Organometallics **1992,** *11,* 171–176

slope of 0.9. The pK_a values of the dihydride complexes and those of the free phosphines are related by eq 15. Thus, the basicity of the phosphine is efficiently transferred to the metal center.

$$pK_a(RuH_2^+) = 8.4 + 0.9[pK_a(HPR_3^+)] \quad (15)$$

Conclusion

The Cp*RuHL$_2$ complexes can be readily prepared by the reaction of NaOMe (excess) with Cp*RuClL$_2$, which can be prepared in situ by the reactions of Cp*RuCl$_2$ with L$_2$ in the presence of Zn. Protonation of Cp*RuH(dppp) or CpRuHL$_2$ at low temperature gives exclusively the dihydrogen complexes [Cp*Ru(η^2-H$_2$)(dppp)]$^+$ or [CpRu(η^2-H$_2$)L$_2$]$^+$ when L$_2$ = dppe, dape, dtfpe. This is consistent with the microscopic reverse of this reaction, where the η^2-dihydrogen form has a higher kinetic acidity than the dihydride form. However, protonation at the metal as well as the hydride might be concurrent processes for Cp*RuH(dppm) and Cp*RuH(PMePh$_2$)$_2$. The most thermodynamically stable products for the electron-rich Cp* complexes are the *trans*-dihydrides in a square-based piano-stool geometry with monodentate phosphines or a bidentate phosphine with a large enough bite angle (i.e. dppp) to span trans sites without much strain. Bidentate ligands forming four- or five-membered rings with the metal allow both the *trans*-dihydride and η^2-dihydrogen tautomers to coexist. The η^2-H$_2$ ligand is thought to have hindered rotation on the Ru binding sites and have an H–H distance of approximately 1.1 Å. An increase in the basicity of the phosphine results in an increase in the basicity of the metal center and a decrease in the acidity of the resulting metal dihydride or dihydrogen complex. A range of pK_a values from 10 to 16 has been determined here, but the overlapping equilibrium method results in large uncertainties in the values greater than 11. The Ru–H bond energy of the *trans*-dihydride complexes appears to vary by about 5 kal mol^{-1} depending on the type of phosphine ligand in the complex.

Acknowledgment. This research was supported by grants to R.H.M. from the Natural Sciences and Engineering Research Council of Canada and from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by a loan of ruthenium chloride from Johnson Matthey Co. We thank Nick Plavac and Samantha Drouin for their assistance in obtaining T_1 data.

Registry No. Cp*RuH(dppm), 131296-11-2; Cp*RuH(dppp), 137436-50-1; Cp*RuH(PPh$_3$)$_2$, 112861-28-6; Cp*RuH(PMePh$_2$)$_2$, 108083-42-7; Cp*RuH(PMe$_2$Ph)$_2$, 137436-51-2; [Cp*Ru(H)$_2$(dppm)]BF$_4$, 137436-53-4; [Cp*Ru(η^2-H$_2$)(dppm)]BF$_4$, 131296-13-4; [Cp*Ru(H)$_2$(dppp)]BF$_4$, 137436-55-6; [Cp*Ru(η^2-H$_2$)(dppp)]BF$_4$, 137436-57-8; [Cp*Ru(H)$_2$(PPh$_3$)$_2$]BF$_4$, 121183-76-4; [Cp*Ru(H)$_2$(PMePh$_2$)$_2$]BF$_4$, 131274-36-7; [Cp*Ru(H)$_2$(PMe$_2$Ph)$_2$]BPh$_4$, 137436-59-0; [Cp*Ru(H)$_2$(PMe$_3$)$_2$]BPh$_4$, 137436-61-4; [Cp*Ru(η^2-HD)(dppp)]BF$_4$, 137436-63-6; Cp*RuCl$_2$, 92390-47-1; Cp*RuH(PMe$_3$)$_2$, 87640-53-7; [Cp*Ru(H$_2$)(dppm)]$^+$, 131296-12-3; [Cp*Ru(H)$_2$(PMePh$_2$)$_2$]$^+$, 131274-35-6; [Cp*Ru(H)$_2$(PMe$_2$Ph)$_2$]$^+$, 137436-58-9; [Cp*Ru(H)$_2$(dppp)]$^+$, 137436-54-5; [Cp*Ru(H)$_2$(PPh$_3$)$_2$]$^+$, 121183-75-3; [Cp*Ru(H)$_2$(PMe$_3$)$_2$]$^+$, 137436-60-3; HP(t-Bu)$_3$$^+$, 137436-49-8.

Supplementary Material Available: Listings of H atom coordinates and anisotropic thermal parameters (3 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Preparation and Reactions of (π-Allyl)palladium and -platinum Carbonate Complexes

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Received June 3, 1991

The tertiary-phosphine-coordinated Pd(0) complexes Pd(styrene)L$_2$ (L = PMe$_3$, PMe$_2$Ph, PMePh$_2$) react readily with allylic carbonates (methyl 2-methylallyl carbonate and allyl ethyl carbonate) in THF to afford cationic (π-allyl)palladium complexes having an alkyl carbonate anion [(π-allyl)PdL$_2$]$^+$[OCOOR]$^-$ (allyl = 2-MeC$_3$H$_4$, R = Me, L = PMe$_3$ (**1a**), PMe$_2$Ph (**1c**), PMePh$_2$ (**1d**); allyl = C$_3$H$_5$, R = Et, L = PMe$_3$ (**1b**)). Complexes **1a**–**1d** are extremely moisture sensitive and readily react with water to give the corresponding hydrogen carbonate complexes [(π-allyl)PdL$_2$]$^+$[OCOOH]$^-$. X-ray analysis of the hydrogen carbonate complex (**2a**) derived from **1a** has revealed that **2a** has a dimeric structure, in which two [(η^3-2-MeC$_3$H$_4$)Pd(PMe$_3$)$_2$]$^+$[OCOOH]$^-$ units are associated with each other by hydrogen bonds between the hydrogen carbonate anions. Crystal data for **2a**: C$_{11}$H$_{26}$O$_3$P$_2$Pd, a = 12.055 (2) Å, b = 14.497 (2) Å, c = 9.602 (2) Å, β = 97.93 (1)°, monoclinic, $P2_1/a$, Z = 4. Treatment of **1a** with active hydrogen compounds including 2,4-pentanedione, dimethyl malonate, and cyclohexanone gives the allylation products, whereas **1a** reacts with CO to afford methyl 3-methyl-3-butenoate together with methyl 2-methylallyl ether. Preparation of related (π-allyl)platinum carbonate complexes [(η^3-2-MeC$_3$H$_4$)Pt(PMe$_3$)$_2$]$^+$[OCOOR]$^-$ (R = Me (**3**), H (**4**)) are reported.

