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Synthesis and Properties of (η^3-1-Methylallyl)palladium(II) Formates as Models of Intermediates in the Palladium-Catalyzed Reductive Cleavage of Allylic Carboxylates and Carbonates with Formic Acid

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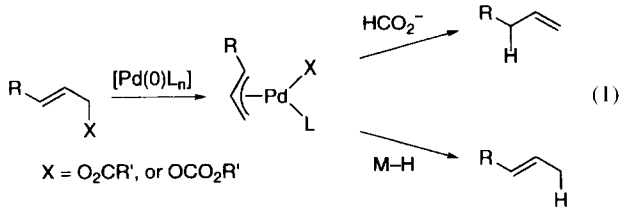
In order to gain insight into the mechanism of the regioselective formation of alkenes in the palladium-catalyzed reductive cleavage of allylic carboxylates or carbonates with formic acid, two types of (η^3-1-methylallyl)palladium formates (P1 and P2 types) have been prepared as simple models of catalytic intermediates. The P1 type is a neutral complex coordinated with one tertiary phosphine ligand and a formato ligand: [Pd(η^3-MeCHCHCH$_2$)(O$_2$CH)(L)] (L = PMePh$_2$, PMe$_2$Ph, PMe$_3$, P(*o*-tolyl)$_3$); the P2 type is a cationic complex bearing two tertiary phosphine ligands and a formate counter anion: [Pd(η^3-MeCHCHCH$_2$)L$_2$]$^+$CO$_2$H$^-$ (L = PMePh$_2$, PMe$_2$Ph, PMe$_3$). The structures and dynamic behavior of the complexes in solution have been examined in detail by NMR spectroscopy. Studies on the thermolysis of the P1 and P2-type complexes have clearly provided the following mechanistic viewpoints: (1) 1-butene and 2-butene are formed from the P1 species; (2) butadiene is liberated from the P2 species; (3) the ratio of 1-butene to 2-butene increases as the bulkiness of phosphine ligand increases. A mechanism involving two geometrical isomers of [Pd(η^3-MeCHCHCH$_2$)(H)(L)], which are formed by decarboxylation of the P1-type complexes, has been proposed for the formation of butenes.

Among various catalytic reactions utilizing palladium catalysts,[1,2] the catalytic reduction of allylic carboxylates (or carbonates) by formic acid or by metal hydrides (e.g. Na[BH$_4$] and Na[BH$_3$CN]) provides a useful means for the regioselective synthesis of alkenes.[2—8] It has been documented that the regiochemistry of product alkene is effectively controlled by the sort of reducing agent employed (Eq. 1). Thus, the reactions with formic acid as the reducing agent predominantly give terminal alkenes,[2—5] whereas the reactions with metal hydrides afford internal alkenes in high selectivities.[6] It has been further established by Keinan that the reduction of a cyclic allylic acetate with Na[BD$_4$] catalyzed by [Pd(PPh$_3$)$_4$] proceeds with the inversion of the stereochemistry at the acetoxy-substituted carbon, suggesting an internal attack of deuteride on the η^3-allyl ligand from the side of the palladium center.[7b] An internal attack of hydride on the η^3-allyl ligand was also confirmed for the reduction of alkenyloxiranes with formic acid.[8] Therefore, it seems quite likely that an (η^3-allyl)palladium hydride species is involved as the key intermediate in both catalytic systems, while the exact reason for the selective formation of terminal and internal alkenes with the respective reducing agents has remained unclarified.



(1)

In this paper we wish to examine the mechanism of reductive cleavage of allylic substrates with formic acid. In previous work[9] we confirmed the essential features of the catalytic cycle depicted in Scheme 1, in which the supporting ligand is omitted for simplicity. The first step is the oxidative addition of allylic substrates to a palladium(0) species (**A**) with cleavage of the C–O bond[10] to form (η^3-allyl)palladium complexes (**B**). This step has been documented with allylic acetates[11] and carbonates[12] in stoichiometric systems. The carboxylato or carbonato ligand (X) in **B** is subsequently replaced by a formato ligand by the reaction with formic acid, giving (η^3-allyl)palladium formate (**C**). This process was observed by NMR spectroscopy. Finally, complex **C** undergoes decarboxylation to give terminal and internal alkenes with regeneration of the palladium(0) species (**A**), as confirmed by thermolysis experiments of independently prepared (η^3-allyl)palladium formates.

As can be seen from this scheme, the regioselectivity must be determined at the final stage. Therefore, we prepared in

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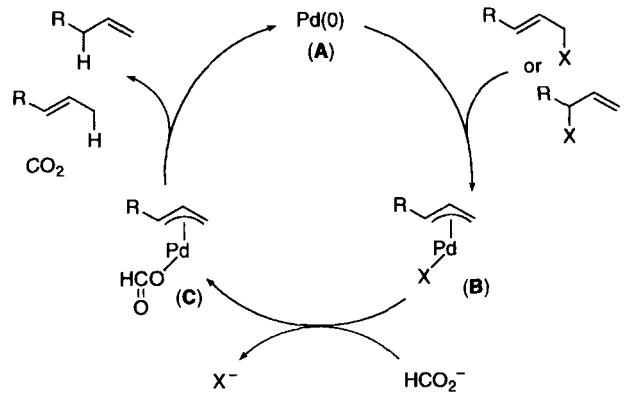


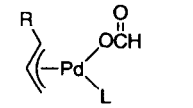
Scheme 1. X = O_2CR' or OCO_2R'.

this study a series of (η^3-1-methylallyl)palladium formates as simple models of the key intermediate **C** and examined in detail their structures and thermolysis behavior in solution. The selectivity to give either 1-butene or 2-butene has been found to vary significantly with the bulkiness of the tertiary phosphine ligands.

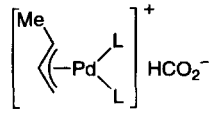
Results

Preparation of (η^3-1-Methylallyl)palladium Formates. Two types of (η^3-allyl)palladium(II) formates, listed in Chart 1, were prepared. One is the (η^3-1-methylallyl)-palladium formate coordinated with one tertiary phosphine ligand (P1 type, **1a**—**1d**), and the other is the cationic (η^3-1-methylallyl)palladium bearing two tertiary phosphine ligands and a formate counter anion (P2 type, **4a**—**4c**).

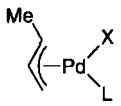
The P1-type complexes **1a**—**1d** were prepared according to Eq. 2 by treating a chloro-bridged (η^3-1-methylallyl)-palladium dimer[13] with 1 equiv/Pd of phosphine (L) followed by conversion of the resulting **2** into the formate complex **1** by reaction with silver formate at low temperature.



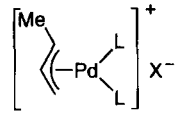
1a: R = Me, L = $PMePh_2$
1b: R = Me, L = PMe_2Ph
1c: R = Me, L = PMe_3
1d: R = Me, L = P(*o*-tolyl)$_3$
1e: R = H, L = $PMePh_2$



4a: L = $PMePh_2$
4b: L = PMe_2Ph
4c: L = PMe_3

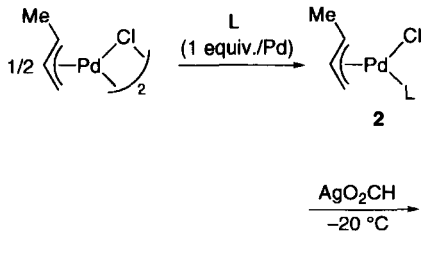


2a: X = Cl, L = $PMePh_2$
3a: X = OAc, L = $PMePh_2$



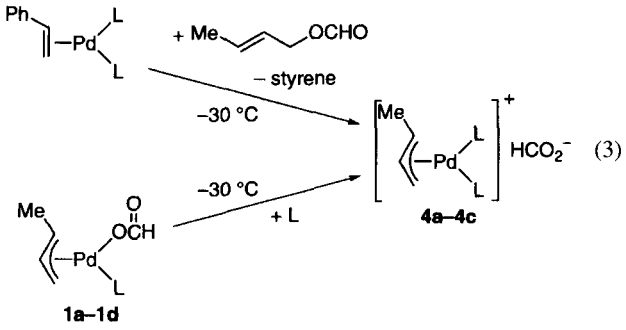
5a: X = BF_4, L = $PMePh_2$
6a: X = Cl, L = $PMePh_2$

Chart 1.



