-1,4-diol was recovered and acetylacetone which remained unreacted was detected by TLC and GLC.

12: ^{1}H NMR ($CDCl_3$) (keto form) δ=5.72—5.62 (overlapping m, 2H), 4.01 (dd, *J*=5.6, 1.5 Hz, 2H), 3.68 (t, *J*=7.2 Hz, 1H), 2.54 (t, *J*=7.2 Hz, 2H), 2.14 (s, 6H), 2.11 (br s, 1H), (enol form) δ=16.64 (s, 1H), 5.62—5.48 (overlapping m, 2H), 4.08 (dd, *J*=5.6, 1.5 Hz, 2H), 2.95 (dd, *J*=5.1, 1.5 Hz, 2H), 2.11 (br s, 1H), 2.07 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) (keto form) δ=203.8, 129.3, 127.2, 67.9, 62.8, 30.8, 29.2, (enol form) δ=191.4, 132.2, 129.5, 107.5, 63.0, 29.7, 22.9; IR (neat) 3420 (br), 1726 (sh), 1696 (s) cm^{-1}; HRMS. Found: *m/z* 170.0895 M. Calcd for $C_9H_{14}O_3$: M, 170.0943.

13: ^{1}H NMR ($CDCl_3$) δ=5.88 (ddd, 17.1, 10.3, 6.6, 1H), 5.25 (d, *J*=17.2 Hz, 1H), 5.16 (d, *J*=10.3 Hz, 1H), 5.04—4.95 (m, 1H), 3.07 (dd, *J*=13.9, 11.5, 1H), 2.68 (dd, *J*=13.9, 8.3 Hz, 1H), 2.18 (s,

3H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=194.2, 167.2, 136.5, 116.6, 111.7, 82.4, 36.1, 29.2, 14.8; IR (neat) 1622 (s), 1228 (s), 938 (s) cm^{-1}; HRMS. Found: *m/z* 152.0819 M. Calcd for $C_9H_{12}O_2$: M, 152.0838.

14: ^1H NMR ($CDCl_3$) (keto form) δ=5.39—5.36 (overlapping m, 2H), 3.65 (t, *J*=7.3 Hz, 2H), 2.48 (m, 4H), 2.13 (s, 12H), (one enol form) δ=16.66 (s, 1H), 5.52—5.46 (m, 1H), 5.30—5.24 (m, 1H), 3.63 (t, *J*=7.3 Hz, 1H), 2.89 (dd, *J*=5.5, 1.5 Hz, 2H), 2.54 (dd, *J*=7.4, 7.2 Hz, 2H), 2.14 (s, 6H), 2.06 (s, 6H), (another enol form) δ=16.66 (s, 2H), 5.39—5.36 (overlapping m, 2H), 2.93 (d, *J*=3.3 Hz, 4H), 2.04 (s, 12H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) (keto form) δ=203.6 or 203.5, 128.8, 68.3, 30.9, 29.3 or 29.2, (one enol form) δ=203.6 or 203.5, 191.3, 130.8, 126.0, 107.7 or 107.4, 68.1, 30.9, 30.0 or 29.9, 29.3 or 29.2, 22.9, (another enol form) δ=191.3, 128.0, 107.7 or 107.4, 30.0 or 29.9, 22.9; IR (neat) 3396 (br), 1724 (sh), 1700 (s) cm^{-1}; Mass. Found: *m/z* 253 M+H, 209 M−CH_3CO.

15:[30] ^1H NMR ($CDCl_3$) (keto form) δ=5.68—5.05 (overlapping m), 4.02 (d, *J*=5.5 Hz, 2H), 3.61 (t, *J*=7.3 Hz, 1H), 2.58—2.50 (overlapping m), 2.47 (t, *J*=7.3 Hz, 2H), 2.11 (s, 6H), 2.03 (s, 6H), (enol form) δ=16.65 (s, 1H), 5.68—5.05 (overlapping m), 4.02 (d, *J*=5.5 Hz, 2H), 2.88 (d, *J*=4.0 Hz, 2H), 2.58—2.50 (overlapping m), 2.04 (s, 6H), 2.03 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) (keto form) δ=205.6, 203.6, 133.9, 130.3, 126.6, 124.9, 70.2, 68.1, 62.9, 33.5, 33.4 or 33.3, 30.9, 29.1, 27.1, (enol form) δ=205.6, 191.3, 133.8, 132.4, 124.8, 123.7, 107.3, 70.3, 62.9, 33.5, 33.4 or 33.3, 30.1, 27.2, 22.8; IR (neat) 3392 (br), 1717 (sh), 1696 (s) cm^{-1}; Mass. Found: *m/z* 323 M+H, 304 M−H_2O.

