Palladium(0)-Catalyzed Alkoxycarbonylation of Allyl Phosphates and Acetates

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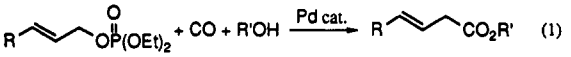
Received November 30, 1992

Palladium-catalyzed alkoxycarbonylation of allyl phosphates under CO (1 atm) at 50 °C proceeds highly efficiently to give the corresponding β,γ-unsaturated esters. The carbonylation of geranyl phosphate ((*E*)-11) under CO (1 atm) at 50 °C gave ethyl ester of homogeranic acid ((*E*)-12) stereoselectively. The carbonylation takes place at the least substituted allylic positions with *inversion of configuration*. Typically, the methoxycarbonylation of *cis*-5-(methoxycarbonyl)-2-cyclohexen-1-yl phosphate (*cis*-16) gave *trans*-dimethyl 2-cyclohexene-1,5-dicarboxylate (*trans*-17) selectively. Alkoxycarbonylation of allyl acetates is performed for the first time in the presence of a catalytic amount of bromide ion. The reaction can be rationalized by assuming the mechanism which involves oxidative addition of palladium(0) species to allyl acetates to give π-allylpalladium acetate, fast ligand exchange of the acetate with bromide, insertion of carbon monoxide to give acylpalladium species, and alkoxylation.

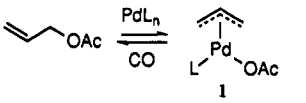
Introduction

Carbonylation of allylic compounds is one of the most attractive methods for the synthesis of β,γ-unsaturated carbonyl compounds, which are versatile building blocks. Allylic halides undergo carbonylation with ease by using nickel,[1] cobalt,[2] and palladium complex catalysts.[3,4] However, carbonylation of synthetically more important allylic alcohol derivatives such as allyl acetates[3b,5-7] and ethers[3b,8] is difficult and usually requires severe reaction conditions. Recently, palladium(0)-catalyzed carbonylation of allyl alkyl carbonates[9] was reported by Tsuji to proceed under mild reaction conditions, although contamination of allyl alkyl ethers is observed in some cases. We have shown that allyl phosphates are excellent allylating agents for the palladium-catalyzed alkylation, amination,[10] hydroxylamination,[11] and azidation.[12] Allyl phosphates are highly reactive toward palladium(0) species, and phosphoryloxy groups have extremely low nucleophilicity. We have found that alkoxycarbonylation of allyl phosphates proceeds highly selectively under mild reaction conditions (eq 1).



(1)

Allylic acetates are important substrates and have been used for various palladium-catalyzed allylic transformations.[13] However, many attempts at carbonylation of allyl acetates were in vain. This is due to the fact that π-allylpalladium acetates (1), which are formed readily by oxidative addition of palladium(0) species to allyl acetates, undergo back-reaction to give the starting allyl acetates[14] rather than insertion of carbon monoxide to give β,γ-unsaturated esters upon treatment with carbon monoxide. This is in contrast to the facile carbonylation



(2)

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of allyl halides via π-allylpalladium halide complexes.[15] In order to overcome this difficulty, palladium(0)-catalyzed carbonylation of cinnamyl acetate has been carried out in the presence of a stoichiometric amount of $NaCo(CO)_4$ in methanol under CO atmosphere to give methyl 4-phenyl-3-butenoate.[5] In this reaction, the intermediate π-allylpalladium acetate complex is converted into allylcobalt carbonyl, which undergoes facile carbonylation.

We focused on the effect of the leaving groups of allylic substrates and found that the carbonylation of allyl acetates proceeds smoothly under mild reaction conditions, when bromide ion is used as a cocatalyst (eq 3). We report

(1) (a) Chiusoli, G. P.; Cassar, L. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 124-133. Cassar, L.; Chiusoli, G. P.; Guerrieri, F.; *Synthesis* **1973**, 509-523. (b) Foá, M.; Cassar, L. *Gazz. Chim. Ital.* **1979**, *109*, 619-621. (c) Joó, F.; Alper, H. *Organometallics* **1985**, *4*, 1775-1778.

(2) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1963**, *85*, 2779-2782.

(3) Synthesis of β,γ-unsaturated carboxylic acids derivatives: (a) Dent, W. T.; Long, R.; Whitfield, G. H. *J. Chem. Soc.* **1964**, 1588-1594. (b) Tsuji, J.; Kiji, J.; Imamura, S.; Morikawa, M. *J. Am. Chem. Soc.* **1964**, *86*, 4350-4354. (c) Medema, D.; van Helden, R.; Kohll, C. F. *Inorg. Chim. Acta* **1969**, *3*, 255-265. (d) Knifton, J. F. *J. Organomet. Chem.* **1980**, *188*, 223-236. (e) Kiji, J.; Okano, T.; Konishi, H.; Nishiumi, W. *Chem. Lett.* **1989**, 1873-1876.

(4) Synthesis of allyl ketones and aldehydes: Merrifield, J. H.; Godschalx, J. P.; Stille, J. K. *Organometallics* **1984**, *3*, 1108-1112. Baillargeon, V. P.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 452-461.

(5) Hegedus, L. S.; Tamura, R. *Organometallics* **1982**, *1*, 1188-1194.

(6) Cyclocarbonylation of 3-arylallyl acetates: Matsuzaka, H.; Hiroe, Y.; Iwasaki, M.; Ishii, Y.; Koyasu, Y.; Hidai, M. *J. Org. Chem.* **1988**, *53*, 3832-3838. Iwasaki, M.; Kobayashi, Y.; Li, J.-P.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *J. Org. Chem.* **1991**, *56*, 1922-1927.

(7) Kiji, J.; Okano, T.; Ono, I.; Konishi, H. *J. Mol. Catal.* **1987**, *39*, 355-358.

(8) Neibacker, D.; Poirier, J.; Tkatchenko, J. *J. Org. Chem.* **1989**, *54*, 2459-2462.

(9) Tsuji, J.; Sato, K.; Okumoto, H. *J. Org. Chem.* **1984**, *49*, 1341-1344.

(10) Tanigawa, Y.; Nishimura, K.; Kawasaki, A.; Murahashi, S.-I. *Tetrahedron Lett.* **1982**, *23*, 5549-5552.

(11) Murahasi, S.-I.; Imada, Y.; Taniguchi, Y.; Kodera, Y. *Tetrahedron Lett.* **1988**, *29*, 2973-2976.

(12) Murahashi, S.-I.; Tanigawa, Y.; Imada, Y.; Taniguchi, Y. *J. Org. Chem.* **1989**, *54*, 3292-3303.

(13) For reviews: Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Heidelberg, 1980. Trost, B. M.; Verhoeven, T. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, pp 800-938.

(14) (a) Takahashi, Y.; Tsujiyama, K.; Sakai, S.; Ishii, Y. *Tetrahedron Lett.* **1970**, 1913-1916. (b) Bäckvall, J.-E.; Nordberg, R. E.; Björkman, E. E.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1980**, 943-944. (c) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559-1567.

(15) Milstein, D. *Organometallics* **1982**, *1*, 888-890. Milstein, D. *Acc. Chem. Res.* **1988**, *21*, 428-434.

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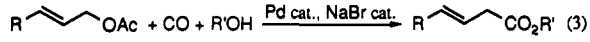
Table I. Carbonylation of Allylic Compounds[a]

entry	leaving group, X	convn, %[b]	yield, %[b,c]
1	Br	100	83
2	Cl	77	60
3	$OP(O)(OEt)_2$ (2)	81	84
4	OCO_2Et	71	82
5	$OCOCF_3$ (5)	72	35
6	OCOPh (6)	22	90
7	$OCOCH_3$ (3)	19	74
8	OPh	0	0
9	NEt_2	0	0
10	OH	0	0

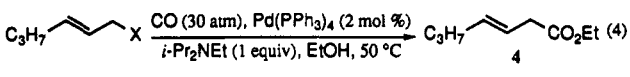
[a] General conditions: 1 mmol of substrate in 1 mL of ethanol, 1 mol % of $Pd_2(dba)_3$·$CHCl_3$, 4 mol % of PPh_3, 1 equiv of *i*-Pr_2NEt, 30 atm of CO, 50 °C, 1 h. [b] Determined by GC. [c] Yield of 4 based on the consumed substrate.

here full details of the palladium-catalyzed carbonylations of both allyl phosphates and allyl acetates with respect to scope, limitation, and mechanism.[16]



Results and Discussion

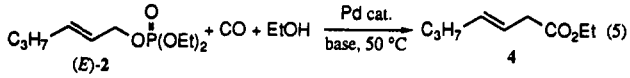
Carbonylation of Allyl Phosphates. In order to clarify the effect of the leaving groups of allylic compounds toward palladium-catalyzed carbonylation, carbonylations of a series of 2-hexenyl derivatives, such as 2-hexenyl halides, phosphate (**2**), and acetate (**3**), were examined. The reactivity of allylic compounds was monitored by the conversion and the yield of ethyl 3-heptenoate (**4**). The carbonylations were carried out in the presence of 1 mol % of $Pd_2(dba)_3$·$CHCl_3$ catalyst, 4 mol % of PPh_3, and 1 equiv of *i*-Pr_2NEt as a base in ethanol under CO pressure (30 atm) at 50 °C for 1 h (eq 4).