(2)

On the other hand, P2-type formates **4a**—**4c** were prepared by the oxidative addition of 2-butenyl formate to Pd(0)–styrene complexes having two phosphine ligands (L) in THF at −30 °C (Eq. 3). The starting styrene complexes were prepared in situ by the thermolysis of *trans*-[$PdEt_2L_2$] in a THF solution containing styrene.[14] The P2-type complexes could also be prepared by the treatment of P1 complexes **1a**—**1c** with 1 equivalent of phosphine in solution. The reactions took place instantly at −30 °C to give **4a**—**4c** in quantitative yields, as confirmed by ^1H and ^{31}P NMR spectroscopy. In contrast, the P1-type complex **1d** bearing tri-*o*-tolylphosphine ligand showed no sign of the formation of the P2-type complex in a THF solution containing 3 equivalents of free P(*o*-tolyl)$_3$.



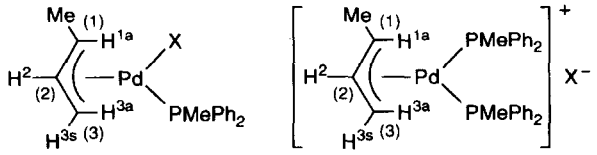
(3)

Although P1-type complexes **1a**—**1d** are thermally unstable in solution as well as in the solid state and therefore could not be isolated as analytically pure compounds, their formation was unequivocally confirmed by NMR spectroscopy. On the other hand, P2-type complexes **4a**—**4c** were isolated as white solids from the reaction systems, though their elemental analyses were infeasible due to the highly hygroscopic nature. As typical examples, we describe in the following sections the characterization of P1 and P2-type complexes having η^3-1-methylallyl and $PMePh_2$ ligand(s) (**1a** and **4a**) in detail. The identification of the other formate complexes is reported in the Experimental Section.

Characterization of 1a. Table 1 lists the NMR data of **1a**. For a comparison, NMR data of the related P1-type 1-methylallyl complexes bearing chloro and acetato ligands (**2a** and **3a**, respectively) are included. The acetate complex **3a** was synthesized by the reaction of **2a** with silver acetate. The assignments of the ^1H NMR signals were based on homospin-decoupling experiments.

Except for the formate signal observed at δ = 8.48, the other features of the ^1H NMR spectrum of **1a** are quite similar to those of **2a** and **3a**. The H^2 proton attached to the central

Table 1. NMR Data for (η^3-1-Methylallyl)palladium Complexes Coordinated with $PMePh_2$ Ligand(s)[a]



1a, 2a, 3a **4a, 5a, 6a**

Complex (X)	^{1}H NMR δ	J_{HH}	J_{HP}	Assignment	^{13}C{^{1}H} NMR δ	J_{CP}	Assignment	^{31}P{^{1}H} NMR δ	J_{PP}
1a (O_2CH)	8.48 (s)	—	—	O_2CH	168.2 (s)	—	O_2CH	11.9 (s)	
	5.40 (ddd)	12.9, 11.5, 6.9	—	H^2	117.2 (d)	4	C^2		
($CDCl_3$)	4.73 (ddq)	12.9, 6.6	8.9	H^{1a}	97.7 (d)	27	C^1		
(at −50 °C)	2.94 (dd)	6.9	1.5	H^{3s}	48.0 (s)	—	C^3		
	2.38 (d)	11.5	—	H^{3a}	17.7 (d)	4	1-Me		
	1.92 (d)	—	8.9	PMe	13.5 (d)	24	PMe		
	1.62 (dd)	6.6	8.6	1-Me					
2a (Cl)	5.32 (ddd)	12.9, 11.9, 6.6	—	H^2	117.0 (d)	4	C^2	12.3 (s)	
	4.41 (ddq)	12.9, 6.3	9.6	H^{1a}	99.0 (d)	28	C^1		
($CDCl_3$)	3.07 (dd)	6.6	2.0	H^{3s}	53.6 (s)	—	C^3		
(at −50 °C)[b]	2.54 (d)	11.9	—	H^{3a}	17.7 (d)	5	1-Me		
	2.07 (d)	—	9.2	PMe	14.2 (d)	27	PMe		
	1.83 (dd)	6.3	9.2	1-Me					
3a (O_2CMe)	5.29 (ddd)	12.9, 11.5, 5.9	—	H^2	177.2 (s)	—	O_2CMe	12.3 (s)	
	4.58 (ddq)	12.9, 6.9	—	H^{1a}	116.7 (d)	3	C^2		
($CDCl_3$)	2.86 (d)	5.9	—	H^{3s}	96.9 (d)	26	C^1		
(at −50 °C)[c]	2.86 (d)	6.9	1.5	H^{3a}	47.2 (s)	–	C^3		
	1.87 (d)	—	8.9	PMe	24.3 (s)	—	O_2CMe		
	1.85 (s)	—	—	O_2CMe	17.6 (d)	4	1-Me		
	1.72 (dd)	6.6	8.6	1-Me	13.2 (d)	25	PMe		
4a (OCHO)	8.94 (s)	—	—	O_2CH	168.5 (s)	—	O_2CH	8.0 (d)	43
	5.48 (m)	d)	d)	H^2	121.4 (t)	6	C^2	7.5 (d)	43
	4.19 (m)	d)	d)	H^{1a}	94.0 (dd)	22, 7	C^1		
($CDCl_3$)	3.66 (m)	d)	d)	H^{3s}	70.8 (dd)	22, 7	C^3		
(at −50 °C)	3.22 (m)	d)	d)	H^{3a}	17.2 (d)	3	1-Me		
	1.73 (d)	—	7.9	PMe	13.8 (dd)	22, 6	PMe		
	1.65 (d)	—	7.6	PMe	12.0 (dd)	23, 5	PMe		
	1.09 (td)	7.6	8.0[e]	1-Me					
5a (BF_4)	5.53 (m)	d)	—	H^2	121.8 (t)	6	C^2	8.2 (d)	43
	4.33 (m)	d)	d)	H^{1a}	94.7 (dd)	22, 7	C^1	7.7 (d)	43
($CDCl_3$)	3.65 (m)	d)	d)	H^{3s}	71.3 (dd)	22, 7	C^3		
(at 26 °C)	3.33 (m)	d)	d)	H^{3a}	17.1 (d)	2	1-Me		
	1.80 (d)	—	8.6	PMe	13.7 (dd)	22, 6	PMe		
	1.77 (d)	—	7.9	PMe	12.3 (dd)	22, 5	PMe		
	1.16 (td)	7.8	8.1[e]	1-Me					
6a (Cl)	5.41 (m)	d)	—	H^2	117.9 (t)	6	C^2	9.0 (d)	44
	4.59 (m)	d)	d)	H^{1a}	92.0 (dd)	23, 7	C^1	8.6 (d)	44
($CDCl_3$)	3.54 (m)	d)	d)	H^{3s}	68.6 (dd)	22, 8	C^3		
(at −50 °C)	3.51 (m)	d)	d)	H^{3a}	17.3 (d)	2	1-Me		
	1.89 (d)	—	8.3	PMe	14.1 (dd)	21, 6	PMe		
	1.73 (d)	—	7.6	PMe	12.3 (dd)	22, 5	PMe		
	1.01 (td)	7.6	8.2[e]	1-Me					

a) 270.05 MHz (^{1}H), 67.80 MHz (^{13}C), and 109.25 MHz (^{31}P). b) ^{13}C and ^{31}P NMR were measured at −30 °C. c) ^{31}P NMR was measured at −20 °C. d) The coupling constants are obscure due to the high multiplicity. e) Coupling constant for the apparent triplet due to the coupling between the 1-methyl protons and the two phosphorus nuclei.

carbon of the 1-methylallyl ligand (C^2) appeared to be a doublet of doublets of doublets due to the couplings to the two *anti* (^3J(H–H) = 12.9 and 11.5 Hz) and one *syn* protons (^3J(H–H) = 6.9 Hz). The *anti* proton (H^{1a}) at the methyl-substituted allylic carbon (C^1) exhibited a relatively large coupling to the phosphorus nucleus (^3J(P–H) = 8.9 Hz). A relatively large coupling to the phosphorus was also observed in the signal arising from the 1-methyl protons (^4J(P–H) = 8.6 Hz). In contrast, no or only a small coupling to the phosphorus was observed in the allylic protons at the C^3-carbon (H^{3a} and H^{3s}). These coupling patterns are fully consistent with the stereochemically frozen structure of **1a** having a phosphine ligand at the site *trans* to the methyl-substituted terminus of the allylic ligand. The $^{13}C\{^1H\}$ NMR data in Table 1 also support the structural assignment for **1a**.[15] Thus, the C^1-carbon *trans* to the phosphine ligand showed a large coupling to the phosphorus nucleus (^2J(P–C) = 27 Hz), whereas the C^3-carbon exhibited no coupling to the phosphorus.