3-(2-Propenyl)-5-hexen-2-one[31] **(19):** A mixture of allyl alcohol **1** (2.04 mL, 30.0 mmol), diketene **16** (764 μL, 10.0 mmol), and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (5 mL), and stirred under CO_2 (40 atm) at room temperature for 20 h to give **19** as colorless oil in 51% isolated yield. ^1H NMR ($CDCl_3$) δ=5.67 (dddd, *J*=17.1, 10.3, 7.4, 7.4 Hz, 2H), 5.01 (d, *J*=17.1 Hz, 2H), 4.99 (d, *J*=10.3 Hz, 2H), 2.61 (quint, *J*=6.5 Hz, 1H) 2.29 (ddd, *J*=13.3, 7.4, 6.5 Hz, 2H), 2.17 (ddd, *J*=13.3, 7.4, 6.5 Hz, 2H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=211.0, 135.2, 116.9, 52.0, 35.1, 29.5; IR (neat) 1714 (s) cm^{-1}; HRMS. Found: *m/z* 138.1035 M. Calcd for $C_9H_{14}O$: M, 138.1045.

General Procedure for Reactions of Allylic Alcohols with CO. A 100-mL stainless steel autoclave filled with argon was charged with allyl alcohol, solvent, Pd-complex, and a tertiary phosphine. After introduction of pressurized CO_2 and CO, the mixture was stirred at 110 °C for 40 h. Then the pressure was released and the solution was filtered through a Celite column or filter paper. The filtrate was poured into an aq NaOH solution (2—3 g/40 mL) and the organic layer was separated. Dilute hydrochloric acid was added into the water layer and the mixture was extracted several times with ether. After drying over $MgSO_4$, the solvent was evaporated and the residue was purified by using silica-gel chromatography or by Kugelrohr distillation to give the corresponding carboxylic acids. Detailed conditions of the reactions perfomed for producing various unsaturated carboxylic acids are as follows;

3-Butenoic Acid (20) and *trans*-2-Butenoic Acid (21): Allyl alcohol (1.36 mL, 20.00 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.5 mol%) were mixed in dioxane (10 mL) under CO (50 atm) and CO_2 (50 atm). After heating the system at 110 °C for 40 h, GLC analysis showed the formation of **20** (7%) and **21** (92%). Isolation of the products according to the general procedure gave a mixture of the carboxylic acids. All the spectroscopic data of the acids were identical with those for commercially available authentic samples.

3-Pentenoic Acid (22) (Table 4, Entry 2): 2-Buten-1-ol (*E*/*Z*=81/19) (1.70 mL, 20.00 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.5 mol%) in dioxane (10 mL) were treated with CO (50 atm) and CO_2 (50 atm) at 110 °C for 40 h. Compound **22** was isolated as slightly yellow oil in 60% yield as an *E* and a *Z* mixture (*E*/*Z*=66/34). ^1H NMR ($CDCl_3$) **22**-(***E***): δ=9.71 (br s, 1H), 5.67—5.49 (overlapping, m, 2H), 3.06 (d, *J*=5.9 Hz, 1H), 1.70 (d, *J*=5.5 Hz, 1H), **22**-(***Z***): δ=9.52 (br s, 1H), 5.67—5.49 (overlapping, m, 2H), 3.14 (d, *J*=7.0 Hz, 1H), 1.64 (d, *J*=6.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) **22**-(***E***): δ=178.6, 130.1, 121.9, 37.7, 17.9, **22**-(***Z***): δ=178.4, 128.1, 121.0, 32.3, 12.9; IR (neat) 2932 (br), 1710 (s) cm^{-1}; HRMS. Found: *m/z* 100.0544 M. Calcd for $C_5H_8O_2$: M, 100.0524.