Introduction

The palladium complex-catalyzed organic reactions using allylic carbonates have wide applications in organic synthesis.[1] In the presence of tertiary-phosphine-coordinated palladium catalysts, allylic carbonates serve as efficient allylating reagents for active hydrogen compounds without assistance of a base, whereas palladium-catalyzed carbonylation of allylic carbonates proceeds under very

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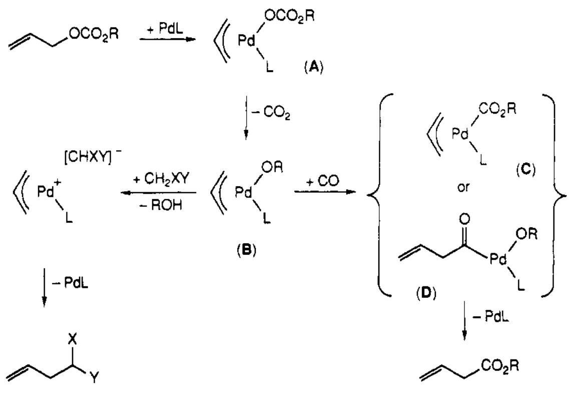
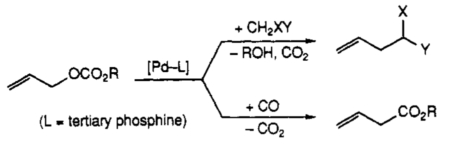
0276-7333/92/2311-0171$03.00/0

Scheme I



L = tertiary phosphine

mild conditions to give synthetically useful 3-butenoic acid esters (eq 1).[2]

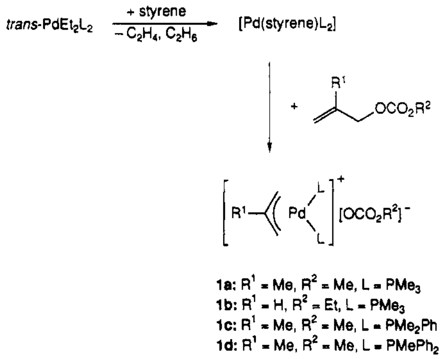


(1)

A mechanism involving a (π-allyl)palladium carbonate intermediate has been proposed (Scheme I).[1] Oxidative addition of an alkyl allyl carbonate to Pd(0) complex gives (π-allyl)palladium carbonate A, which undergoes decarboxylation to give palladium alkoxide B. In the presence of active hydrogen compounds, the alkoxo ligand in B serves as a base and abstracts a proton from active hydrogen compounds to give carbonucleophiles which attack the (π-allyl)palladium moiety to afford the allylation products. Under CO atmosphere complex B undergoes CO insertion into the Pd–OR bond[3] or Pd–allyl bond[4] to give an allyl alkoxycarbonyl (C) or alkoxo(butenoyl)palladium intermediate (D), respectively. The resulting complex C or D reductively eliminates the carbonylation products. While the mechanism reasonably accounts for the reaction patterns observed in the catalytic systems, no direct information has been reported so far on the structure and reactivity of the putative intermediate A.

As our continuous effort to elucidate structure and reactivity of (π-allyl)palladium complexes generated in the palladium-catalyzed allylation reactions,[5] we examined synthesis and reactions of (π-allyl)palladium carbonate complexes.[6] The (π-allyl)palladium carbonate complexes having two tertiary phosphine ligands [(π-allyl)PdL$_2$]$^+$[OCOOR]$^-$ (R = alkyl, H) have been prepared by oxidative addition of allylic carbonates to Pd(0) complexes. The spectroscopic data for the carbonate complexes indicated the ionic structure having a carbonate anion. An X-ray diffraction study on the PMe$_3$-coordinated hydrogen carbonate complex also supported its ionic structure. The isolated alkyl carbonate complexes exhibited the reactivity features expected for (π-allyl)palladium intermediates in the palladium-catalyzed reactions using allylic carbonates.

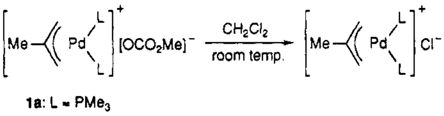
Scheme II



Results

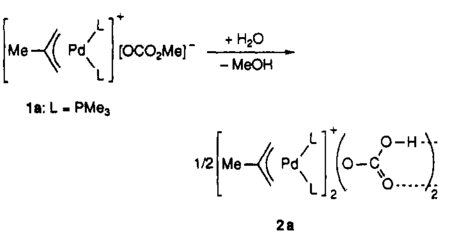
Synthesis. The (π-allyl)palladium complexes having an alkyl carbonate anion (**1a**–**1d**) were prepared by oxidative addition of allylic carbonates to styrene-coordinated Pd(0) complexes generated in situ from diethylpalladium precursors (Scheme II).[7] The oxidative addition proceeded instantly at −40 °C in THF to give **1a**–**1d**. The PMe$_3$-coordinated complexes (**1a** and **1b**) were isolated as analytically pure white solids. Complexes **1c** and **1d** having bulkier tertiary phosphines could not be isolated as analytically pure materials probably due to their susceptibility to moisture (vide infra), while their formation could be confirmed by spectroscopy.