Upon raising the temperature, the ^1H NMR spectrum of **1a** showed a sign of fluxional behavior. At 10 °C in $CDCl_3$, the *syn* and *anti* protons attached to the C^3-carbon significantly broadened, while the 1-methyl and H^{1a} protons retained their coupling patterns at −50 °C, which involve a relatively large coupling to the phosphorus nucleus. In addition, the coupling constants $^3J(H^2–H^{3s})$ and $^3J(H^2–H^{3a})$ appearing in the H^2 signal became very close to each other (ca. 9 Hz) at 10 °C; the value was almost the average of those at −50 °C (J = 6.9 and 11.5 Hz). These NMR observations at 10 °C may be taken as an indication of the η^3–η^1–η^3 type interconversion involving the dissociation of the C^1 terminus of the allylic ligand. However, the fact that the 1-methyl and H^{1a} signals still retained the coupling to the phosphorus nucleus indicates that the η^3-allyl structure having the phosphine and formato ligands at the *trans* and *cis* positions of the C^1-carbon, respectively, is maintained most of the time. At room temperature, although the *syn* and *anti* protons showed a sign of coalescence, further observation of the spectroscopic change was not feasible due to the thermal decomposition of **1a**.

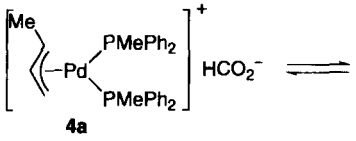
The rate of η^3–η^1–η^3 interconversion of **1a** was strongly affected by the solvent. Thus, in THF-d_8 the H^{3a} and H^{3s} signals broadened even at −30 °C, the temperature of which is significantly lower than that in $CDCl_3$ (10 °C). It was also noted that the fluxional nature of the (η^3-1-methylallyl)-palladium moiety varies with anionic ligands. As described above, the fluxional behavior of **1a** having the formato ligand was observed at above 10 °C in $CDCl_3$. On the other hand, the acetate complex **3a** showed a similar behavior at −20 °C in $CDCl_3$. The chloride complex **2a** exhibited no sign of fluxionality, even at room temperature.

Characterization of 4a. The NMR data of **4a** (Table 1) were very similar to those of the cationic (η^3-1-methylallyl)-palladium complexes having BF_4^- and Cl^- anions (**5a** and **6a**, respectively), except that the formate signal at δ = 8.94 was observed at a lower field than that of the corresponding P1-type complex **1a**. The methyl groups of the two $PMePh_2$ ligands were observed as two nonequivalent doublets, indicating that the two phosphine ligands are coordinated nonequivalently with palladium in the square-planar environment. Since the signals arising from the 1-methylallyl ligand were too complicated to be analyzed, further identification of **4a** was performed by ^{13}C NMR spectroscopy.[15]

The methyl-substituted and non-substituted allylic carbons (C^1 and C^3) were observed at δ = 94.0 and 70.8 as a doublet of doublets, respectively, due to coupling to the two phosphorus nuclei. The central C^2-carbon and the 1-methyl-carbon appeared at δ = 121.4 and 17.2 as a triplet and a doublet, respectively. The formate carbon was observed at δ = 168.5 as a singlet. These chemical shifts and coupling patterns are fully consistent with the cationic (η^3-1-methylallyl)palladium structure having two $PMePh_2$ ligands and a formate counter anion.

At elevated temperatures, the ^1H NMR spectrum of **4a** showed a sign of η^3–η^1–η^3 interconversion of the 1-methylallyl ligand on an NMR time scale (270 MHz). At −30 °C the signals arising from the two allylic protons at the C^3-carbon (H^{3s} and H^{3a}) turned into broad signals (δ = 3.32 and 3.66, respectively), and the H^2 proton was observed as a doublet of triplets due to the coupling to H^{1a} (^3J(H–H) = 12.9 Hz) and to H^{3s} and H^{3a} in apparently the same coupling constants (^3J(H–H) = 10.2 Hz). Upon raising the temperature further to −10 °C, the signals arising from H^{3s} and H^{3a} coalesced into a broad singlet at δ = 3.51 and the signals of two PMe groups coalesced into a broad peak at δ = 1.78. At 25 °C the protons at C^3-carbon and the PMe-protons were observed as doublets, respectively (H^3: δ = 3.51, $^3J(H^3–H^2)$ = 10.2 Hz; PMe: δ = 1.81, ^2J(P–H) = 7.8 Hz). The other signals of **4a** observed at 25 °C are as follows: δ = 8.96 (s, OCHO), 5.48 (dt, ^3J = 12.9 and 10.2 Hz, H^2), 4.47 (dq, ^3J = 12.9 and 6.3 Hz, H^{1a}), 1.17 (d, ^3J = 6.3 Hz, 1-Me).

These NMR observations strongly suggest the η^3–η^1–η^3 interconversion involving a (2-buten-1-yl)palladium species. The kinetic parameters derived from the exchange rates of the H^{3s} and H^{3a} signals measured at five different temperatures are as follows: E_a = 9.6 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −163 J K^{-1} mol^{-1}, $\Delta G^{\ddagger}$ = 11.7 kJ mol^{-1}, $k = 6.0\times10^2$ s^{-1} (at 258 K).[16] The large negative value of the activation entropy indicates an associative process involving coordination of the formate anion to give a four-coordinated (2-buten-1-yl)palladium species (Eq. 4). In contrast to the formate complex **4a**, complex **5a** having the BF_4^- anion as a good leaving group showed no sign of dynamic behavior, even at room temperature. This fact also supports the associative process involving the coordination of formate anion to palladium, as shown in Eq. 4.



4a

(4)

Thermolysis of (η^3-1-Methylallyl)palladium Formates. Seven kinds of P1 and P2-type (η^3-1-methylallyl)palladium formates (**1a**—**1d** and **4a**—**4c**) were subjected to thermolysis in a THF or toluene solution. All of the complexes examined were thermally unstable and decomposed smoothly at 10 °C to liberate 1-butene, 2-butene, and/or butadiene together with 1 equiv/Pd of CO_2, as confirmed by GLC and/or ^{1}H NMR analysis. The thermolysis was examined in the presence of styrene. In the absence of styrene, 1-butene formed in the system subsequently underwent isomerization to thermodynamically more stable 2-butene. The addition of over 10 equiv/Pd of styrene to the system effectively suppressed the isomerization, and the product distribution in the thermolysis was exactly determined.