X = Br, Cl, $OP(O)(OEt)_2$ (2), $OCOCH_3$ (3), ...

Allyl phosphate **2** (entry 3) and allyl carbonate (entry 4) undergo carbonylation readily as well as allyl halides (entries 1 and 2). Carbonylations of 2-hexenyl trifluoroacetate (**5**) (entry 5), benzoate (**6**) (entry 6), and acetate (**3**) (entry 7) gave poor results, and other substrates such as phenyl ether are inactive under the present reaction conditions (entries 8–10).

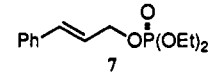
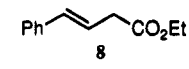
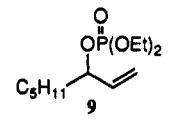
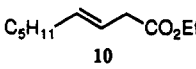
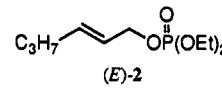
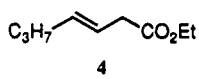
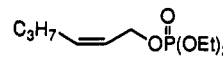
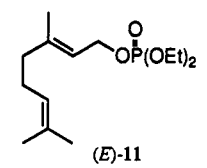
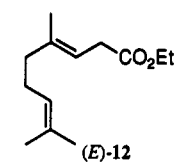
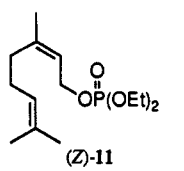
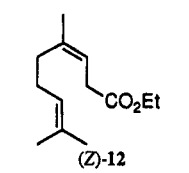
The carbonylation of diethyl 2-hexen-1-yl phosphate (**2**) has been examined as a complicated example with respect to catalysts and bases (eq 5). Palladium(0)–



phosphine complexes such as $Pd_2(dba)_3$·$CHCl_3$–$4PPh_3$ and $Pd(PPh_3)_4$ were found to be the most effective catalysts. A base is required to remove phosphoric acid liberated. Without a base, **4** could not be obtained. More basic and sterically bulky amines such as *i*-Pr_2NEt gave satisfactory results. When the carbonylation of 2-hexenyl phosphate (**2**) was carried out in the presence of 0.5 mol % of $Pd_2(dba)_3$·$CHCl_3$, 2 mol % of PPh_3, and 1 equiv of *i*-Pr_2NEt in ethanol, ester **4** was obtained in 92% yield. The *E*:*Z* ratio of **4** obtained was determined to be 84:16.

(16) Murahashi, S.-I.; Imada, Y.; Taniguchi, Y.; Higashiura, S. *Tetrahedron Lett.* **1988**, *29*, 4945–4948.

Table II. Carbonylation of Allyl Phosphates[a]

entry	allyl phosphate	product	yield, %[b] (*E*:*Z* ratio)[c]
1	 7	 8	90 (100:0)
2	 9	 10	91 (85:15)
3	 (*E*)-2	 4	88 (84:16)
4	 (*Z*)-2	4	74 (84:16)
5	 (*E*)-11	 (*E*)-12	76 (97:3)[d]
6	 (*Z*)-11	 (*Z*)-12	95 (4:96)[d]

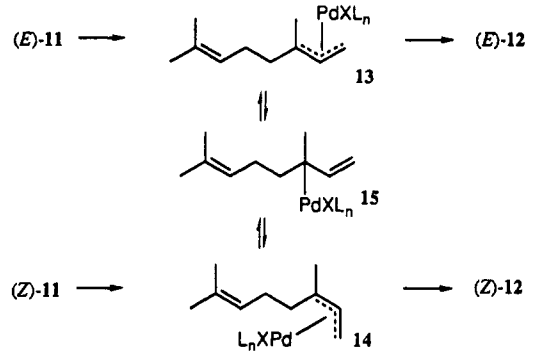
[a] General conditions: 2 mmol of substrate in 1 mL of ethanol, 0.5 mol % of $Pd_2(dba)_3$·$CHCl_3$, 2 mol % of PPh_3, 1 equiv of *i*-Pr_2NEt, 30 atm of CO, 50 °C, 5 h. [b] Isolated yield based on starting substrate. [c] Determined by ^1H and ^{13}C NMR. [d] Determined by capillary GLC.

As shown in Table II, various allyl phosphates are carbonylated smoothly to give the corresponding β,γ-unsaturated esters in good yields, and high regioselectivity is attained in all cases. Insertion of carbon monoxide occurs at the least substituted terminal allylic carbon to give linear esters rather than branched esters. It is noteworthy that the branched allyl phosphate, 1-octen-3-yl phosphate (**9**), was converted into ethyl 3-nonenoate (**10**), predominantly (entry 2). α,β-Unsaturated esters could not be detected among the products, although isomerizations of β,γ-unsaturated esters to α,β-unsaturated isomers occurs readily.[17] An isomeric mixture of β,γ-unsaturated esters were obtained irrespective of the stereochemistry of the starting substrates. To prove the question of double bond integrity of the product, the carbonylations of (*E*)- and (*Z*)-diethyl 2-hexen-1-yl phosphates ((*E*)- and (*Z*)-**2**) has been examined under the same conditions (entries 3 and 4). (*E*)- and (*Z*)-phosphates **2** can be converted into a mixture of (*E*)- and (*Z*)-ethyl 3-heptenoate ((*E*)- and (*Z*)-**4**) in a same ratio (ca. 8:2), irrespective of the stereochemistry of the starting phosphate. Lost of the stereochemistry of the carbon–carbon double bond seems to be due to the π–σ–π-isomerization of intermediate π-allylpalladium complexes.[18] Thermodynamically stable (*E*)-isomers are obtained preferentially, irrespective of the stereochemistry of the starting substrates. Diethyl cinnamyl phosphate (**7**) was carbonylated

(17) Alcock, S. G.; Baldwin, J. E.; Bohlmann, R.; Harwood, L. M.; Seeman, J. I. *J. Org. Chem.* **1985**, *50*, 3526–3535.

(18) (a) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642–2653. (b) Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107* 2046–2054.

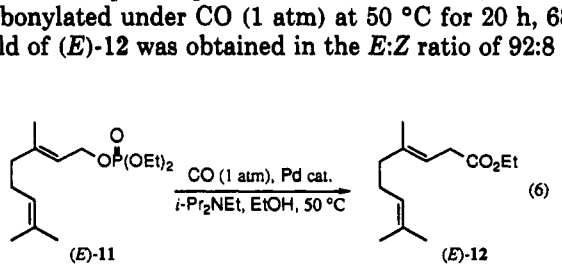
Scheme I



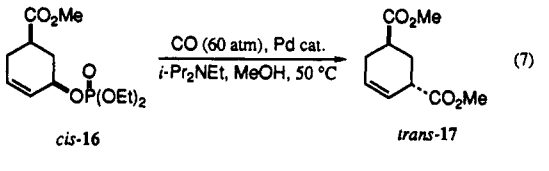
to give (*E*)-ethyl 4-phenyl-3-butenoate ((*E*)-**8**) stereoselectively (entry 1).