Complexes **1a**–**1d** are insoluble in nonpolar solvents such as toluene and benzene and sparingly soluble in THF. These complexes may be dissolved in chlorinated solvents including dichloromethane and chloroform at low temperature (<0 °C), while they readily react with these solvents at room temperature to give the corresponding (π-allyl)palladium chloride complexes. For example, treatment of **1a** with CH$_2$Cl$_2$ at room temperature gave the chloride complex quantitatively (eq 2).



(2)

The alkyl carbonate complexes reacted rapidly with water to give the corresponding hydrogen carbonate complexes (eq 3).[8] The PMe$_3$-coordinated hydrogen carbonate complex **2a** derived from **1a** was isolated as white crystals (90% yield) and fully characterized by NMR and IR spectroscopy and X-ray crystallography.



(3)

2a

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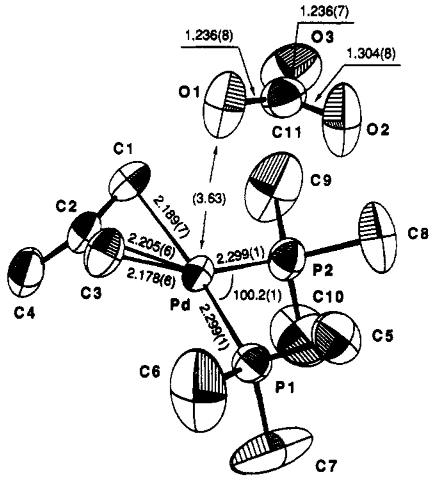
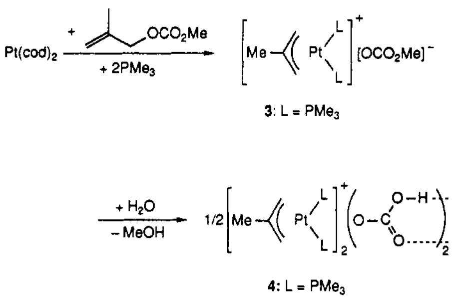


Figure 1. ORTEP diagram of complex **2a**. The ellipsoids are drawn at the 50% probability level.

Preparation of (π-allyl)platinum carbonates analogous to **1** and **2** were examined. Treatment of $Pt(cod)_2$ with 2-methylallyl methyl carbonate (1 equiv/Pt) at −40 °C in CD_2Cl_2 in the presence of 2 equiv of PMe_3 gave a yellow homogeneous solution. The NMR spectra indicated the formation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pt(PMe_3)_2]^+[OCOOMe]^-$ (**3**). Several attempts to isolate **3** as a pure compound were not successful due to concomitant formation of the hydrogen carbonate complex **4**, formed by hydrolysis of **3**. In the presence of water, the reaction of $Pt(cod)_2$, PMe_3, and 2-methylallyl methyl carbonate afforded **4** selectively (eq 4).



(4)

Characterization. Table I summarizes the spectroscopic data of the palladium complexes. The ^1H NMR data are consistent with the ionic (π-allyl)palladium structure with two tertiary phosphine ligands. Thus, the (2-methylallyl)palladium moiety in **1a** and **2a** exhibits chemical shifts and coupling patterns very similar to those of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2]^+BF_4^-$.

In the IR spectra, the alkyl carbonate complexes **1a–1d** show strong absorptions at about 1640 and 1430 cm^{-1} assignable to the $\nu(CO_3)$ bands of the carbonate anion. The hydrogen carbonate complex **2a** exhibits a very broad peak at about 2600 cm^{-1}, in addition to the very strong $\nu(CO_3)$ absorptions at 1620–40 and 1410 cm^{-1}. The value of 2600 cm^{-1} is typical of $\nu(OH)$ absorption for metal hydrogen carbonates in which the hydrogen carbonate groups are associated with each other by hydrogen bonds.[8,9] The presence of the hydrogen bond is suggested also by the appearance of a singlet peak of the hydrogen carbonate proton at very low magnetic field (δ 12.10) in the ^1H NMR spectrum.

X-ray Structure of 2a. Single crystals suitable for X-ray diffraction study were obtained by slow cooling of an acetone solution of **2a**. As seen from the ORTEP diagram in Figure 1, **2a** has a typical (π-allyl)palladium structure having the P–Pd–P angle of 100.2°. The hydrogen carbonate anion is located above the coordination plane without direct interaction with the palladium; the nearest oxygen atom (O1) being 3.63 Å distant from the palladium. The C11–O2 bond (1.304 Å) is slightly longer than the other C–O bonds (1.236 Å) in the carbonate anion, indicating that the hydrogen atom is bound to the O2 atom.

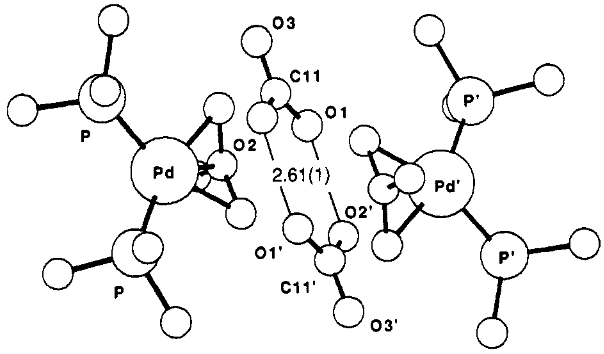
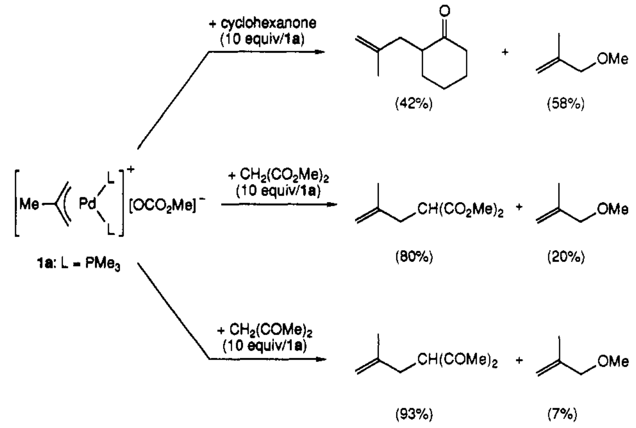