3-Methyl-3-butenoic Acid (23) and 3-Methyl-2-butenoic Acids (24) (Table 4, Entry 4): 2-Methyl-2-propen-1-ol (1.69 mL, 20.00 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.5 mol%) dissolved in dioxane (10 mL) were treated with CO (50 atm) and CO_2 (50 atm) at 110 °C for 40 h to give a mixture of **23** and **24** (**23**/**24**=66/34) in a combined yield of 72%. ^1H NMR ($CDCl_3$) **23**: δ=11.2 (br s, 1H), 4.95 (s, 1H), 4.89 (s, 1H), 3.08 (s, 2H), 1.83 (s, 3H), **24**: δ=11.2 (br s, 1H), 5.69 (s, 1H), 2.16 (s, 3H), 1.92 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) **23**: δ=178.1, 137.9, 115.2, 43.2, 22.3, **24**: δ=172.4, 160.1, 115.6, 27.7, 20.4; IR (neat) 2932 (br), 1712 (s), 1700 (s) cm^{-1}; HRMS for **23**: Found: *m/z* 100.0531 M. Calcd for $C_5H_8O_2$: M, 100.0524. HRMS for **24**: Found: *m/z* 100.0557 M. Calcd for $C_9H_8O_2$: M, 100.0524.

2-Isopropyl-3-butenoic Acid (25) and (*E*)-3,4-Dimethyl-2-pentenoic Acid (26) (Table 4, Entry 6): 2-Isopropyl-2-propen-1-ol (2.3 mL, 20 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.5 mol%) were dissolved in dioxane (10 mL), and treated with CO (50 atm) and CO_2 (50 atm) at 110 °C for 40 h to give a mixture of **25** and **26** in a ratio of 55 : 45 and in a combined yield of 69%. ^1H NMR ($CDCl_3$) **25**: δ=11.1 (br s, 1H), 4.99 (s, 1H), 4.92 (s, 1H), 3.10 (s, 2H), 2.39 (sept, *J*=7.0 Hz, 1H), 1.06 (d, *J*=7.0 Hz, 6H), **26**: δ=11.1 (br s, 1H), 5.70 (s, 1H), 2.36 (sept, *J*=6.6 Hz, 1H), 2.13 (s, 3H), 1.07 (d, *J*=6.6 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) **25**: δ=178.6, 147.8, 111.9, 40.3, 38.4, 21.3, **26**: δ=172.9, 169.0, 113.1, 33.7, 20.8, 16.7; IR (neat) 2964 (br), 1698 (s), 1642 (s) cm^{-1}; HRMS for **25**: Found: *m/z* 128.0854 M. Calcd for $C_7H_{12}O_2$: M, 128.0838. HRMS for **26**: Found: *m/z* 128.0872 M. Calcd for $C_7H_{12}O_2$: M, 128.0838.

(*E*)-4-Phenyl-3-butenoic Acid (27): Cinnamyl alcohol (1.34 g, 10.00 mmol) was mixed with $Pd(PPh_3)_4$ (58 mg, 0.05 mmol, 0.5 mol%) in dioxane (5 mL) and treated with CO (50 atm) and CO_2 (50 atm) at 110 °C for 40 h. An oily solid consisting of carboxylic acid **27** (33%) and 62% of the starting material (cinnamyl alcohol) was obtained. ^1H NMR ($CDCl_3$) δ=7.44—7.28 (m, 5H), 6.55 (d, *J*=15.8 Hz, 1H), 6.33 (dt, *J*=15.8, 7.3 Hz, 1H), 4.98 (br, 1H),[32] 3.33 (d, *J*=7.0 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=176.6, 136.6, 133.8, 128.5, 127.6, 126.3, 121.1, 38.0; IR (KBr disc) 1730 (s) cm^{-1}; HRMS. Found: *m/z* 162.0703 M. Calcd for $C_{10}H_{10}O_2$: M, 162.0681.

(*E*)-3-Phenyl-2-butenoic Acid (28): 2-Phenyl-2-propen-1-ol (138 mg, 1.03 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol, 4.9 mol%) dissolved in dioxane (2 mL) were stirred under CO (50 atm) and CO_2 (50 atm) at 110 °C for 40 h. **28** was isolated (73%) as colorless micro crystals. ^1H NMR ($CDCl_3$) δ=11.0—7.8 (br, 1H), 7.51—7.39 (m, 5H), 6.19 (s, 1H), 2.62 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=172.1, 158.5, 142.0, 129.3, 128.6, 126.4, 116.4, 18.3; IR (KBr disc) 3052 (br), 1688 (s), 1620 (s) cm^{-1}; HRMS. Found: *m/z* 162.0707 M. Calcd for $C_{10}H_{10}O_2$: M, 162.0681.