Homogeranic acid and homoneric acid, which are precursors of tetrahydroactinidiolides,[19] can be obtained stereoselectively from geraniol and nerol, respectively. Thus, the carbonylation of diethyl geranyl phosphate ((*E*)-**11**) afforded (*E*)-ethyl 4,8-dimethyl-3,7-nonadienoate ((*E*)-**12**) in the *E*:*Z* ratio of 97:3 (entry 5), while that of diethyl neryl phosphate ((*Z*)-**11**) gave (*Z*)-**12** in the *E*:*Z* ratio of 4:96 (entry 6). Virtually, the geometric integrity of the double bonds in (*E*)- and (*Z*)-**11** is maintained during the reaction. Control experiments show that the isomerization of (*Z*)-**12** to (*E*)-**12** does not occur under the reaction conditions. The ratio of π-allylpalladium complexes **13**:**14** derived from geranyl chloride is close to 1:1 at equilibrium in solution;[20] however, the product ratio of the carbonylation does not reflect the equilibrium ratio of π-allylpalladium complexes. This indicates that the CO insertion into π-allylpalladium intermediate **13** or **14** proceeds much faster than the syn–anti isomerization (π–σ–π mechanism)[18] between **13** and **14** under the present reaction conditions (Scheme I). In the carbonylation of trisubstituted allylic substrates such as **11**, syn–anti isomerization via sterically hindered tertiary σ-allylpalladium **15** is an unfavorable process.[18a] In contrast, in the carbonylation of 1,2-disubstituted substrates such as **2** and **9**, syn–anti isomerization via secondary σ-allylpalladium proceeds faster than CO insertion, giving the same *E*:*Z* ratio of carbonylation products irrespective of the stereochemistry of the starting substrates (entries 2–4 in Table II).

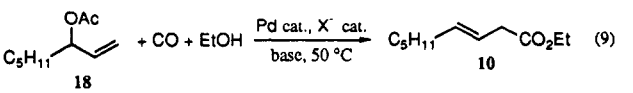
Carbonylation of allyl phosphates can be performed even under atmospheric pressure of CO. When (*E*)-**11** was carbonylated under CO (1 atm) at 50 °C for 20 h, 68% yield of (*E*)-**12** was obtained in the *E*:*Z* ratio of 92:8 (eq 6).



In order to determine the stereochemistry of the carbonylation at the allylic carbon center, the reactions of *cis*- and *trans*-5-(methoxycarbonyl)-2-cyclohexen-1-ol[21] have been examined. The methoxycarbonylation of *cis*-diethyl 5-(methoxycarbonyl)-2-cyclohexen-1-yl phosphate (*cis*-**16**) (100% cis) gave *trans*-dimethyl 2-cyclohexene-1,5-dicarboxylate (*trans*-**17**) stereoselectively (eq 7). The cis:trans ratio of **17** obtained was determined to be 4:96 on the basis of the capillary GC analysis. The similar carbonylation of the trans enriched phosphate **16** (cis:trans = 36:64) afforded the cis enriched diester **17** (cis:trans = 63:37) (eq 8). Therefore, the carbonylation of **16** takes place with inversion of configuration at the allylic carbon center. Since the oxidative addition occurs with inversion of configuration,[22] the present result indicates that the insertion of CO into σ-alkylpalladium complexes proceeds with retention of configuration. This is consistent with the results obtained by palladium-promoted alkoxycarbonylation of olefins.[23]



Carbonylation of Allyl Acetates. Although allyl phosphates undergo carbonylation readily under mild conditions, allyl acetates show quite low reactivity toward the carbonylation. When 1-octen-3-yl acetate (**18**) was treated under the optimized conditions for the carbonylation of allyl phosphates, ethyl 3-nonenoate (**10**) was obtained only in 10% yield. The oxidative addition of allyl acetates to palladium(0) complexes proceeds quite efficiently at room temperature to give π-allylpalladium acetate complexes **1** (eq 1), and various palladium-catalyzed transformations of allyl acetates have been explored.[13] However, the complexes **1** are known to be converted into allyl acetate upon treatment with carbon monoxide.[14] Considering the facile insertion of carbon monoxide into π-allylpalladium bromide complexes, we examined the ligand exchange of acetate with bromide in aming at acceleration of the carbonylation of allyl acetates. In order to clarify the effect of bromide, ethoxycarbonylation of **18** has been examined precisely by using $Pd_2(dba)_3$·$CHCl_3$–PPh_3 catalyst in the presence of 1 equiv of *i*-Pr_2NEt and catalytic amount of halide (0.1 equiv) in ethanol at 50 °C (eq 9). The representative results of the effect of halides are listed in Table III.



The carbonylation of **18** without halide gave **10** in a low yield; however, the addition of halide enhances the carbonylation dramatically. When NaBr is used as a cocatalyst, the reaction proceeds quite efficiently to give

(19) (a) Kato, T.; Kumazawa, S.; Kitahara, Y. *Synthesis* **1972**, 573–574. (b) Hoye, T. R.; Caruso, A. J.; Kurth, M. J. *J. Org. Chem.* **1981**, *46*, 3550–3552. (c) Gnonlonfoun, N.; Zamarlik, H. *Tetrahedron Lett.* **1987**, *28*, 4035–4056.

(20) Akermark, B.; Vitagliano, A. *Organometallics* **1985**, *4*, 1275–1283.

(21) Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215–3216.

(22) (a) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730–4743. (b) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767–7768.

(23) (a) Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 485–490. (b) James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810–1823. (c) Stille, J. K.; Divakarumi, R. *J. Org. Chem.* **1979**, *44*, 3474–3482.

Table III. Effect of Halide on the Carbonylation of 18[a]

entry	halide	convn of 18, %[b]	yield, %[b,c]
1	none	44	82
2	LiCl	90	76
3	LiBr	87	74
4	NaCl	82	71
5	NaBr	96	83
6	NaI	88	81
7	Bu_4NBr	92	80

[a] General conditions: 1 mmol of **18** in 1 mL of ethanol, 1 mol % of $Pd_2(dba)_3{\cdot}CHCl_3$, 4 mol % of PPh_3, 0.1 equiv of halide, 1 equiv of *i*-Pr_2NEt, 30 atm of CO, 50 °C, 20 h. [b] Determined by GC. [c] Yield of **10** based on the consumed substrate.

10 in 80% yield. Addition of the other halides such as NaI and Bu_4NBr also enhances the carbonylation but is not so effective in comparison with that of NaBr.

The addition of a base also enhances the reaction dramatically. Sterically bulky basic amines ($pK_a \approx 10$) such as *i*-Pr_2NEt, *t*-$BuNMe_2$, and 2,2,6,6-tetramethylpiperidine give excellent results. The use of secondary amines such as *i*-Pr_2NH leads to the formation of *N,N*-diisopropyl-2-octenylamine (45%). When simple tertiary amines such as NEt_3 and pyridine are used, the conversions of **18** are high; however, the yields of **10** are low, because (i) tertiary amines react with π-allylpalladium intermediates to give quaternary allylammonium salts[20] and (ii) the elimination of acetic acid from allyl acetate occurs to give 1,3-dienes.[24] The use of less basic amines such as imidazole and inorganic bases such as Na_2CO_3 results in low yields of **10**.

The catalytic activity of various palladium catalysts (5 mol %) has been examined for the carbonylation of **18** in the presence of NaBr (50 mol %) at 50 °C. Pd(0)–PPh_3 complexes are found to be the best catalysts among those examined. The palladium complexes, which have no phosphine ligand such as $Pd_2(dba)_3{\cdot}CHCl_3$, have no catalytic activity. Monodentate arylphosphines such as PPh_3 are more effective in comparison with bidentate phosphines such as dppe and dppp and trialkylphosphines such as PBu_3. The molar ratio of PPh_3 to Pd is important, and 2:1 with the combination of $Pd_2(dba)_3{\cdot}CHCl_3$ and PPh_3 gives the best result among those examined. A large excess of PPh_3 decreases the yield of **10** because of the formation of quaternary allylphosphonium salts.[25] The catalytic activity is in the order of $Pd_2(dba)_3{\cdot}CHCl_3$–$4PPh_3 \approx Pd(PPh_3)_4 \approx Pd(CO)(PPh_3)_3 > Pd(OAc)_2$–$2PPh_3 \gg PdCl_2(PPh_3)_2$. The ratio of *E* to *Z* of the ester **10** is not dependent on bases, halide ions, and catalysts. The yield of **10** increases with increase of CO pressure, and 30 atm of CO pressure is required. The β,γ-unsaturated ester **10** are obtained at 50–80 °C in high yields. Allyl alkyl ether could not be detected among the products of the present reactions.[26]