Table 2 summarizes the results. P1 complexes **1a**—**1d** provided 1-butene and 2-butene (Entries 1—4). The ratio of 1-butene to 2-butene lowered in the order **1d** > **1a** > **1b** ≈ **1c**, probably reflecting the decreasing bulkiness of the phosphine ligands bound to palladium. Figure 1 shows the time-course of the thermolysis of **1d** in toluene-d_8 at 10 °C. The reaction was first-order in the concentration of **1d** up to 80% conversion ($k_{obsd} = 3.1\times10^{-4}$ s^{-1}). The reaction rate was little affected by the addition of free tri-*o*-tolylphosphine (3 equiv/Pd) ($k_{obsd} = 2.7\times10^{-4}$ s^{-1}), and the product ratio was approximately constant regardless of the presence or absence of free tri-*o*-tolylphosphine. As described above, complex **1d** did not form a P2-type complex, even in the presence of an excess amount of tri-*o*-tolylphosphine. This behavior is attributable to the bulkiness of tri-*o*-tolylphosphine and differs from that of **1a**—**1c** bearing more compact phosphine ligands, which readily form P2-type complexes (Eq. 3).[17]

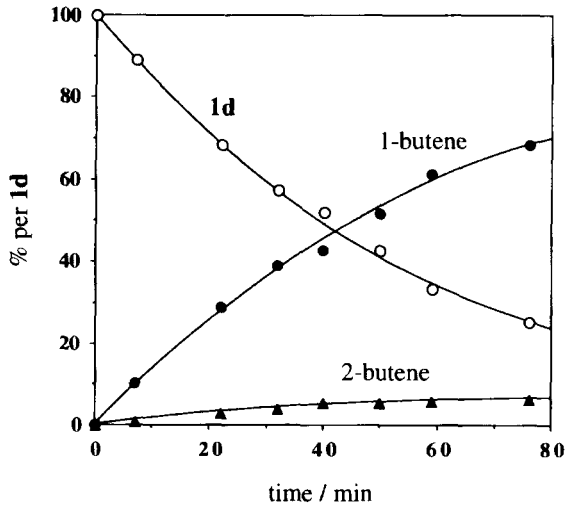


Fig. 1. Time-course of the thermolysis of **1d** in toluene-d_8 at 10 °C in the presence of 10 equivalents of styrene.

The thermolysis of P2-type complexes **4a**—**4c** liberated butadiene in addition to 1-butene and 2-butene (Entries 5—10 in Table 2). Particularly, **4a** formed a considerable amount of butadiene in the presence of free $PMePh_2$ (Entry 6). The thermolysis of **4a** was slower than that of the P1 complex **1a**[18a] and was retarded by the addition of free $PMePh_2$ to the system.[18b]

Interestingly, despite the formation of butadiene, the ratio of 1-butene to 2-butene in the thermolysis of P2 complex was almost identical to that observed for the corresponding P1 complex bearing the same phosphine ligand. This situation can be more clearly seen from Fig. 2, in which the ratios of 1-butene to 2-butene are plotted as a function of the cone angles of the phosphine ligands. Apparently, the more sterically demanding phosphine tends to give a higher ratio of 1-butene, irrespective of the number of phosphine ligands bound to palladium. The selectivity of 1-butene was somewhat improved at higher reaction temperatures (Entries 5, 7 and 8 in Table 2).

The thermolysis of a P0-type formate complex was also examined. Since the (η^3-1-methylallyl)palladium formate without tertiary phosphine ligands could not be prepared as a stable species, the chloro-bridged (η^3-1-methylallyl)-palladium dimer was treated with formic acid (5 equiv/Pd) and Et_3N (2 equiv/Pd) in THF at 10 °C. This reaction gave 1-butene and 2-butene in a 42 : 58 ratio (Eq. 5).

Table 2. Product Distribution in the Thermolysis of (η^3-1-Methylallyl)palladium Formate Complexes[a)]

Entry	Complex (L)	Reaction temp/°C	Product ratio 1-Butene	2-Butene	Butadiene	Ratio of 1-butene/ 2-butene
1	**1d** ($P(o\text{-tolyl})_3$)	10	0.91	0.09	0.00	91/9 (10.1)
2	**1a** ($PMePh_2$)	10	0.76	0.24	0.00	76/24 (3.2)
3	**1b** (PMe_2Ph)	10	0.39	0.61	0.00	39/61 (0.57)
4	**1c** (PMe_3)	10	0.38	0.62	0.00	38/62 (0.61)
5	**4a** ($PMePh_2$)	10	0.57	0.17	0.26	77/23 (3.3)
6[b)]	**4a** ($PMePh_2$)	10	0.34	0.11	0.55	76/24 (3.2)
7	**4a** ($PMePh_2$)	30	0.60	0.12	0.28	83/17 (4.9)
8	**4a** ($PMePh_2$)	50	0.64	0.09	0.27	88/12 (7.3)
9	**4b**(PMe_2Ph)	10	0.40	0.55	0.05	43/57 (0.75)
10	**4c** (PMe_3)	10	0.36	0.62	0.02	37/63 (0.59)

a) All of the reactions were run in solutions containing 10 equiv/Pd of styrene. Solvent: toluene (Entry 1); THF (Entries 2—10). The product ratio was determined by GLC. b) The reaction was carried out in the presence of 1 equiv/Pd of added $PMePh_2$.

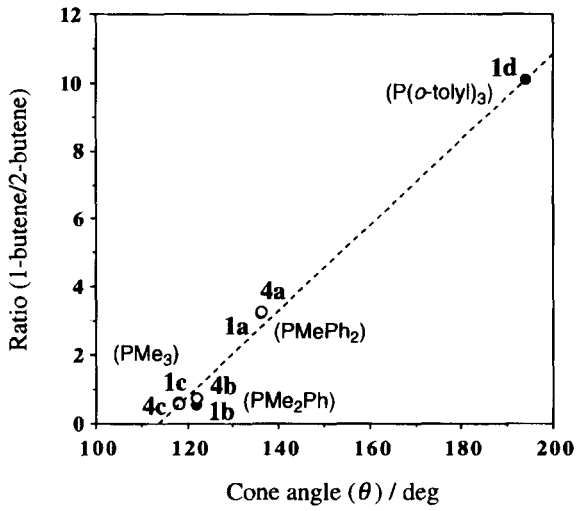
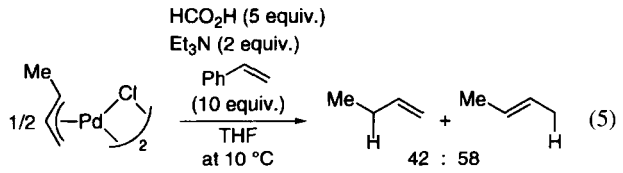


Fig. 2. Plot of 1-butene/2-butene ratios vs. cone angles (θ) of tertiary phosphine ligands for the thermolysis of (η^3-1-methylallyl)palladium formates.



Catalytic Decarboxylation of Allylic Formates. The P1 and P2-type (η^3-1-methylallyl)palladium complexes (**1a**, **1d**, **4a**) proved to be catalytically active in the decarboxylation of (*E*)-2-butenyl formate (Entries 1—3 in Table 3). All of the complexes examined satisfactorily reproduced the ratios of 1-butene to 2-butene observed in the stoichiometric systems (Table 2), though the amount of butadiene formed in the catalytic system with **4a** (Entry 3) was much less than that obtained in the corresponding stoichiometric system (Entry 5 in Table 2). These tendencies were also observed in the catalytic reactions using palladium(0) catalysts generated in situ from [$Pd_2(dba)_3$] (dba = 1,5-diphenyl-1,4-pentadien-3-one) and phosphines (Entries 4—7 in Table 3). The dppe-coordinated catalyst **E** released a large amount of butadiene (Entry 8).