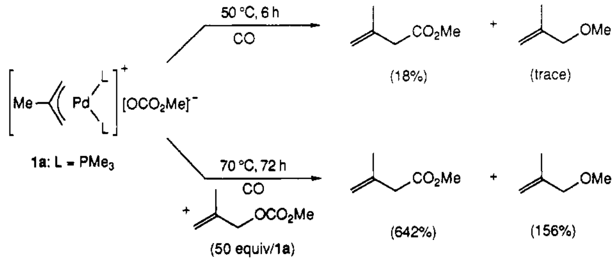
Figure 2. PLUTO drawing of complex **2a** showing the association of two molecules by hydrogen bonds.

Scheme III[a]



[a] Reaction conditions: in THF, at 50 °C, for 3 h.

Scheme IV[a]



[a] Reaction conditions: in THF, under CO (1 atm).

It is noted that the two (π-allyl)palladium carbonate units are associated with each other by hydrogen bonds between the carbonate anions (Figure 2). The internal distances between carbonate oxygens (O1–O2′ and O2–O1′) are 2.61 Å, the value being in the typical range of a hydrogen bond.[10]

Reactions. The methyl carbonate complex **1a** reacted with active hydrogen compounds such as 2,4-pentanedione, dimethyl malonate, and cyclohexanone to afford the cor-

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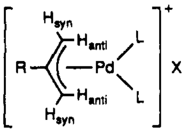
(10) *The Hydrogen Bond. II. Structure and Spectroscopy*; Schuster, P., Zundel, G.; Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976.

Table I. IR and NMR Data for π-Allylpalladium Complexes[a]



complex				^1H NMR						
R	L	X		H_{anti}	H_{syn}	R	X	L(PMe)	$^{31}P\{^1H\}$NMR	IR
Me	PMe_3	OCO_2Me	(**1a**)	3.10 (vt)[b]	4.09 (s)	1.85 (s)	3.56 (s)	1.68 (vt)[c]	−17.2 (s)	1620–60, 1440
Me	PMe_3	OCO_2H	(**2a**)	3.06 (vt)[b]	4.05 (s)	1.81 (s)	12.1 (s)	1.62 (vt)[c]	−17.0 (s)	1620–40, 1410, 2600
Me	PMe_3	BF_4		3.04 (vt)[b]	4.07 (s)	1.82 (s)		1.62 (vt)[c]	−16.9 (s)	
H	PMe_3	OCO_2Et	(**1b**)	3.31 (m)[d,f]	4.32 (d)[f]	5.55 (m)[f]	1.25 (t)[e] 3.75 (q)[e]	1.44 (vt)[c]	−17.1 (s)	1620–60, 1438
Me	PMe_2Ph	OCO_2Me	(**1c**)	3.60 (br)	4.15 (s)	1.87 (s)	3.56 (s)	1.78 (br t)	−6.0 (s)	1620–60, 1430
Me	$PMePh_2$	OCO_2Me	(**1d**)	3.58 (br)	3.34 (s)	1.94 (s)	3.81 (s)	1.85 (br t)	10.4 (s)	1620–60, 1410

[a] ^1H NMR: 100 MHz, at −40 °C; chemical shifts are in δ relative to an internal $SiMe_4$ standard. $^{31}P\{^1H\}$ NMR: 40 MHz, at −40 °C; chemical shifts are in δ relative to an external 85% H_3PO_4 standard. Solvent: CD_2Cl_2 (**1a**, **2a**, and the BF_4 complex), $CDCl_3$ (**1b**, **1c**, and **1d**). IR: KBr disks; frequencies are in cm^{-1}. [b] Virtual triplet[15] ($^3J_{PH}$ = 10 Hz). [c] Virtual triplet[15] ($^2J_{PH}$ = 8 Hz). [d] $^3J_{PH(anti)}$ = 10 Hz. [e] $^3J_{HH}$ = 7 Hz. [f] $^3J_{HH}$ = 12 and 7 Hz.

responding allylation products in good to excellent yields (Scheme III). It is noted that the yield of allylation product increases with increasing acidity of the active hydrogen compounds.

Treatment of **1a** with an atmospheric pressure of CO gave methyl 3-methyl-3-butenoate together with 2-methylallyl methyl ether. In the presence of an excess amount of 2-methylallyl methyl carbonate, catalytic formation of butenoic acid ester proceeded (Scheme IV).

Discussion

In this study we have succeeded for the first time in isolating the (π-allyl)palladium alkyl carbonate complexes formed by oxidative addition of allyl alkyl carbonates to tertiary-phosphine-coordinated Pd(0) complexes. The isolated complexes reacted in the manner expected for (π-allyl)palladium intermediates in the palladium-catalyzed reactions using allylic carbonates.

The spectroscopic data showed that the present (π-allyl)palladium complexes have ionic structure with alkyl carbonate anion. The ionic structure is supported also by the X-ray structure of the related hydrogen carbonate complex **2a**. From reactivities of the complexes, the highly nucleophilic property of the anionic alkyl carbonate group in **1a**–**1d** is suggested. Thus, the alkyl carbonate anion reacts with dichloromethane and chloroform at room temperature to generate the chloride anion, whereas in the presence of water the alkyl carbonate anion is rapidly converted into the hydrogen carbonate anion. It should be noted that the related, neutral (alkyl carbonato)- and carbamatopalladium complexes in the type *trans*-PdMe(OCOY)L_2 (Y = OMe, NR_2; L = tertiary phosphine) are fairly stable toward water and chlorinated solvents at least at room temperature.[11] Thus, the alkyl carbonate anion in **1** may be regarded as a potential alkoxide anion whose potent nucleophilicity is modified by binding with the acidic carbon dioxide moiety. On interaction with active hydrogen compounds, the masked property of the alkoxide anion may be revealed to deprotonate the active hydrogen compounds or directly attack the π-allyl ligand to give an allylic alkyl ether. The reaction pathway may be determined by the acidity of the active hydrogen compound employed.