A variety of allyl acetates can be carbonylated upon treatment with CO (30 atm) in ethanol in the presence of a $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol %)–PPh_3 (8 mol %) catalyst, NaBr (20 mol %), and *i*-Pr_2NEt (1.0 equiv) at 50 °C. The representative results are summarized in Table IV. Carbonylation of allyl acetates proceeds highly regioselectively to give the corresponding linear β,γ-unsaturated esters

Table IV. Carbonylation of Allyl Acetates[a]

entry	allyl acetate	product	yield, %[b] (*E*:*Z* ratio)[c]
1	C_3H_7, OAc, **3**	C_3H_7, CO_2Et, **4**	68 (80:20)
2	OAc, C_3H_7, **19**	**4**	78 (82:18)
3	Ph, OAc, **20**	Ph, CO_2Et, **8**	84 (100:0)
4	TMS, OAc, **21**	TMS, CO_2Et, **22**	76 (100:0)
5	BnO, OAc, **23**	BnO, CO_2Et, **24**	85 (88:12)
6	OAc, **25**	CO_2Et, **26**	80
7[d]	OAc, **27**	CO_2Et, **28**	57
8[d]	OAc, **29**	CO_2Et, **30**	59 (95:5)

[a] General conditions: 1 mmol of substrate in 1 mL of ethanol, 2 mol % of $Pd_2(dba)_3{\cdot}CHCl_3$, 8 mol % of PPh_3, 0.2 equiv of NaBr, 1 equiv of *i*-Pr_2NEt, 30 atm of CO, 50 °C, 20 h. [b] Isolated yield based on starting substrate. [c] Determined by ^1H and ^{13}C NMR. [d] 0.5 equiv of NaBr, 60 atm of CO, 80 °C.

without formation of α,β-unsaturated esters. Cinnamyl acetate (**20**) and 3-(trimethylsilyl)-2-propenyl acetate (**21**) undergo the carbonylation stereoselectively to give (*E*)-ethyl 4-phenyl-3-butenoate ((*E*)-**8**) and (*E*)-ethyl 4-(trimethylsilyl)-3-butenoate ((*E*)-**22**), respectively (entries 3 and 4). The reaction of secondary allyl acetates (entries 7 and 8) requires severe reaction conditions (60 atm of CO and 0.5 equiv of NaBr at 80 °C) because of the steric effect on the insertion of CO into secondary carbons.

The carbonylations of linalyl (**31**), geranyl ((*E*)-**32**), and neryl acetates ((*Z*)-**32**) have been examined in detail (Table V). The carbonylation of **31** under the standard conditions (condition A: CO (30 atm) at 50 °C) gave a 60:40 mixture of (*E*)- and (*Z*)-isomers of ethyl 4,8-dimethyl-3,7-nonadienoate (**12**) in >99% yield. The carbonylation of (*E*)-**32** under the same conditions gave (*E*)-**12** stereoselectively (*E*:*Z* = 93:7) but only in 6% yield. These results indicate that the oxidative addition of allyl acetates to palladium(0) complex occurs in an S_N2'-fashion at the γ-position.[27] Under more severe conditions (condition B: CO (60 atm) at 80 °C), the carbonylation of (*E*)-**32** proceeded efficiently to give (*E*)-**12** stereoselectively (*E*:*Z* = 93:7) in 74% yield, while that of (*Z*)-**32** gave (*Z*)-**12** preferentially in 78% yield (*E*:*Z* = 14:86).

Allyl esters having low reactivities can be also carbonylated under the present conditions using bromide ion. 2-Hexenyl benzoate (**6**) showed quite low reactivity for carbonylation (entry 6 in Table I); however, the carbon-

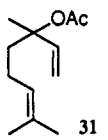
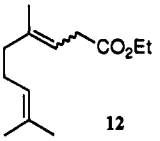
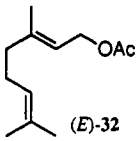
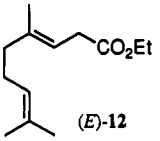
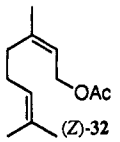
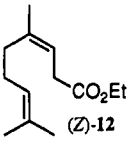
(24) (a) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075–2078. (b) Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301–2304.

(25) Tamura, R.; Kato, M.; Saegusa, K.; Kaihana, M.; Oda, D. *J. Org. Chem.* **1987**, *52*, 4121–4124.

(26) Guibe, F.; M'leux, Y. S. *Tetrahedron Lett.* **1981**, *22*, 3591–3594.

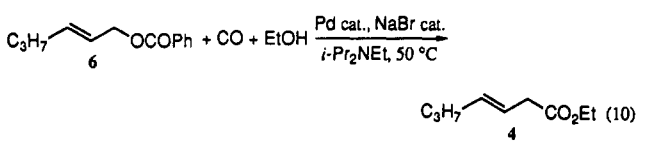
(27) Osakada, K.; Chiba, T.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1589–1591.

Table V. Carbonylation of Acetates 31, (E)-32, and (Z)-32

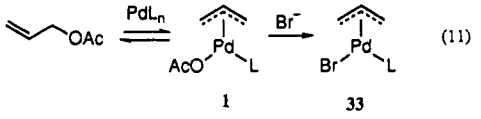
entry	allyl acetate	conditions[a]	product	yield, %[b]	E:Z ratio[c]
1	 31	A	 12	90 (99)	60:40
2	 (E)-32	A	 (E)-12	(6)	93:7
3		B		74 (74)	93:7
4	 (Z)-32	B	 (Z)-12	68 (78)	14:86

[a] General conditions: 1 mmol of substrate in 1 mL of ethanol, 2 mol % of $Pd_2(dba)_3{\cdot}CHCl_3$, 8 mol % of PPh_3, 1 equiv of $i\text{-}Pr_2NEt$, and other conditions are as follows: (A) 0.2 equiv of NaBr, 30 atm of CO, 50 °C, 20 h; (B) 0.5 equiv of NaBr, 60 atm of CO, 80 °C, 20 h. [b] Isolated yield based on substrate, and GC yield in parentheses. [c] Determined by capillary GC and ^{13}C NMR.

ylation of 6 in the presence of a catalytic amount of NaBr proceeds quite efficiently to give ester 4 in 83% yield (eq 10). Similar carbonylation of 2-hexenyl trifluoroacetate (5) gives ester 4 in 75% yield.



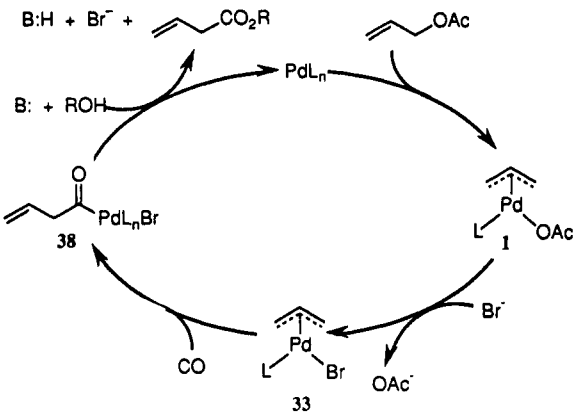
Mechanistic Aspect. Oxidative addition of allyl acetates to palladium(0) complexes gives π-allylpalladium acetate complex 1 readily;[14c] however, the carbonylation of allyl acetates proceeds very slowly, because 1 undergoes back reaction to give allyl acetate upon treatment with carbon monoxide.[14] The addition of a catalytic amount of NaBr enhances the carbonylation dramatically. The key step of the carbonylation seems to be the ligand exchange of the acetate complex 1 with bromide ion to form complex 33 (eq 11). Exclusive formation of ethyl



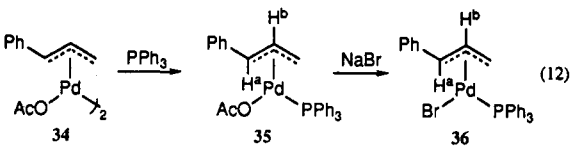
3-heptenoate (4) from either 2-hexen-1-yl acetate (3) or 1-hexen-3-yl acetate (19) clearly shows the intermediacy of π-allyl complexes. The ligand exchange of π-allylpalladium acetate complex 1 with bromide ion has been established precisely. The ^1H NMR spectra clearly shows that monomeric π-allyl(triphenylphosphine)palladium acetate (35), $Pd(\eta^3\text{-}1\text{-}Ph\text{-}allyl)(OAc)PPh_3$, wss obtained exclusively upon treatment of dimeric π-allylpalladium acetate $[Pd(\eta^3\text{-}1\text{-}Ph\text{-}allyl)(OAc)]_2$ (34) with 1 equiv of PPh_3[28] in CD_3OD–$CDCl_3$. Further, the NMR spectrum shows that the π-allylpalladium acetate complex 35 can be converted to π-allylpalladium bromide complex 36 by

(28) Powell, J.; Shaw, B. L. J. Chem. Soc. A 1967, 1839–1851.