Table 3. Product Distribution in the Catalytic Decarboxylation of (*E*)-2-Butenyl Formate[a)]

Entry	Complex (L)	Reaction temp/°C	Product ratio			Ratio of 1-butene/ 2-butene
			1-Butene	2-Butene	Butadiene	
1	**1d** (P(*o*-tolyl)$_3$)	10	0.91	0.09	0.00	91/9 (10.1)
2	**1a** (PMePh$_2$)	20	0.79	0.21	0.00	79/21 (3.8)
3	**4a** (PMePh$_2$)	20	0.79	0.20	0.01	80/20 (4.0)
4	**A** (P(*o*-tolyl)$_3$)	10	0.91	0.09	0.00	91/9 (10.1)
5	**B** (PMePh$_2$)	20	0.77	0.23	0.00	77/23 (3.3)
6	**C** (PMePh$_2$)	20	0.75	0.20	0.05	79/21 (3.8)
7	**D** (PMePh$_2$)	20	0.64	0.19	0.17	77/23 (3.3)
8	**E** (dppe)	50	0.11	0.44	0.45	20/80 (0.25)

a) All of the reactions were run in THF using 2.5 mol% of catalyst for 5 h (Entries 1, 2, 4, 5) or 24 h (Entries 3, 6—8) and analyzed by means of GLC. Catalysts **A**—**D** in Entries 4—7 were generated in situ from [$Pd_2(dba)_3$]·$CHCl_3$ and phosphine ligand. **A**, **B**: L/Pd = 1; **C**: L/Pd = 2; **D**: L/Pd = 3. Catalyst **E** in Entry 8 was prepared in situ from [Pd(η^3-1-methylallyl)(μ-Cl)]$_2$ and dppe (1,2-bis(diphenylphosphino)ethane) (Pd/dppe = 1).

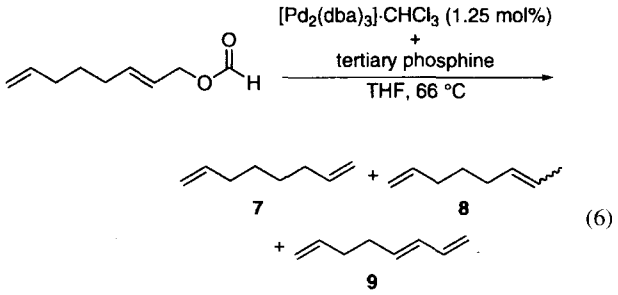
Table 4. Effect of Tertiary Phosphine Ligands on the Catalytic Decarboxylation of 2,7-Octadienyl Formate[a)]

Entry	Ligand (equiv/Pd)	Product ratio			Ratio of
		7	**8**	**9**	**7/8**
1	PPh_3 (4)	0.95	0.05	0.00	95/5 (19)
2	PPh_3 (2)	0.96	0.04	0.00	96/4 (24)
3	PPh_3 (1)	0.87	0.13	0.00	87/13 (6.7)
4	$PMePh_2$ (2)	0.92	0.08	0.00	92/8 (11.5)
5	PMe_2Ph (2)	0.93	0.07	0.00	93/7 (13.3)
6	PBu_3 (2)	0.96	0.03	0.01	97/3 (32.3)
7	PMe_3 (2)	0.29	0.71	0.00	29/71 (0.41)
8	dppe (1)	0.08	0.70	0.22	10/90 (0.11)
9	dppp (1)	0.80	0.10	0.10	89/11 (8.1)
10	dppb (1)	0.92	0.08	0.00	92/8 (11.5)

a) All of the reactions were run in THF under reflux using 2.5 mol% of catalysts generated in situ from [$Pd_2(dba)_3$]·$CHCl_3$ and phosphines. dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane.

The experimental results described above indicate the following tendencies associated with the stoichiometric as well as the catalytic conversion of 2-butenyl formate into butenes and butadiene. (1) The complex coordinated with more sterically demanding phosphine(s) tends to provide a higher ratio of 1-butene to 2-butene. (2) The ratio of 1-butene to 2-butene is independent of the number of phosphines bound to palladium. (3) Butadiene is formed only from P2 complexes. In order to see if these tendencies are observed in catalytic reactions closer to practical systems as well and to study the effect of a more variety of phosphine ligands on the product distribution, we next examined the catalytic decarboxylation of 2,7-octadienyl formate.

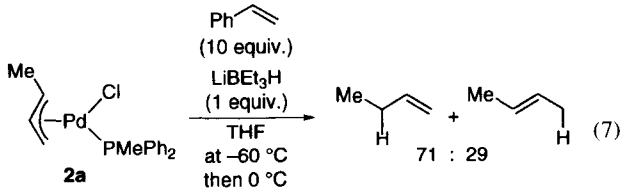
Table 4 summarizes the results. All of the reactions listed were performed in THF under reflux (66 °C) to be completed within 2 h, giving three types of products **7**, **8**, and **9** (Eq. 6). Compounds **7** and **8** correspond to 1-butene and 2-butene, and **9** to butadiene in the decarboxylation of 2-butenyl formate, respectively. Notable amounts of β-elimination product **9** were formed only in those reactions using dppe and dppp as potential chelating ligands (Entries 8 and 9). In the reactions with monodentate ligands, the product ratio of **7** to **8** tended to increase as the amount of phosphine increased from 1 equivalent to 2 equivalents, and became almost constant in the presence of over 2 equiv/Pd of phosphine (see Entries 1—3 as typical examples). This variation, not observed in the decarboxylation of 2-butenyl formate, may be associated with the more facile dissociation of phosphine ligand at higher reaction temperature (66 °C). Therefore, the reactions given in Table 4 were examined with 2 equiv/Pd of monodentate phosphines.



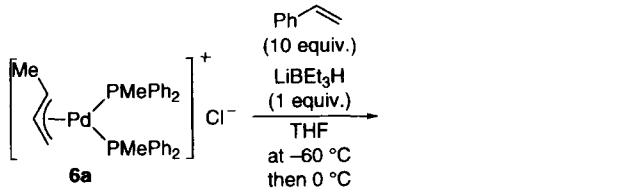
(6)

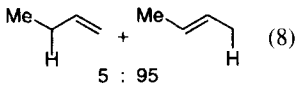
As can be seen from Table 4, although the relation is somewhat ambiguous compared with the data in Table 2, there is still a tendency that the bulkier ligand provides a higher ratio of terminal alkene **7**. It may also be seen that the more basic phosphine is preferable for the formation of **7** when the bulkiness is similar.

Reductive Cleavage with Metal Hydride. In the stoichiometric and catalytic decarboxylation of 2-butenyl formate, the ratio of 1-butene to 2-butene was little affected by the number of phosphine ligands. On the other hand, the product distribution in the reduction of (η^3-1-methylallyl)palladium with $LiBEt_3H$ was reversed, depending on the number of phosphine ligands attached to palladium. Thus, the treatment of (η^3-1-methylallyl)palladium chloride **2a** with $LiBEt_3H$ in THF in the presence of an excess amount of styrene at −60 °C, followed by thermolysis at 0 °C, gave 1-butene and 2-butene in a 71 : 29 ratio (Eq. 7), whereas the reaction of P2-type (η^3-1-methylallyl)palladium chloride **6a** with $LiBEt_3H$ under similar reaction conditions liberated 2-butene, the internal alkene, predominantly (Eq. 8). It is noted that, even in the reduction with a metal hydride, terminal alkene (1-butene) is the major product when the η^3-allyl complex possesses only one monophosphine ligand.



(7)



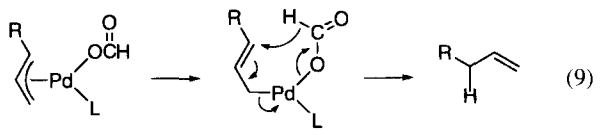


(8)

Discussion

The P1 and P2-type (η^3-1-methylallyl)palladium formates have been found to provide almost the same ratio of 1-butene to 2-butene when the complexes have the same tertiary phosphine ligand, though the P2 complexes also give butadiene. The product ratios observed in the stoichiometric systems have been satisfactorily reproduced in the catalytic reactions converting 2-butenyl formate into 1-butene and 2-butene. These results, in conjunction with the fact that the thermolysis of P2 complex is slower than that of the corresponding P1 complex, and is retarded by the addition of free phosphine to the system, strongly suggest that both 1-butene and 2-butene are formed from a common P1 species.

Previously, Hatchins and others proposed the mechanism depicted in Eq. 9 to account for the predominant formation of terminal alkenes in the catalytic reductive cleavage of allylic carboxylates with formic acid in the presence of an amine base.[8a] They postulated the conversion of the allylic ligand from the η^3 to η^1 form prior to the decarboxylation of the formate entity. The terminal alkene is formed by the subsequent hydride transfer from the formato ligand to the vinyl carbon substituted with R via an S_Ni process involving a quasi seven-membered cyclic transition state.