In the presence of CO, which may coordinate to the allylpalladium moiety, the alkoxide anion liberated from the alkyl carbonate anion may attack the CO ligand to give the alkoxycarbonyl complex C in Scheme I, which reductively eliminates 3-butenoic acid ester as the carbonylation product.[12] Alternatively, insertion of CO into the Pd–allyl bond[4] followed by attack of the alkoxide anion on the resulting butenoylpalladium species may also give the carbonylation product. It is presently uncertain that either process is operative in the carbonylation reactions of allylic carbonates.

Experimental Section

All manipulations were carried out under an atmosphere of argon or nitrogen or in vacuo. ^1H, ^{13}C and ^{31}P NMR spectra were measured on JEOL FX-100, GX-270, and GX-500 spectrometers by Dr. Y. Nakamua, Ms. R. Ito, and Ms. A. Kajiwara of our laboratory. ^1H and ^{13}C NMR signals were referred to Me_4Si as an internal standard, and ^{31}P NMR signals, to 85% H_3PO_4 as an external reference. IR spectra were recorded on a JASCO IR-810 spectrometer. Elemental analyses were carried out by Dr. M. Tanaka of our laboratory by using a Yanagimoto CHN autocorder Type MT-2 and a Yazawa halogen analyzer. THF and Et_2O were dried over sodium benzophenone ketyl and distilled just before using. CD_2Cl_2 and $CDCl_3$ were dried over P_2O_5 and vacuum-transferred and stored in flasks equipped with Teflon screw valves. Other solvents including hexane, toluene, and acetone were dried in the usual manner, distilled, and stored under argon atmosphere. Carbon monoxide was used as purchased (Nippon Sanso) without further purification. Allylic carbonates were prepared by esterification of allylic alcohols with alkyl chloroformates in dichloromethane in the presence of pyridine. Diethylpalladium complex *trans*-$PdEt_2L_2$ (L = PMe_2Ph, $PMePh_2$) were prepared as described previously.[13] $Pt(cod)_2$ was prepared by the reported method.[14]

Preparation of *trans*-$PdEt_2(PMe_3)_2$. A heterogeneous mixture of $Pd(acac)_2$ (1.5 g, 4.9 mmol) in Et_2O (10 mL) was cooled at −70 °C with a dry ice ethanol bath, and an Et_2O solution of PMe_3 (17 mL, 12.4 mmol) and then $Al_2Et_3(OEt)_3$ (3 mL) were added by means of a syringe. The mixture in the alcohol bath was allowed to warm to 0 °C with stirring to give a yellow ho-

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[11] Ozawa, F.; Ito, T.; Yamamoto, A. *Chem. Lett.* **1979**, 735.

[12] A similar process is operative in the palladium-catalyzed carbonylation of aryl halides and secondary amines to give amides. In this case nucleophilic attack of amine to an arylpalladium carbonyl intermediate gives aryl(carbamoyl)palladium species, which reductively eliminates amide: Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics* **1990**, *9*, 2603. Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1985**, *107*, 3235.

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mogeneous solution. After the system was stirred at 0 °C for about 1 h, the solution was concentrated under reduced pressure to two-thirds in volume and allowed to stand at −20 °C overnight to give a white solid, which was collected by filtration, washed with cold hexane (10 mL), and dried under vacuum. The crude product was dissolved in Et_2O at room temperature and cooled to −20 °C to form white crystals of *trans*-$PdEt_2(PMe_3)_2$ (2.2 g, 70%). Anal. Calcd for $C_{10}H_{28}P_2Pd$: C, 37.93; H, 8.91. Found: C, 37.93; H, 8.89. ^1H NMR ($CDCl_3$, −20 °C): δ 0.39 (tq, J_{HH} = J_{PH} = 8 Hz, 4 H, $PdCH_2$), 1.07 (t, J_{HH} = 8 Hz, 6 H, $PdCH_2CH_3$).

Preparation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2][OCOOMe]$ (1a). To a Schlenk tube containing *trans*-$PdEt_2(PMe_3)_2$ (0.44 g, 1.4 mmol) were added styrene (0.8 mL, 7.0 mmol) and THF (5 mL). The mixture was heated at 55 °C for 3 h to give a homogeneous yellow solution. The solution was cooled to −30 °C, and methyl 2-methylallyl carbonate (363 μL, 2.8 mmol) was added. The homogeneous system instantly changed to a white heterogeneous mixture. The mixture was stirred at 0 °C for 2 h, and the resulting white solid of **1a** was collected by filtration, washed with cold Et_2O (10 mL × 2), and dried under vacuum at 0 °C (0.33 g, 60%). Anal. Calcd for $C_{12}H_{28}O_3P_2Pd$: C, 37.08; H, 7.26. Found: C, 36.83; H, 7.34.

Similarly prepared was $[(\eta^3\text{-}C_3H_5)Pd(PMe_3)_2][OCOOEt]$ (**1b**) by using allyl ethyl carbonate in place of methyl 2-methylallyl carbonate (0.80 g, 82%). Anal. Calcd for $C_{12}H_{28}O_3P_2Pd$: C, 37.08; H, 7.26. Found: C, 36.79; H, 7.32.