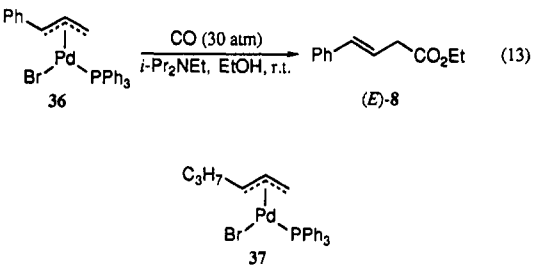
Scheme II



addition of 1 equiv of NaBr (eq 12). Thus, the double-triplet signal at 6.24 ppm (H^b) is shifted immediately to 6.14 ppm, and the double-doublet signal at 5.69 ppm (H^a) is shifted to 5.33 ppm. The spectrum obtained is exactly same with that of $Pd(\eta^3\text{-}1\text{-}Ph\text{-}allyl)(Br)PPh_3$ (36), which can be obtained upon treatment of $[Pd(\eta^3\text{-}1\text{-}Ph\text{-}allyl)(Br)]_2$ with 1 equiv of PPh_3.[28] These results clearly show



that the ligand exchange of π-allylpalladium acetate complexes with bromide ion proceeds very fast to give the π-allylpalladium bromide complexes. When bromo(1–3-η-1-phenylallyl)(triphenylphosphine)palladium(II) (36) was treated with CO (30 atm) in ethanol at room temperature for 2 h in the presence of $i\text{-}Pr_2NEt$, the ester (E)-8 was obtained in >99% yield (eq 13). Furthermore,



the carbonylation of 36 under CO (1 atm) gave 10% yield of 8 after 2 h, and 8 was obtained in >99% yield after 24 h. Similarly, the carbonylation of bromo(1–3-η-2-hexenyl)-(triphenylphosphine)palladium(II) (37), which was prepared by the reaction of dimeric $[Pd(\eta^3\text{-}2\text{-}hexenyl)(Br)]_2$ with 1 equiv of PPh_3,[28] under 30 atm of CO gave the ester 4 in 85% yield (E:Z = 85:15). The stereochemistry of the carbonylations of the palladium complexes 36 and 37 is similar to that of the catalytic carbonylations with these allyl acetates (entries 1 and 3 in Table IV). Apparently, the π-allylpalladium bromide complex 33 is a key intermediate for the carbonylation of allyl acetates.

The present carbonylation reaction can be rationalized by assuming Scheme II. The first step is the oxidative addition of allyl acetate to Pd(0) species to give π-allylpalladium acetate complex 1, which undergoes substitution of the acetate ligand with bromide ion to give π-allylpalladium bromide complex 33. Insertion of CO to 33 gives acylpalladium complex 38. This is supported by

the isolation of acylpalladium complexes by the carbonylation of π-allylpalladium bromide complexes.[29] Alkoxycarbonylation of **38** with alcohols would give β,γ-unsaturated esters, bromide ion, and palladium(0) species to complete catalytic cycle. An alternative pathway which involves the formation of (alkoxycarbonyl)(σ-allyl)palladium complex,[15] derived from direct base-induced nucleophilic attack of alcohol to co-ordinated CO, cannot be eliminated.

Conclusion. The palladium(0)-catalyzed alkoxycarbonylation of allyl phosphates under mild reaction conditions gives β,γ-unsaturated esters selectively. Allyl acetates are also carbonylated in the presence of catalytic amount of bromide ion. These carbonylation occur highly regioselectively at the less hindered allylic terminal carbon to give linear esters. The stereochemistry is the inversion of configuration at the allylic carbon center.

Experimental Section

General. NMR spectra were measured in $CDCl_3$ solution at 35 °C unless otherwise noted. $Pd_2(dba)_3{\cdot}CHCl_3$[30] and $Pd_4(PPh_3)_4$[31] was prepared by the reported methods. Allyl acetates and phosphates were prepared from the corresponding alcohols according to the reported procedure.[12]

Palladium-Catalyzed Carbonylation of Various 2-Hexenol Derivatives. In a 10-mL stainless-steel autoclave were placed $Pd_2(dba)_3{\cdot}CHCl_3$ (0.01 mmol), PPh_3 (0.04 mmol), allylic compounds (1.0 mmol), *i*-Pr_2NEt (1.0 mmol), and ethanol (1.0 mL). After CO was introduced up to 30 atm, the mixture was stirred at 50 °C for 1 h. The conversion of 2-hexenol derivatives and the yield of ethyl 3-heptenoate (**4**) based on consumed substrate were calculated by GC using tridecane as an internal standard. These results were listed in Table I.

Palladium-Catalyzed Carbonylation of Diethyl (*E*)-2-Hexen-1-yl Phosphate ((*E*)-2). (A) Influence of Catalyst. A solution of catalyst (0.01 mmol), (*E*)-**2** (1.0 mmol), and *i*-Pr_2NEt (1.0 mmol) in ethanol (1.0 mL) was stirred under CO (30 atm) at 50 °C for 5 h. The conversion of (*E*)-**2** and the yield of **4** based on consumed substrate were calculated by GC using octadecane as an internal standard. These results are as follows: catalyst $Pd_2(dba)_3{\cdot}CHCl_3$–4PPh_3 (97%, 95%), $Pd(PPh_3)_4$, (97%, 93%), $PdCl_2(CH_3CN)_2$ (93%, 86%), $PdCl_2(PPh_3)_2$ (77%, 61%) Pd–C (46%, 83%), and $Pd(OAc)_2$ (47%, 79%). **(B) Influence of Base.** A solution of $Pd(PPh_3)_4$ (0.01 mmol), (*E*)-**2** (1.0 mmol), and base (1.0 mmol) in ethanol (1.0 mL) was stirred under CO (30 atm) at 50 °C for 5 h. The conversion of (*E*)-**2** and the yield of **4** are as follows: base *i*-Pr_2NEt (98%, 96%), *i*-Pr_2NH (97%, 42%), NEt_3 (92%, 16%), pyridine (90%, 2%), and without any base (55%, 0%).