General Procedure for the Disproportionation Reaction of Diallylamine. A 100-mL stainless steel autoclave filled with argon was charged with diallylamine (2.46 mL, 20.00 mmol) and

$Pd(PPh_3)_4$ (116 mg, 0.10 mmol). After introduction of pressurized CO_2, the mixture was warmed in an oil bath and stirred for several hours. As a control experiment, the system with the same composition was treated similarly under argon. After completion of the reaction, the autoclave was cooled down to room temperature with a stream of water and the pressure was released. Formation of triallylamine and allylamine[33] was detected by GLC and/or NMR. Characterization of the products was achieved by comparing with NMR data of the commercially available samples.

Proportionation Reaction of Triallylamine and Allylamine. Triallylamine (1.72 mL, 10.00 mmol) and allylamine (751 μL, 10.00 mmol) were reacted with $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) at 110 °C for 20 h to give diallylamine in 20% (under argon) and 12% (under CO_2, 50 atm), respectively, with recovery of the starting materials.

General Procedure for the Reaction of [Pd{η^3-$CH_2C(R)CH_2$}$(PMe_3)_2$](OCO_2H) (R=H: 31a, R=Me: 31b) with Various Nucleophiles. Into an NMR tube (5 mm diameter) filled with argon was added **31**, and the tube was cooled down to −78 °C. Into the tube CD_2Cl_2 was added slowly, followed by addition of a nucleophile. The tube was capped, brought to room temperature, and shaken vigorously (or put into a water bath with a supersonic device). After several hours ^1H NMR was measured. Conditions of the reactions are shown below.

Reaction of [Pd(η^3-CH_2CHCH_2)$(PMe_3)_2$](OCO_2H) (31a) with Ethyl 2-Methylacetoacetate (3) (Table 5, Entry 1). Complex **31a** (15.9 mg, 0.0441 mmol) was treated with ethyl 2-methylacetoacetate **3** (6.4 μL, 0.0441 mmol) in CD_2Cl_2 (520 μL) at room temperature for 14 h. Compound **6** was obtained in 95% (NMR) yield.

Reaction of [Pd{η^3-$CH_2C(Me)CH_2$}$(PMe_3)_2$](OCO_2H) (31b) with Ethyl 2-Methylacetoacetate (3) (Table 5, Entry 2). Complex **31b** (13.0 mg, 0.0347 mmol) was treated with ethyl 2-methylacetoacetate **3** (5.0 μL, 0.0347 mmol) in CD_2Cl_2 (520 μL) at room temperature for 19 h. **7** was obtained in 85% (NMR) yield.

Reaction of [Pd{η^3-$CH_2C(Me)CH_2$}$(PMe_3)_2$](OCO_2H) (31b) with Et_2NH (Table 3, Entry 3). Complex **31b** (25.0 mg, 0.0667 mmol) dissolved in CD_2Cl_2 (520 μL) was reacted with Et_2NH (7.0 μL, 0.0667 mmol) at room temperature for 6 h to give *N,N*-diethyl-2-methylallylamine in 21% yield (NMR).

Reaction of [Pd(η^3-CH_2CHCH_2)$(PMe_3)_2$](OCO_2H) (31a) with Methyl 2-Oxoclopentanecarboxylate (5) (Table 5, Entry 4). Complex **31a** (18.9 mg, 0.0524 mmol) was mixed with methyl 2-oxoclopentanecarboxylate **5** (6.5 μL, 0.0524 mmol) in CD_2Cl_2 (520 μL) at room temperature for 14 h to give **9** in the yield of 96% (NMR).

Reaction of [Pd{η^3-$CH_2C(Me)CH_2$}$(PMe_3)_2$](OCO_2H) (31b) with Ethyl 2-Oxocyclopentanecarboxylate (5) (Table 5, Entry 5). Complex **31b** (14.0 mg, 0.0374 mmol) was mixed with methyl 2-oxocyclopentanecarboxylate **5** (4.6 μL, 0.0374 mmol) in CD_2Cl_2 (520 μL) at room temperature for 25 h to give methyl 1-(2-methyl-2-propenyl)-2-oxocyclopentanecarboxylate in the yield of 92% (NMR). $^{13}C\{^1H\}$ NMR δ=214.2, 171.2, 141.9, 114.8, 60.5, 52.7, 41.8, 37.8, 32.2, 23.3, 19.7.

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