Preparation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_2Ph)_2][OCOOMe]$ (1c). A yellow solution of $Pd(styrene)(PMe_2Ph)_2$ was prepared by thermolysis of *trans*-$PdEt_2(PMe_2Ph)_2$ (0.28 g, 0.63 mmol) in THF (3 mL) at 40 °C in the presence of styrene (0.36 mL, 3.2 mmol). The solution was cooled to −30 °C, and methyl 2-methylallyl carbonate (165 μL, 1.3 mmol) was added. The homogeneous system instantly changed to a white heterogeneous mixture. The mixture was stirred at 0 °C for 2 h and Et_2O (10 mL) was added at −30 °C. The resulting white solid of **1c** was collected by filtration, washed with cold Et_2O (10 mL × 2), and dried under vacuum at −20 °C (0.20 g, 62%). The ^1H NMR spectrum indicated the formation of the title compound (Table I), while the product did not give the correct analytical values. Attempts to obtain **1c** as a pure compound by recrystallization were unsuccessful due to contamination by the corresponding hydrogen carbonate complex during the recrystallization, as confirmed by the appearance of the signal of the hydrogen carbonate proton at δ 12.1 in the ^1H NMR spectrum.

Preparation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMePh_2)_2][OCOOMe]$ (1d). A yellow solution of $Pd(styrene)(PMePh_2)_2$ was prepared by thermolysis of *trans*-$PdEt_2(PMePh_2)_2$ (0.33 g, 0.58 mmol) in toluene (5 mL) containing styrene (0.34 mL, 3.0 mmol) at 30 °C for 2 h. The solution was cooled to −30 °C, and methyl 2-methylallyl carbonate (190 μL, 1.5 mmol) was added. The homogeneous system instantly changed to a white heterogeneous mixture. The mixture was stirred at −20 °C for 2 h, and Et_2O (10 mL) was added at −30 °C. The resulting white solid of **1d** was collected by filtration, washed with cold Et_2O (10 mL × 2), and dried under vacuum at −20 °C (0.13 g, 35%). The ^1H NMR spectrum indicated the formation of the title compound (Table I). Several attempts to obtain **1d** as an analytically pure compound by recrystallization were unsuccessful.

Reaction of 1a with CH_2Cl_2. Preparation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2]Cl$. Complex **1a** (0.30 g, 0.77 mmol) was dissolved in CH_2Cl_2 (2 mL) at −30 °C. The solution was stirred at room temperature for 4 h, and then the solvent was evaporated under reduced pressure to give a white powder of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2]Cl$ (0.27 g, 100%). The ^1H NMR spectrum (CD_2Cl_2) was identical with the authentic sample.

The authentic compound was prepared as follows. To a Schlenk tube containing *trans*-$PdEt_2(PMe_3)_2$ (0.30 g, 0.96 mmol) were added styrene (0.55 mL, 4.8 mmol) and THF (6 mL). The mixture was heated at 55 °C for 6 h to give a homogeneous yellow solution. The solution was cooled to −30 °C, and 2-methylallyl chloride (188 μL, 1.9 mmol) was added. The homogeneous system instantly changed to a white heterogeneous mixture. The mixture was stirred at room temperature for 1 h, and then the solvent was evaporated to dryness under vacuum. The resulting white solid was recrystallized from a CH_2Cl_2–Et_2O mixture to give $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2]Cl$ as white crystals (0.22 g, 66%). Anal. Calcd for $C_{10}H_{25}ClP_2Pd$: C, 34.40; H, 7.22; Cl, 10.16. Found: C, 34.23; H, 7.43; Cl, 10.21. ^1H NMR (CD_2Cl_2): δ 1.72 (virtual triplet, $^2J_{PH}$ = 9 Hz, 18 H, PMe), 1.87 (s, 3 H, allyl–Me), 3.08 (virtual triplet, $^3J_{PH}$ = 10 Hz, 2 H, anti-allyl), 4.11 (s, 2 H, syn-allyl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −17.5 (s).

Preparation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2]BF_4$. To a Schlenk tube containing a heterogeneous mixture of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2]Cl$ (0.12 g, 0.33 mmol) and acetone (3 mL) was added $AgBF_4$ (0.065 g, 0.33 mmol) at −30 °C. The system was stirred at the same temperature for 1 h, and the resulting precipitate of AgCl was removed by filtration to give a pale yellow solution, which was concentrated to dryness to give a white solid of the title compound. The crude product was recrystallized from a CH_2Cl_2–Et_2O mixture to give white crystals of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2]BF_4$ (0.082 g, 62%). Anal. Calcd for $C_{10}H_{25}BF_4P_2Pd$: C, 29.99; H, 6.29. Found: C, 29.50; H, 6.73.

Preparation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2][OCOOH]$ (2a). To a Schlenk tube containing *trans*-$PdEt_2(PMe_3)_2$ (0.44 g, 1.4 mmol) were added styrene (0.81 mL, 7.0 mmol) and toluene (3 mL). The mixture was heated at 55 °C for 3 h to give a homogeneous yellow solution. The solution was cooled to −30 °C, and methyl 2-methylallyl carbonate (410 μL, 3.2 mmol) and water (29 mL, 1.6 mmol) were added. The homogeneous system instantly changed to a white heterogeneous mixture. The mixture was stirred at 0 °C for 3 h, and the resulting white solid of **2a** was collected by filtration, washed with cold Et_2O (10 mL × 2), and dried under vacuum at 0 °C (0.47 g, 90%). Anal. Calcd for $C_{11}H_{26}O_3P_2Pd$: C, 35.26; H, 7.00. Found: C, 35.36; H, 7.41. The ^1H and ^{31}P NMR data are reported in Table I. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.0 (virtual triple, $^1J_{PC}$ = 32 Hz, PMe), 24.7 (s, allyl–Me), 69.7 (virtual triple, $^2J_{PC}$ = 28 Hz, allylic carbons), 137.1 (t, $^2J_{PC}$ = 5 Hz, center carbon), 160.4 (s, OCOOH).