Palladium-Catalyzed Carbonylation of 1-Octen-3-yl Acetate (18). (A) Influence of Halide. A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.01 mmol), PPh_3 (0.04 mmol), halide (0.10 mmol), **18** (1.0 mmol), and *i*-Pr_2NEt (1.0 mmol) in ethanol (1.0 mL) was stirred under CO (30 atm) at 50 °C for 20 h. The conversion of **18** and the yield of ethyl 3-nonenoate (**10**) based on consumed substrate were calculated by GC. These results are listed in Table III. **(B) Influence of Base.** A solution of $Pd(PPh_3)_4$ (0.05 mmol), NaBr (0.50 mmol), **18** (1.0 mmol), and base (1.0 mmol) in ethanol (3.0 mL) was stirred under CO (30 atm) at 50 °C for 5 h. The conversion of **18** and the yield of **10** are as follows: base *i*-Pr_2NEt (99%, 75%), *t*-$BuNMe_2$ (95%, 73%), 2,2,6,6-tetramethylpiperidine (99%, 62%), NEt_3 (97%, 46%), *i*-Pr_2NH (99%, 40%), pyridine (87%, 39%), imidasole (75%, 5%), Na_2CO_3 (65%, 52%), and without any base (48%, 44%). **(C) Influence of Catalyst.** A solution of catalyst (0.05 mmol), NaBr (0.50 mmol), **18** (1.0 mmol), and *i*-Pr_2NEt (1.0 mmol) in ethanol (2.0 mL) was stirred under CO (30 atm) at 50 °C for 5 h. The conversion of **18** and the yield of **10** are as follows: catalyst $Pd_2(dba)_3{\cdot}CHCl_3$ (0%, 0%), $Pd_2(dba)_3{\cdot}CHCl_3$–2PPh_3 (75%, 93%), $Pd_2(dba)_3{\cdot}CHCl_3$–4PPh_3 (94%, 91%), $Pd_2(dba)_3{\cdot}CHCl_3$–4PBu_3 (27%, 63%), $Pd_2(dba)_3{\cdot}CHCl_3$–2dppe (27%, 41%), $PdCO(PPh_3)_4$ (93%, 73%), $Pd(dba)_2$–2PPh_3 (84%, 80%), $Pd(OAc)_2$–2PPh_3 (63%, 99%), $Pd(acac)_2$–2PPh_3 (80%, 74%), $PdCl_2(PPh_3)_2$ (13%, 15%), $Pd(PPh_3)_4$ (99%, 73%), $Pd(PCy_3)_2$ (16%, 69%). **(D) Influence of CO Pressure.** A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.025 mmol), PPh_3 (0.10 mmol), NaBr (0.50 mmol), **18** (1.0 mmol), and *i*-Pr_2NEt (1.0 mmol) in ethanol (2.0 mL) was stirred under CO at 50 °C for 5 h. The conversion of **18** and the yield of **10** are as follows: P_{CO} 1 (24%, 33%), 5 (57%, 63%), 10 (68%, 78%), 20 (78%, 77%), 30 (96%, 77%), and 50 (94%, 80%) atm. **(E) Temperature Dependency.** A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.025 mmol), PPh_3 (0.10 mmol), NaBr (0.50 mmol), **18** (1.0 mmol), and *i*-Pr_2NEt (1.0 mmol) in ethanol (2.0 mL) was stirred under CO (30 atm) for 5 h. The conversion of **18** and the yield of **10** are as follows: *T* 30 (61%, 75%), 40 (89%, 78%), 50 (92%, 88%), 60 (97%, 84%), 70 (97%, 77%), and 80 (97%, 81%) °C.

General Procedure for Carbonylation of Allylic Phosphates. In a 10-mL stainless-steel autoclave were placed under argon $Pd_2(dba)_3{\cdot}CHCl_3$ (0.010 g, 0.01 mmol), PPh_3 (0.010 g, 0.04 mmol), allylic phosphate (2.0 mmol), *i*-Pr_2NEt (0.35 mL, 2.0 mmol), and ethanol (1.0 mL). CO was introduced up to 30 atm, and the mixture was stirred at 50 °C for 5 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with water. The organic phase was separated and dried over $MgSO_4$. After removal of the solvents, the residue was purified by using SiO_2 column chromatography to afford β,γ-unsaturated ester. When a mixture of (*E*)- and (*Z*)-β,γ-unsaturated esters was obtained, the stereoisomeric ratio of *E*:*Z* was determined on the basis of ^{13}C and ^1H NMR and capillary GC analyses. The results for carbonylation of various kinds of allylic phosphates are listed in Table II.

General Procedure for Carbonylation of Allylic Acetates. Condition A. A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.020 g, 0.02 mmol), PPh_3 (0.021 g, 0.08 mmol), NaBr (0.020 g, 0.20 mmol), allylic acetate (1.0 mmol), and *i*-Pr_2NEt (0.17 mL, 1.0 mmol) in ethanol (1.0 mL) was stirred under CO (30 atm) at 50 °C for 20 h. The workup, purification, and analyses were performed as described above. The results for the carbonylation of various kinds of allylic acetates are listed in Tables IV (entries 1–6) and V (entries 1 and 2). Carbonylations of 2-hexenyl benzoate (**6**) and 2-hexenyl trifluoroacetate (**5**) were carried out according the same procedure. **Condition B.** The reaction conditions were same to the condition A except the following factors: NaBr (0.50 mmol), CO (60 atm), and temperature (80 °C). These results are summarized in Tables IV (entries 7 and 8) and V (entries 3 and 4).

Ethyl 3-heptenoate (4): bp 80–85 °C (9 mmHg) (Kugelrohr); IR (neat) 1740 (C=O), 1250 (CO) cm^{-1}; ^1H NMR (500 MHz) δ 0.89 (t, *J* = 7.1 Hz, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 1.39 (tq, *J* = 7.3 and 7.1 Hz, 2 H, H-6), 2.11 (dt, *J* = 5.7 and 7.3 Hz, 2 H, H-5), 3.01 (d, *J* = 5.7 Hz, 2 H, H-2), 4.13 (q, *J* = 7.1 Hz, 2 H), 5.52 (dt, *J* = 16 and 5.7 Hz, 1 H H-3), 5.57 (dt, *J* = 16 and 5.7 Hz, 1 H, H-4) for (*E*)-**4**; 0.91 (t, *J* = 7.1 Hz, 3 H), 3.07 (d, *J* = 5.4 Hz, 2 H, H-2) for (*Z*)-**4**; $^{13}C\{^1H\}$ NMR (25 MHz) δ 13.6, 14.2 22.4 (C-5), 34.6, 38.2 (C-2), 60.5, 121.8 (C-4), 134.5 (C-3), 172.1 (C=O) for (*E*)-**4**; 29.4 (C-5), 33.1 (C-2), 121.1 (C-4), 133.2 (C-3), 171.9 (C=O) for (*Z*)-**4**. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.75; H, 10.21.

(*E*)-Ethyl 4-phenyl-3-butenoate ((*E*)-8): R_f = 0.20 (SiO_2, CH_2Cl_2–hexane, 3:7); bp 75–80 °C (0.2 mmHg) (Kugelrohr); IR (neat) 1735 (C=O), 1650 (C=C), 1250 (CO) cm^{-1}; ^1H NMR (270 MHz) δ 1.26 (t, *J* = 7.2 Hz, 3 H), 3.21 (dd, *J* = 1.3 and 7.0 Hz, 2 H, H-2), 4.15 (q, *J* = 7.2 Hz, 2 H), 6.28 (dt, *J* = 16 and 7.0 Hz, 1 H, H-3), 6.48 (dt, *J* = 16 and 1.3 Hz, 1 H, H-4), 7.10–7.40 (m, 5 H, Ph); $^{13}C\{^1H\}$ NMR (25 MHz) δ 14.2, 38.3 (C-2), 60.6, 122.0 (C-4), 126.3, 127.5, 128.5, 133.2, 136.9 (i), 171.2 (C=O). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.45.

Ethyl 3-nonenoate (10): R_f = 0.23 (SiO_2, CH_2Cl_2–hexane, 3:7); bp 70–71 °C (4 mmHg); IR (neat) 1740 (C=O), 1250 (CO) cm^{-1}; ^1H NMR (270 MHz) δ 0.88 (t, *J* = 6.9 Hz, 3 H), 1.26 (t, *J* = 6.9 Hz, 3 H), 1.30–1.45 (m, 6 H), 1.96–2.08 (m, 2 H, H-5), 3.01 (d, *J* = 5.4 Hz, 2 H, H-2), 4.13 (q, *J* = 6.9 Hz, 2 H), 5.51 (dt, *J* = 15.6 and 5.6 Hz, 1 H, H-4), 5.57 (dt, *J* = 15.6 and 5.4 Hz, 1 H,

(29) Ozawa, F.; Son, T.; Osakada, K.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1067–1068.

(30) (a) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253–260. (b) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 134–140.

(31) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121–125.

H-3) for (*E*)-**10**; 3.09 (d, J = 5.4 Hz, 2 H, H-2) for (*Z*)-**10**; $^{13}C\{^1H\}$ NMR (25 MHz) δ 14.0, 14.2, 22.6, 28.9, 31.4, 32.5 (C-5), 38.2 (C-2), 60.5, 121.6 (C-4), 134.7 (C-3), 172.1 (C=O) for (*E*)-**10**; 27.1 (C-5), 33.1 (C-2), 120.9 (C-4), 133.4 (C-3), 171.9 (C=O) for (*Z*)-**10**. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.62; H, 10.90.