(9)

On the other hand, we confirmed in this study that all of the P1-type (η^3-1-methylallyl)palladium formates bearing

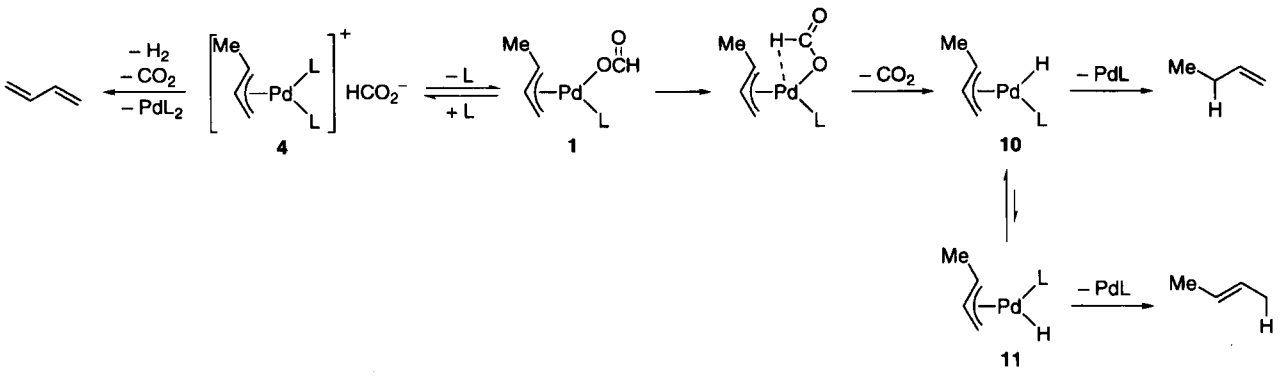
a variety of tertiary phosphine ligands (**1a—1e**) exist as a single isomer having the formato ligand cis to the methyl-substituted terminus of the allylic ligand. This geometry is stable at the temperatures for NMR measurements (−70 °C—room temperature). Therefore, if the mechanism in Eq. 9 should operate, one must expect the selective formation of 1-butene as the terminal alkene irrespective of the tertiary phosphine ligand bound to palladium. However, the result indeed showed is a clear dependence of the regioselectivity upon the sort of tertiary phosphine ligand. Hence, the mechanism in Eq. 9 is incompatible with the present observation.

We herein propose the mechanism in Scheme 2, where the P1-type (η^3-1-methylallyl)palladium formate **1** gives 1-butene and 2-butene and the P2-type formate **4** affords butadiene. Complexes **1** and **4** are in an rapid equilibrium with each other when the reaction system contains more than 2 equiv/Pd of phosphine (L). Although complex **1** exists as a single isomer irrespective of the sort of phosphine ligand, it is assumed that (η^3-1-methylallyl)palladium hydride formed by decarboxylation of **1** exists as a mixture of two geometrical isomers **10** and **11**. Since the decarboxylation of transition metal formates is known to proceed with retention of the geometry around the metal center,[19—21] the product initially formed by decarboxylation must be **10** having the hydrido and phosphine ligands at the sites cis and trans to the methyl-substituted terminus of the allylic ligand, respectively. The geometrical isomer **11** is formed by the isomerization of **10**. Finally, complexes **10** and **11** reductively eliminate 1-butene and 2-butene, respectively.[22] The C–H reductive elimination is assumed to take place selectively at the allylic carbon *cis* to the hydrido ligand. Accordingly, the structures of the product alkenes (i.e. terminal or internal) are prescribed by the geometries of **10** and **11**, respectively.

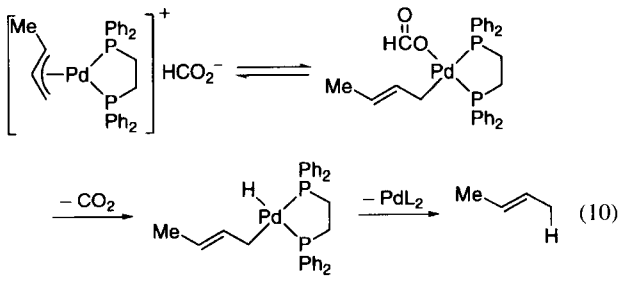
The above-mentioned mechanism, especially concerning the thermolysis processes of **10** and **11**, is compatible with studies of the reductive elimination of (η^3-allyl)(aryl)(phosphine)palladium complexes reported by Kurosawa et al.[24,25] It has been confirmed that (i) the η^3-allyl form is preferable to the η^1-allyl form for reductive elimination,[23] (ii) reductive elimination takes place between the allylic carbon and the aryl ligand in mutually *cis* positions, (iii) [Pd(η^3-1-methylallyl)(Ar)(PR_3)] complexes can take two geometries that correspond to **10** and **11**, respectively, and are interconverted to each other, (iv) reductive elimination involving the methyl-substituted allylic carbon is slower than that involving the non-substituted allylic carbon.[24] Based on Kurosawa's finding (iv), the reductive elimination from **10** is considered to be slower than that from **11**. This is partly due to the greater steric congestion around the methyl-substituted carbon, as suggested for [Pd(η^3-1-methylallyl)(Ar)(PR_3)] complexes.

Despite the slower reductive elimination of 1-butene from **10** than 2-butene from **11**, however, 1-butene is the major product in the thermolysis of (η^3-1-methylallyl)palladium formates bearing bulky phosphine ligands (**1d**, **1a**, **4a**). This is probably because the equilibrium between **10** and **11** lies on the far side of **10**. Thus, the steric repulsion between the phosphine ligand and the 1-methyl group of allylic ligand in **11** will destabilize the complex significantly. In contrast, steric congestion around **10** should be modest, since in this configuration phosphine is located at a less hindered site and the compact hydrido ligand is situated at the side of the 1-methyl group. Thus, the overall situation gives rise to much higher thermodynamic stability of **10** than **11**, particularly when the phosphine is bulky.

We have described that the dependence of the product distribution upon the size of the phosphine ligand in the thermolysis of (η^3-1-methylallyl)palladium formates can be rationalized by the mechanism in Scheme 2. However, the present discussion is not conclusive, owing to the lack of a direct observation on the chemical properties of presumed (η^3-1-methylallyl)palladium hydride intermediates **10** and **11**. Therefore, we can not presently exclude other possible mechanisms. For example, the exceptionally high 2-butene ratio in the catalytic decarboxylation of (*E*)-2-butenyl formate using a dppe-coordinated catalyst (Entry 8 in Table 3) may be accounted for by the following mechanism involving a (2-buten-1-yl)palladium species (Eq. 10), whose analogs have already been confirmed for allylic arylation systems.[24,25]



Scheme 2.



(10)

Experimental

General Methods and Materials. Unless otherwise stated, all manipulations were carried out under an atmosphere of argon or nitrogen. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL FX-100, GSX-400, EX-270, and Varian inova-400 spectrometers. ^{1}H and ^{13}C signals are 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 Shimadzu IR-400 spectrometer. GLC analyses were carried out on a Shimadzu GC-3BT instrument equipped with a TCD detector and a VZ-9 column (3 mm×6 m). Elemental analyses were performed by the Hokkaido University Analytical Center. The solvents were dried in the usual manners, distilled, and stored under an argon atmosphere. (η^3-1-Methylallyl)palladium chloride dimer [di(μ-chloro)di{(1,2,3-η)-2-butenyl)}dipalladium][13] and *trans*-[$PdEt_2L_2$] (L = PMe_3,[12] PMe_2Ph,[25a] $PMePh_2$,[25b]) were prepared according to literature methods.