Preparation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pt(PMe_3)_2][OCOOMe]$ (3) (NMR Tube Reaction). To a suspension of $Pt(cod)_2$ (32.1 mg, 0.078 mmol) in CD_2Cl_2 (0.7 mL) in an NMR sample tube equipped with a rubber septum cap were added methyl 2-methylallyl carbonate (10.5 μL, 0.082 mmol) and PMe_3 (16.2 μL, 0.156 mmol) at −40 °C. The system quickly turned to a yellow homogeneous solution. The ^1H and ^{31}P NMR spectra indicated the formation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pt(PMe_3)_2][OCOOMe]$ (**3**). ^1H NMR (CD_2Cl_2, −40 °C): δ 1.71 (d, J_{PH} = 10 Hz, J_{PtH} = 36 Hz, 18 H, PMe), 1.84 (s, J_{PtH} = 55 Hz, 3 H, allyl–Me), 2.57 (d, J_{PH} = 8.3 Hz, J_{PtH} = 44 Hz, 2 H, anti-allyl), 3.33 (s, 3 H, OCOOMe), 3.87 (s, 2 H, syn-allyl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C): −24.6 (s, J_{PtP} = 3590 Hz).

Preparation of $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pt(PMe_3)_2][OCOOH]$ (4). To a Schlenk tube containing $Pt(cod)_2$ (0.122 g, 0.296 mmol) was added THF (5 mL) at room temperature. The system was cooled to −20 °C, and PMe_3 (62 μL, 0.60 mmol), methyl 2-methylallyl carbonate (153 μL, 1.19 mmol), and water (10 μL, 0.55 mmol) were added. The mixture was stirred for 10 h at −20 °C, and the resulting white precipitate of **4** was collected by filtration, washed with Et_2O, and dried under vacuum (0.067 g, 47%). Anal. Calcd for $C_{11}H_{26}O_3P_2Pt$: C, 28.51; H, 5.66. Found: C, 28.77; H, 5.95. ^1H NMR (CD_2Cl_2, −40 °C): δ 1.73 (d, J_{PH} = 10 Hz, J_{PtH} = 36 Hz, 18 H, PMe), 1.82 (s, J_{PtH} = 56 Hz, 3 H, allyl–Me), 2.62 (d, J_{PH} = 8.6 Hz, J_{PtH} = 43 Hz, 2 H, anti-allyl), 3.85 (s, 2 H, syn-allyl), 11.85 (br, 1 H, OCOOH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ 18.1 (d, J_{PC} = 40 Hz, J_{PtC} = 45 Hz, PMe), 24.9 (s, J_{PtC} = 28 Hz, allyl–Me), 61.4 (dd, J_{PC} = 28 and 4 Hz, J_{PtC} = 74 Hz, allylic carbons), 133.2 (t, J_{PC} = 2.4 Hz, J_{PtC} = 23 Hz, center carbon), 160.0 (s, OCOOH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ −24.7 (s, J_{PtP} = 3592 Hz). IR (KBr): 2600 (br), 1632 (s), 1620 (s), 1420 (s) cm^{-1}.

X-ray Diffraction Study of 2a. A single crystal of dimensions ca. 0.5 × 0.5 × 0.5 mm was obtained from acetone and sealed in a glass capillary tube under argon. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer. Unit cell dimensions and an orientation matrix were obtained by a least-squares calculation for 25 automatically centered reflections in the range $20 \le 2\theta \le 25°$. Diffraction intensities were measured at 19 °C in the range $3 \le 2\theta \le 60°$ using the ω–2θ scan technique at a scan rate of 4°/min. Three standard reflections, measured at every 100 reflection measurements, showed no appreciable decrease in the intensities during the data collection. No absorption correction was made. Of the 4828 unique reflections measured, 3892 were

Table II. Crystal Data for $[(\eta^3\text{-2-MeC}_3H_4)Pd(PMe_3)_2][OCOOH]$ (2a)

formula	$C_{11}H_{26}O_3P_2Pd$
fw	374.68
habit	prismatic
temp, K	292
cryst syst	monoclinic
space group	$P2_1/a$
a, Å	12.055 (2)
b, Å	14.497 (2)
c, Å	9.602 (2)
β, deg	97.93 (1)
V, Å^3	1662.0 (4)
Z	4
d_{calcd}, g cm^{-3}	1.50
cryst size, mm	0.5 × 0.5 × 0.5
μ(Mo Kα), cm^{-1}	12.9
radiation	Mo Kα (λ = 0.71068 Å)
diffractometer	Rigaku AFC-5
monochromator	graphite
data collcd	$\pm h,+k,+l$
scan type	ω–2θ
2θ range, deg	3.0–60.0
scan speed, deg min^{-1}	4, fixed
no. of unique reflns	4828
no. of reflns used	3892 ($F_o \geq 3\sigma(F_o)$)
no. of variables	154
R	0.052
R_w	0.054

Table III. Selected Bond Distances (Å) and Angles (deg) for $[(\eta^3\text{-2-MeC}_3H_4)Pd(PMe_3)_2][OCOOH]$ (2a)

(a) Bond Distances			
Pd–C1	2.189 (7)	C2–C4	1.472 (9)
Pd–C(2)	2.205 (6)	C11–O1	1.236 (8)
Pd–C3	2.178 (6)	C11–O2	1.304 (8)
Pd–P1	2.299 (1)	C11–O3	1.236 (7)
Pd–P2	2.299 (1)	Pd–O1	3.630 (5)
C1–C2	1.404 (9)	O1–O2′	2.61 (1)
C2–C3	1.396 (9)	O2–O1′	2.61 (1)
(b) Bond Angles			
C1–Pd–P1	162.3 (2)	C1–C2–C4	120.6 (6)
C1–Pd–P2	95.9 (2)	C3–C2–C4	121.3 (6)
C3–Pd–P1	96.9 (2)	O1–C11–O2	115.8 (6)
C3–Pd–P2	161.8 (2)	O1–C11–O3	125.6 (6)
P1–Pd–P2	100.2 (1)	O2–C11–O3	118.6 (6)
C1–C2–C3	117.3 (5)		

classed as observed ($F_o > 3\sigma(F_o)$) and these were used for the solution and refinement of the structure. The crystal data and details of data collection are listed in Table II.