(*E*)-Ethyl 4,8-dimethyl-3,7-nonadienoate ((*E*)-12): R_f = 0.37 (SiO_2, CH_2Cl_2–hexane, 1:9); bp 65–70 °C (0.2 mmHg) (Kugelrohr); IR (neat) 1740 (C=O), 1255 (CO) cm^{-1}; ^1H NMR (270 MHz) δ 1.25 (t, J = 7.1 Hz, 3 H), 1.60 (br s, 3 H), 1.63 (br s, 3 H, 4-CH_3), 1.67 (br s, 3 H), 1.95–2.20 (m, 4 H), 3.03 (dq, J = 7.1 and 1.0 Hz, 2 H, H-2), 4.13 (q, J = 7.1 Hz, 2 H), 5.05–5.15 (m, 1 H, H-7), 5.33 (tq, J = 7.1 and 1.2 Hz, 1 H, H-3); $^{13}C\{^1H\}$ NMR (68 MHz) δ 14.2, 16.4, 17.7, 25.7, 26.6, 33.9 (C-2), 39.6 (C-5), 60.4 115.9 (C-3), 124.1 (C-7), 131.5 (C-8), 138.9 (C-4), 172.4 (C=O). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 73.96; H, 10.56.

(*Z*)-Ethyl 4,8-dimethyl-3,7-nonadienoate ((*Z*)-12): IR (neat) 1740 (C=O), 1270 (CO) cm^{-1}; ^1H NMR (270 MHz) δ 1.25 (t, J = 7.1 Hz, 3 H), 1.60 (br s, 3 H), 1.68 (br s, 3 H), 1.75 (br s, 3 H, 4-CH_3), 1.96–2.23 (m, 4 H), 3.03 (br d, J = 7 Hz, 2 H, H-2), 4.14 (q, J = 7.1 Hz, 2 H), 5.05–5.18 (m, 1 H, H-7), 5.33 (br t, J = 7 Hz, 1 H, H-3); $^{13}C\{^1H\}$ NMR (68 MHz) δ 14.2, 17.6, 23.4, 25.7, 26.4, 32.2 (C-2), 33.7 (C-5), 60.5, 116.6 (C-3), 124.0 (C-7), 131.9 (C-8), 139.0 (C-4), 172.5 (C=O). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 73.86; H, 10.49.

Carbonylation of (*E*)-11 under Atmospheric Pressure of CO. In a 25-mL side-armed flask were placed $Pd_2(dba)_3$·$CHCl_3$ (0.01 mmol), PPh_3 (0.04 mmol), (*E*)-**11** (2.0 mmol), *i*-Pr_2NEt (2.0 mmol), and ethanol (1.0 mL). A rubber balloon filled with CO was attached to the flask, and the mixture was stirred at 50 °C for 20 h. Usual workup afforded (*E*)-**12** in 68% yield.

Control Experiment for the Thermal Isomerization of (*Z*)-12 under Reaction Condition B. In a 10-mL stainless-steel autoclave, control experiment for the thermal isomerization of (*Z*)-**12** (*E*:*Z* = 7:93) was carried out under condition B. After stirring for 20 h, the reaction mixture was analyzed by using capillar GC. No change of isomer ratio was observed.

Dimethyl Cyclohex-4-ene-1,3-dicarboxylate (17). The carbonylation of *cis*-diethyl 5-(methoxycarbonyl)-2-cyclohexyl phosphate (*cis*-**16**) (cis:trans = 100:0) was carried out as described above. Instead of ethanol, methanol was used as a solvent and CO was introduced up to 60 atm. Usual workup gave *trans*-**17** as a colorless oil in 68% yield. This product was contaminated with *cis*-**17** as the another isomer. The cis:trans ratio of **17** was determined to be 4.0:96.0 on the basis of capillary GC analysis. ***trans*-17**: IR (neat) 1735 (C=O), 1160 (CO) cm^{-1}; ^1H NMR (500 MHz) δ 1.88 (ddd, J = 6.2, 10.8, and 13.5 Hz, 1 H, H-2), 2.21–2.35 (m, 3 H, H-2 and H-6), 2.82 (dddd, J = 3.2, 5.7, 8.9, and 10.8 Hz, 1 H, H-1), 3.21 (m, 1 H, H-3), 3.69 (s, 3 H), 3.70 (s, 3 H), 5.75–5.87 (m, 2 H). The carbonylation of the trans-enriched **16** (cis:trans = 36.3:63.7) under the same conditions gave cis-enriched **17** (cis:trans = 62.8:37.2) in 73% yield.

(*E*)-Ethyl 4-(trimethylsilyl)-3-butenoate ((*E*)-22): ^1H NMR (270 MHz) δ 0.07 (s, 9 H), 1.26 (t, J = 7.1 Hz, 3 H), 3.14 (dd, J = 1.5 and 6.4 Hz, 2 H, H-2), 4.15 (q, J = 7.1 Hz, 2 H), 5.79 (dt, J = 18.5 and 1.5 Hz, 1 H, H-4), 6.10 (dt, J = 18.5 and 6.4 Hz, 1 H, H-3); $^{13}C\{^1H\}$ NMR (68 MHz) δ −1.4, 14.1, 42.0 (C-2), 60.6, 134.7 (C-4), 137.6 (C-3), 172.0 (C=O).

Ethyl 5-(benzyloxy)-3-pentenoate (24): bp 115–120 °C (0.2 mmHg) (Kugelrohr); IR (neat) 1740 (C=O), 1250 (CO) cm^{-1}; ^1H NMR (270 MHz) δ 1.25 (t, J = 7.2 Hz, 3 H), 3.08 (dd, J = 1.1 and 6.6 Hz, 2 H, H-2), 4.01 (dd, J = 1.1 and 5.6 Hz, 1 H, H-5), 4.13 (q, J = 7.2 Hz, 2 H), 4.50 (s, 2 H, OCH_2Ph), 5.72 (dtt, J = 15.5, 1.1, and 5.6 Hz, 1 H, H-4), 5.85 (dtt, J = 15.5, 1.1, and 6.6 Hz, 1 H, H-3), 7.20–7.35 (m, 5 H, Ph) for (*E*)-**24**; 4.52 (s, 2 H, OCH_2-Ph) for (*Z*)-**24**; $^{13}C\{^1H\}$ NMR (68 MHz) δ 14.2, 37.8, (C-2), 60.6, 70.3, 72.1, 125.6 (C-4), 127.6, 127.8, 128.4, 130.4 (C-3), 138.3 (i), 171.4 (C=O) for (*E*)-**24**; 33.4 (C-2), 127.7 (C-4), 132.8 (C-3), 172.1 (C=O) for (*Z*)-**24**. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.10; H, 7.89.

Ethyl 3-cyclohexylidenepropanoate (26): R_f = 0.35 (SiO_2, CH_2Cl_2–hexane, 1:1); bp 90–95 °C (6 mmHg) (Kugelrohr); IR (neat) 1740 (C=O), 1240 (CO) cm^{-1}; ^1H NMR (270 MHz) δ 1.22 (t, J = 7.1 Hz, 3 H), 1.40–1.65 (m, 6 H), 2.08–2.15 (m, 4 H), 3.02 (d, J = 7.1 Hz, H-2), 4.13 (q, J = 7.1 Hz, 2 H), 5.22 (t, J = 7.1 Hz, 1 H, H-3); $^{13}C\{^1H\}$ NMR (68 MHz) δ 14.3, 26.8, 27.6, 28.5, 29.0, 33.1, 37.0 (C-2), 60.5, 112.6 (C-3), 143.4 (C-4), 172.6 (C=O). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.28; H, 9.93.

Ethyl 2-cyclohexenecarboxylate (28): R_f = 0.30, (SiO_2, CH_2Cl_2–hexane, 3:7); bp 90–95 °C (17 mmHg) (Kugelrohr); IR (neat) 1730 (C=O), 1200 (CO) cm^{-1}; ^1H NMR (100 MHz) δ 1.27 (t, J = 7.1 Hz, 3 H), 1.42–2.14 (m, 6 H), 2.94–3.21 (m, 1 H, H-1), 4.14 (q, J = 7.1 Hz, 2 H), 5.63–5.97 (m, 2 H, H-2 and H-3); $^{13}C\{^1H\}$ NMR (25 MHz) (25 MHz) δ 14.3, 21.0, 24.9, 25.4, 41.3 (C-1), 60.4, 124.8 (C-3), 129.3 (C-2), 174.0 (C=O). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.65; H, 9.09.