Preparation of Formato(η^3-1-methylallyl)(methyldiphenylphosphine)palladium(II) (1a). (a) Preparation of Chloride Complex 2a. To a Schlenk tube containing (η^3-1-methylallyl)-palladium chloride dimer (1.09 g, 2.77 mmol) was added CH_2Cl_2 (10 mL) at room temperature. The resulting solution was cooled to −10 °C and $PMePh_2$ (1.04 mL, 5.51 mmol) was added. The mixture was stirred for 30 min at room temperature and filtered though a short Al_2O_3 column. The filtrate was concentrated to ca. 3 mL under reduced pressure and Et_2O (10 mL) was carefully layered. The solvent layers were allowed to mix slowly at room temperature, giving yellow crystals of **2a**, which were filtered and dried under vacuum (1.87 g, 85% yield). The NMR data are listed in Table 1. Found: C, 51.69; H, 5.04; Cl, 9.16%. Calcd for $C_{17}H_{20}PClPd$: C, 51.41; H, 5.08; Cl, 8.93%.

(b) Preparation of Silver Formate. After silver carbonate (0.515 g, 1.87 mmol) was added to formic acid (15 mL) in a round-bottom flask at 0 °C, the mixture was stirred at room temperature for 1 h in the dark. An undissolved part of the solid was removed by filtration, and Et_2O (20 mL) was slowly added to the filtrate with stirring to cause precipitation of a fine crystalline solid of silver formate, which was collected by filtration, washed with Et_2O (5 mL×3), and dried under vacuum at room temperature in the dark (0.320 g, 56% yield). The product was used in the preparation of formate complexes without purification.

(c) Preparation of 1a. A solution of **2a** (0.112 g, 0.282 mmol) in CH_2Cl_2 (3 mL) was cooled to −40 °C and silver formate (0.215 g, 1.41 mmol) was added. The mixture was stirred at −20 °C for 2 h in the dark and filtered though a short celite column at −50 °C. The filtrate was concentrated to dryness to give a white solid of **1a** (0.099 g, 86%). Since the solid product thus obtained was readily decomposed at room temperature, its elemental analysis was infeasible. However, the ^{1}H NMR spectrum revealed that the product had over 96% purity (Fig. 1). The NMR data are reported in Table 1.

Complexes **1b**, **1c**, **1d**, and **1e** (Chart 1) were similarly prepared. The starting (η^3-allyl)palladium chlorides having one tertiary phosphine ligand were prepared in situ from the corresponding (η^3-allyl)palladium chloride dimer[13] and 1 equivalent of tertiary phosphine ligand and treated with silver formate.

[1b]: ^{1}H NMR ($CDCl_3$, −30 °C) δ = 1.66 (dd, J_{HH} = 6.0 Hz, J_{PH} = 8.6 Hz, 3H, 1-Me), 1.70 (d, J_{PH} = 9.2 Hz, 3H, PMe), 1.73 (d, J_{PH} = 9.6 Hz, 3H, PMe), 2.38 (d, J_{HH} = 11.2 Hz, 1H, H^{3a}), 3.01 (d, J_{HH} = 6.0 Hz, 1H, H^{3s}), 4.70 (dqd, J_{HH} = 12.8 and 6.0 Hz, J_{PH} = 9.2 Hz, 1H, H^{1a}), 5.38 (ddd, J_{HH} = 12.8, 11.2, and 6.4 Hz, 1H, H^2), 7.43—7.49 (m, 3H, Ph), 7.61—7.69 (m, 2H, Ph), 8.56 (s, 1H, OCHO). ^{13}C{^{1}H} NMR ($CDCl_3$, −30 °C) δ = 14.6 (d, J_{PC} = 25 Hz, PMe_2), 17.5 (d, J_{PC} = 3 Hz, 1-Me), 45.2 (s, C^3), 97.2 (d, J_{PC} = 27 Hz, C^1), 116.7 (d, J_{PC} = 4 Hz, C^2), 128.6 (d, J_{PC} = 11 Hz, Ph), 130.1 (s, Ph-*p*), 130.5 (d, J_{PC} = 12 Hz, Ph), 135.2 (d, J_{PC} = 41 Hz, Ph-*ipso*), 168.0 (s, OCHO). ^{31}P{^{1}H} NMR ($CDCl_3$, −30 °C) δ = −2.5 (s).

[1c]: ^{1}H NMR ($CDCl_3$, −30 °C) δ = 1.46 (d, J_{PH} = 9.2 Hz, 9H, PMe_3), 1.64 (dd, J_{HH} = 6.4 Hz, J_{PH} = 8.6 Hz, 3H, 1-Me), 2.37 (d, J_{HH} = 11.6 Hz, 1H, H^{3a}), 3.07 (d, J_{HH} = 6.4 Hz, 1H, H^{3s}), 4.62 (dqd, J_{HH} = 12.4 and 6.4 Hz, J_{PH} = 8.8 Hz, 1H, H^{1a}), 5.34 (ddd, J_{HH} = 12.4, 11.6, and 6.8 Hz, 1H, H^2), 8.53 (s, 1H, OCHO). ^{13}C{^{1}H} NMR ($CDCl_3$, −30 °C) δ = 15.6 (d, J_{PC} = 26 Hz, PMe_3), 17.4 (d, J_{PC} = 4 Hz, 1-Me), 43.2 (s, C^3), 97.0 (d, J_{PC} = 27 Hz, C^1), 116.6 (d, J_{PC} = 5 Hz, C^2), 167.9 (s, OCHO). ^{31}P{^{1}H} NMR ($CDCl_3$, −30 °C) δ = −12.5 (s).

[1d]: ^{1}H NMR ($CDCl_3$, −30 °C) δ = 1.62 (dd, J_{HH} = 5.6 Hz, J_{PH} = 8.2 Hz, 3H, 1-Me), 2.20 (brs, 9H, tolyl-Me), 3.00 (brs, 2H, H^{3s} and H^{3a}), 4.86 (m, 1H, H^{1a}), 5.40 (m, 1H, H^2), 8.30 (s, 1H, OCHO). ^{13}C{^{1}H} NMR ($CDCl_3$, −30 °C) δ = 18.1 (d, J_{PC} = 5 Hz, 1-Me), 22.8 (d, J_{PC} = 7 Hz, tolyl-Me), 50.8 (s, C^3), 97.0 (d, J_{PC} = 26 Hz, C^1), 116.0 (brs, C^2), 167.6 (s, OCHO). ^{31}P{^{1}H} NMR ($CDCl_3$, −30 °C) δ = 16.5 (s).

[1e]: ^{1}H NMR ($CDCl_3$, −20 °C) δ = 1.98 (d, J_{PH} = 9.2 Hz, 3H, PMe), 2.58 (d, J_{HH} = 12.1 Hz, 2H, H^{3a}), 3.19 (d, J_{HH} = 6.2 Hz, 2H, H^{3s}), 3.90 (dd, J_{HH} = 14.1 Hz, J_{PH} = 9.3 Hz, 1H, H^{1a}), 4.72 (dd, J_{HH} = 6.4 Hz, J_{PH} = 5.4 Hz, 1H, H^{1s}), 5.63 (dddd, J_{HH} = 14.1, 12.1, 6.4, and 6.2 Hz, 1H, H^2), 8.43 (s, 1H, OCHO). ^{13}C{^{1}H} NMR (toluene-d_8, −30 °C) δ = 12.8 (d, J_{PC} = 25 Hz, PMe), 51.2 (s, C^3), 77.7 (d, J_{PC} = 28 Hz, C^1), 117.6 (d, J_{PC} = 5 Hz, C^2), 167.5 (s, OCHO). ^{31}P{^{1}H} NMR (toluene-d_8, −20 °C) δ = 10.8 (s).

Preparation of Acetato(η^3-1-methylallyl)(methyldiphenylphosphine)palladium(II) (3a). Complex **2a** (0.273 g, 0.686 mmol) was dissolved in CH_2Cl_2 (5 mL) at room temperature and silver acetate (0.114 g, 0.683 mmol) was added at −30 °C. The mixture was stirred at −10 °C for 3 h in the dark and filtered twice through a short celite column at room temperature. The filtrate was concentrated to dryness to give a yellow oily material of **3a** (0.183 g, 63% yield). Since the oily product could not be purified by recrystallization, a satisfactory elemental analysis was not obtained. However, the ^{1}H NMR spectrum showed that the product has at least 95% purity. The NMR data are reported in Table 1.