Calculations were performed on a FACOM A-70 computer using the R-CRYSTAN program. The structure was solved by a combination of direct methods (SAPI85) and Fourier techniques. Hydrogen atoms were not located. The structure was refined by full-matrix least-squares calculations with anisotropic thermal parameters for all non-hydrogen atoms. The final R value was 0.052 (R_w = 0.054). The selected bond distances and angles are listed in Table III. Fractional coordinates and equivalent isotropic thermal parameters are given in Table IV.

Reactions of 1a. With Active Hydrogen Compounds. The following procedure for the reaction with cyclohexanone is typical. Complex **1a** (0.039 g, 0.10 mmol) was placed in a Schlenk tube, and THF (1 mL) and cyclohexanone (104 μL, 1.0 mmol) were added at −20 °C. The heterogeneous mixture was heated at 50 °C for 3 h with stirring. Deposition of Pd black during the reaction was noted. GLC analysis (Silicon DC-550, 3-m column) of the resulting solution revealed the formation of the allylation product of cyclohexanone (42%/**1a**) and 2-methylallyl methyl ether (58%).

Table IV. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[(\eta^3\text{-2-MeC}_3H_4)Pd(PMe_3)_2][OCOOH]$ (2a)

atom	x	y	z	B_{eq},[a] Å^2
Pd	0.74322 (2)	0.48647 (2)	0.67420 (2)	3.62 (0)
P1	0.68613 (11)	0.61197 (9)	0.79240 (11)	4.56 (3)
P2	0.62751 (10)	0.37473 (9)	0.74452 (13)	4.39 (2)
C1	0.8448 (5)	0.3923 (4)	0.5660 (6)	6.04 (16)
C2	0.8489 (4)	0.4799 (4)	0.5044 (6)	5.46 (14)
C3	0.8830 (5)	0.5537 (5)	0.5938 (7)	5.97 (16)
C4	0.8005 (6)	0.4952 (5)	0.3570 (7)	6.92 (21)
C5	0.7084 (7)	0.6052 (5)	0.9796 (6)	7.32 (22)
C6	0.7617 (13)	0.7186 (5)	0.7676 (13)	13.8 (5)
C7	0.5434 (8)	0.6464 (8)	0.7504 (12)	12.3 (4)
C8	0.6341 (7)	0.3621 (6)	0.9323 (6)	7.91 (24)
C9	0.6496 (9)	0.2580 (5)	0.6912 (11)	10.4 (4)
C10	0.4820 (6)	0.3857 (8)	0.6826 (11)	10.4 (4)
C11	0.9525 (5)	0.3725 (4)	0.9491 (6)	5.25 (14)
O1	1.0076 (5)	0.4223 (4)	0.8796 (5)	7.74 (15)
O2	0.9302 (5)	0.4073 (4)	1.0674 (5)	8.80 (19)
O3	0.9187 (4)	0.2939 (3)	0.9162 (6)	7.88 (16)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\mathbf{a}_i\cdot\mathbf{a}_j)] = (4/3)\sum_i\sum_j[\beta_{ij}(\mathbf{a}_i\cdot\mathbf{a}_j)]$.

With Carbon Monoxide. (1) Stoichiometric Reaction. Complex **1a** (0.039 g, 0.10 mmol) was placed in a Schlenk tube equipped with a rubber balloon (500 mL), and THF (1 mL) was added. The system was evacuated by pumping, and CO gas (1 atm) was introduced. The heterogeneous mixture was heated with stirring at 50 °C to give a red homogeneous solution. GLC analysis after 6 h revealed the formation of methyl 3-methyl-3-butenoate (18%/**1a**) and methyl 2-methylallyl ether (trace).

(2) Catalytic Reaction. Complex **1a** (0.039 g, 0.10 mmol) was placed in a Schlenk tube equipped with a rubber balloon (500 mL), and THF (1 mL) and 2-methylallyl methyl carbonate (480 μL, 1.5 mmol) were added. The system was evacuated by pumping, and CO gas (1 atm) was introduced. The heterogeneous mixture was heated at 70 °C with stirring for 72 h. GLC analysis of the resulting solution revealed the formation of methyl 3-methyl-3-butenoate (642%/**1a**) and methyl 2-methylallyl ether (156%).

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Registry No. 1a, 137515-70-9; **1b**, 137515-71-0; **1c**, 137540-17-1; **1d**, 137515-73-2; **2a**, 137515-76-5; **3**, 137515-78-7; **4**, 137515-79-8; *trans*-$PdEt_2(PMe_3)_2$, 124717-55-1; $Pd(acac)_2$, 14024-61-4; Pd(styrene)$(PMe_2Ph)_2$, 137515-74-3; *trans*-$PdEt_2(PMe_2Ph)_2$, 75108-70-2; Pd(styrene)$(PMePh_2)_2$, 70316-76-6; *trans*-$PdEt_2(PMePh_2)_2$, 75172-21-3; $[(\eta^3\text{-2-MeC}_3H_4)Pd(PMe_3)_2]Cl$, 126009-37-8; $[(\eta^3\text{-2-MeC}_3H_4)Pd(PMe_3)_2]BF_4$, 137515-75-4; $Pt(cod)_2$, 12130-66-4; methyl 2-methylallyl carbonate, 81112-28-9; allyl ethyl carbonate, 1469-70-1; 2-methylallyl chloride, 563-47-3; cyclohexanone, 108-94-1; 2-(2-methylallyl)-1-cyclohexanone, 936-67-4; 2-methylallyl methyl ether, 22418-49-1; methyl 3-methyl-3-butenoate, 25859-52-3.

Supplementary Material Available: Tables of complete bond distances and angles and anisotropic thermal parameters (2 pages); a table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.