Ethyl 2,5-dimethyl-3-hexenoate (30): R_f = 0.40 (SiO_2, CH_2Cl_2–hexane, 1:1), IR (neat) 1740 (C=O), 1250 (CO) cm^{-1}; ^1H NMR (270 MHz) δ 0.97 (d, J = 5.7 Hz, 6 H), 1.23 (d, J = 7.0 Hz, 3 H), 1.25 (t, J = 7.1 Hz, 3 H), 2.17–2.37 (m, 1 H), 3.054 (dq, J = 7.0 and 7.0 Hz, 1 H, H-2), 4.12 (q, J = 7.1 Hz, 2 H), 5.46 (dd, J = 7.0 and 15.5 Hz, 1 H, H-3), 5.53 (dd, J = 5.8 and 15.5 Hz, 1 H, H-4) for (*E*)-**30**; 3.048 (dq, J = 7.1 and 7.1 Hz, 1 H, H-2) for (*Z*)-**30**; $^{13}C\{^1H\}$ NMR (25 MHz) δ 14.2, 17.6 (2-CH_3), 22.3 (5-CH_3 and C-6), 30.9, 42.8 (C-2), 60.4, 126.0 (C-3), 139.0 (C-4), 175.1 (C=O) for (*E*)-**30**; 38.8 (C-2) for (*Z*)-**30**.

Di-μ-bromobis[1-3-η-(1-phenylallyl)]dipalladium(II) (39). Di-μ-bromo complex **39** was prepared according to the reported procedure:[28] yellow prisms; mp 183–183.5 °C dec; ^1H NMR (270 MHz) δ 3.06 (d, J = 11.7 Hz, 1 H, anti-H-3), 4.03 (d, J = 6.8 Hz, 1 H, syn-H-3), 4.71 (d, J = 11.7 Hz, 1 H, H-1), 5.82 (ddd, J = 6.8 11.7, and 11.7 Hz, 1 H, H-2), 7.10–7.60 (m, 5 H, Ph); $^{13}C\{^1H\}$ NMR (68 MHz) δ 60.6, 84.1, 105.5, 128.0, 128.5, 129.0, 137.0. Anal. Calcd for $C_{18}H_{18}Br_2Pd_2$: C, 35.62; H, 2.99; Br, 26.33. Found: C, 35.81; H, 2.99; Br, 26.70.

Di-μ-bromobis(1-3-η-2-hexenyl)dipalladium(II) (40). Di-μ-bromo complex **40** was prepared as described above: brown crystal; mp 90 °C dec; ^1H NMR (270 MHz) δ 0.96 (t, J = 7.2 Hz, 3 H), 1.4–1.8 (m, 3 H), 1.8–2.0 (m, 1 H), 2.86 (d, J = 12.0 Hz, 1 H, anti-H-1), 3.97 (d, J = 6.7 Hz, 1 H, syn-H-1), 3.9–4.1 (m, 1 H, H-3), 5.28 (ddd, J = 6.7, 11.4, and 12.0 Hz, 1 H, H-2).

Preparation of Di-μ-acetatobis[1-3-η-(1-phenylallyl)]palladium(II) (34). Di-μ-acetato complex **34** was prepared according to the reported procedure[32] as follows. To a solution of **39** (0.955 g, 1.57 mmol) in acetone (25 mL) was added AgOAc (0.577 g, 3.45 mmol). After the mixture was stirred at room temperature for 12 h, the resultant precipiate of AgBr was filtered off, and the filtrate was evaporated to dryness. Recrystallization from CH_2Cl_2–hexane gave **34** as yellow powder (0.609 g, 69%): mp 146–147 °C dec.

Ligand Exchange of Di-μ-acetatobis[1-3-η-(1-phenylallyl)]dipalladium(II) (34). In a 5φ NMR tube was placed a solution of palladium complex **34** (9.2 mg, 0.016 mmol) in a mixture of CD_3OD (0.3 mL) and $CDCl_3$ (0.3 mL) under argon, and the ^1H NMR spectrum was taken. To the solution was added PPh_3 (8.4 mg, 0.032 mmol), and the ^1H NMR spectrum was measured after 1 min. The ^1H NMR spectrum showed the formation of acetato[1-3-η-(1-phenylallyl)](triphenylphosphine)-palladium(II) (**35**), and complex **34** was not observed. To the solution was added powdered NaBr (3.2 mg, 0.032 mmol) at room temperature, and the ^1H NMR spectrum was taken after 1 min. The ^1H NMR spectrum of bromo[1-3-η-(1-phenylallyl)](triphenylphosphine)palladium(II) (**36**) was observed, and the signals corresponding to the complex **35** had disappeared completely. **34**: ^1H NMR (270 MHz) δ 1.60 (s, 6 H, OAc), 3.07 (d, J = 11.4 Hz, 2 H, anti-H-3), 3.94 (d, J = 6.4 Hz, 2 H, syn-H-3), 4.70 (d, J = 11.4 Hz, 2 H, H-1), 6.11 (ddd, J = 6.4, 11.4, and 11.4 Hz, 2 H, H-2), 7.2–7.4 (m, 10 H, Ph). **35**: ^1H NMR (270 MHz) δ 1.50 (s, 3 H, OAc), 2.9–3.1 (br, 2 H, H-3), 5.69 (dd, J = 9.0 and 12.3 Hz, 1 H, H-1), 6.24 (dt, J = 12.3 and 9.2 Hz, 1 H, H-2), 7.2–7.6 (m, 20 H, Ph). **36**: ^1H NMR (270 MHz) δ 3.0–3.3 (m, 2 H, H-3), 5.33 (dd, J = 9.2 and 12.0 Hz, 1 H, H-1), 6.14 (dt, J = 12.0, and 9.0 Hz, H-2), 7.2–7.7 (m, 20 H, Ph).

Bromo[1-3-η-(1-phenylallyl)](triphenylphosphine)-palladium(II) (36): Complex **36** was prepared by the reaction of di-μ-bromo complex **39** with PPh_3 according to the reported procedure:[28] ^1H NMR (270 MHz) δ 2.97 (d, J = 11.8 Hz, 1 H, anti-H-3), 3.11 (d, J = 6.1 Hz, 1 H, syn-H-3), 5.30 (dd, J = 10.3

(32) Robinson, S. D.; Shaw, B. L. *J. Organomet. Chem.* **1965**, *3*, 367–370.

and 13.1 Hz, 1 H, H-1), 6.02 (m, 1 H, H-2), 7.0–8.0 (m, 20 H, Ph); ^{1}H NMR (270 MHz at −30 °C) δ 3.05 (d, J = 12.2 Hz, 1 H, H-3), 3.08 (d, J = 7.0 Hz, 1 H, H-3), 5.30 (dd, J = 10.0 and 13.1 Hz, 1 H, H-1), 6.08 (ddd, J = 7.0, 12.2, and 13.1 Hz, 1 H, H-2), 7.0–8.0 (m, 20 H, Ph). Anal. Calcd for $C_{27}H_{24}PdBrP$: C, 57.32; H, 4.28: Found: C, 57.71; H, 4.56.

Bromo(1-3-η-2-hexenyl)(triphenylphosphine)palladium-(II) (37). Complex **37** was prepared as described above: mp 135 °C dec; ^{1}H NMR (270 MHz) δ 0.99 (t, J = 7.6 Hz, 3 H), 1.4–1.9 (m, 2 H), 1.9–2.2 (m, 1 H, H-4) 2.5–2.7 (m, 1 H, H-4), 2.69 (d, J = 12.1 Hz, 1 H, anti-H-1), 3.02 (dd, J = 1.7 and 6.7 Hz, 1 H, syn-H-1), 4.43 (dddd, J = 3.5, 9.3, 9.3, and 12.7 Hz, 1 H, H-3), 5.34 (ddd, J = 6.7, 12.0, and 12.7 Hz, 1 H, H-2). Anal. Calcd for $C_{24}H_{26}PdPBr$: C, 54.34; H, 4.94: Found: C, 53.93; H, 4.73.

Carbonylation of Palladium Complex 36. A solution of complex **36** (0.0565 g, 0.1 mmol) and i-Pr_2NEt (0.034 mL, 0.2 mmol) in ethanol (1 mL) was stirred under CO (30 atm) at room temperature for 2 h. The yield was determined by GC using tridecane as an internal standard. Usual workup followed by column chromatography on SiO_2 gave (*E*)-**8** (*E*:*Z* = 100:0) in 93% yield. The carbonylation of **36** under an atmospheric pressure of CO was performed in a 10-mL side-armed flask equipped with a rubber ballon filled with CO.

The carbonylation of palladium complex **37** was performed under 30 atm of CO as described above. Usual workup afforded **4** (*E*:*Z* = 85:15) in 85% yield.