Preparation of (η^3-1-Methylallyl)bis(methyldiphenylphosphine)palladium(II) Formate (4a). (a) Preparation of 2-Butenyl Formate. To a solution of formic acid (14.7 g, 320 mmol) and 2-buten-1-ol (14.4 g, 200 mmol) in CH_2Cl_2 (200 mL) was carefully added diphosphorus pentaoxide (31 g) at 0 °C with stirring. The mixture was further stirred for 1 h at the same temperature and then filtered at room temperature. The filtrate was poured into water, and the organic layer was extracted with CH_2Cl_2. The combined extracts were washed with $NaHCO_3$ and then with brine and dried over $MgSO_4$. The solvent was removed by evaporation

and the residue was distilled at atmospheric pressure to give 2-butenyl formate (99% yield). bp 83 °C. ^{1}H NMR ($CDCl_3$) δ = 1.74 (dd, J = 6.3 and 1.3 Hz, 3H), 4.60 (dd, J = 6.6 and 1.0 Hz, 2H), 5.63 (dtd, J = 15.2, 6.6, and 1.0 Hz, 1H), 5.84 (dqd, J = 15.2, 6.3, and 1.3 Hz, 1H), 8.07 (s, 1H).

(b) Preparation of 4a. To a Schlenk tube containing *trans*-[$PdEt_2(PMePh_2)_2$] (0.317 g. 0.562 mmol) were added styrene (0.2 mL) and THF (2 mL) at −20 °C. The mixture was stirred at 30 °C for 1 h to give a yellow homogeneous solution. The solution was cooled to −20 °C, and 2-butenyl formate (0.10 mL, 0.93 mmol) was added. The mixture was stirred at −20 °C for 3 h, and the resulting yellow solution was concentrated to one-fourth in volume at −20 °C by pumping. The addition of Et_2O (4 mL) to the solution at −70 °C gave rise to precipitation of a white solid of **4a**, which was collected by filtration, washed with Et_2O (2 mL×3) and dried under vacuum below 0 °C for 12 h (0.153 g, 45% yield). Because of the thermal instability of the product, its elemental analysis was not feasible. The $^{13}C\{^1H\}$ NMR spectrum of the product is given in Fig. 2. The NMR data are listed in Table 1.

The P2- type formate complexes bearing PMe_2Ph and PMe_3 ligands (**4b**, **4c**) were similarly prepared using *trans*-[$PdEt_2(PMe_2Ph)_2$] and *trans*-[$PdEt_2(PMe_3)_2$] in place of *trans*-[$PdEt_2(PMePh_2)_2$]. The NMR data are as follows.

[4b]: ^{1}H NMR ($CDCl_3$, −50 °C) δ = 1.23 (td, J = 12.1 and 7.4 Hz, 3H, 1-Me), 1.80 (d, J = 12.8 Hz, 12H, PMe_2), 3.28 (m, 1H, H^{3a}), 4.13 (m, 1H, H^{3s}), 4.21 (m, 1H, H^{1a}), 5.51 (dt, J = 11.2 and 11.2 Hz, 1H, H^2), 7.40—7.60 (m, 10H, Ph), 8.92 (s, 1H, OCHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −50 °C) δ = 13.9 (m, PMe), 16.3 (m, PMe), 17.3 (d, J_{PC} = 4 Hz, 1-Me), 66.5 (d, J_{PC} = 24 Hz, C^3), 91.1 (d, J_{PC} = 17 Hz, C^1), 121.2 (b s, C^2), 128.5 (d, J_{PC} = 12 Hz, Ph), 128.5 (d, J_{PC} = 12 Hz, Ph), 128.9 (s, Ph), 129.3 (d, J_{PC} = 10 Hz, Ph), 130.2 (d, J_{PC} = 13 Hz, Ph), 130.9 (s, Ph), 131.6 (s, Ph), 168.0 (s, OCHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) δ = −6.1 (d, J_{PP} = 43 Hz), −7.9 (d, J_{PP} = 43 Hz).

[4c]: ^{1}H NMR ($CDCl_3$, −50 °C) δ = 1.28 (d, J_{PH} = 8.9 Hz, 9H, PMe_3), 1.34 (d, J_{PH} = 9.6 Hz, 9H, PMe_3), 1.64 (dt, J = 9.9 and 6.6 Hz, 3H, 1-Me), 2.64 (t, J = 11.4 Hz, 1H, H^{3a}), 3.65 (m, 1H, H^{1a}), 3.77 (t, J = 6.4 Hz, 1H, H^{3s}), 5.07 (m, 1H, H^2), 8.59 (s, 1H, OCHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −50 °C) δ = 15.3 (d, J_{PC} = 28 Hz, PMe_3), 17.5 (d, J_{PC} = 28 Hz, PMe_3), 17.7 (d, J_{PC} = 4 Hz, 1-Me), 65.2 (d, J_{PC} = 27 Hz, C^3), 88.5 (dd, J_{PC} = 28 and 3 Hz, C^1), 121.0 (t, J_{PC} = 6 Hz, C^2), 167.6 (s, OCHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) δ = −17.3 (d, J_{PP} = 45 Hz), −20.6 (d, J_{PP} = 45 Hz).

Preparation of (η^3-1-Methylallyl)bis(methyldiphenylphosphine)palladium(II) Tetrafluoroborate (5a). To a solution of (η^3-1-methylallyl)palladium chloride dimer (0.224 g, 0.57 mmol) in CH_2Cl_2 (2 mL) was added a CH_2Cl_2 solution (2 mL) of $AgBF_4$ (0.243 g, 1.25 mmol) at −40 °C. The mixture was stirred at −10 °C for 1 h and filtered through a short celite column. The pale-yellow filtrate was concentrated to dryness at room temperature to give a white solid, which was recrystallized from a CH_2Cl_2–Et_2O mixture to give white crystals of **5a** (0.503 g, 68% yield). The NMR data are reported in Table 1. Found: C, 55.16; H, 5.16%. Calcd for $C_{30}H_{33}P_2Pd{\cdot}BF_4$: C, 55.54; H, 5.13%.

Generation and Characterization of (η^3-1-Methylallyl)bis(methyldiphenylphosphine)palladium(II) Chloride (8a). The title compound was generated in situ from **2a** and 1 equivalent of $PMePh_2$ in solution, and used without isolation for the stoichiometric and catalytic reactions. The quantitative formation of **8a** was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy using $CDCl_3$, toluene-d_8, and THF-d_8 as solvents. ^{1}H NMR ($CDCl_3$, −50 °C) δ = 1.01 (td, J_{HH} = 7.6 Hz, J_{PH} = 8.2 Hz, 3H, 1-Me), 1.73 (d, J_{PH} = 7.6 Hz, 3H, PMe), 1.89 (d, J_{PH} = 8.3 Hz, 3H, PMe), 3.51 (m, 1H, H^{3a}), 3.54 (m, 1H, H^{3s}), 4.59 (m, 1H, H^{1a}), 5.41 (m, 1H, H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −50 °C) δ = 12.3 (dd, J_{PC} = 22 and 5 Hz, PMe), 14.1 (dd, J_{PC} = 21 and 6 Hz, PMe), 17.3 (d, J_{PC} = 2 Hz, 1-Me), 68.6 (dd, J_{PC} = 22 and 8 Hz, C^3), 92.0 (dd, J_{PC} = 23 and 7 Hz, C^1), 117.9 (t, J_{PC} = 6 Hz, C^2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) δ = 8.6 (d, J_{PP} = 44 Hz), 9.0 (d, J_{PP} = 44 Hz).

Thermolysis of the P1-Type Formate Complexes 1a—1d. Since the P1-type complexes **1a**—**1d** were thermally unstable and could not be handled at room temperature, their thermolysis was examined using the complexes generated in situ from (1-methylallyl)palladium chloride dimer, 1 equiv/Pd of phosphine, and silver formate. A typical procedure is as follows. To a Schlenk tube containing a solution of (1-methylallyl)palladium chloride dimer (96.7 mg, 246 μmol) in THF (2.5 mL) was added $PMePh_2$ (92 μL, 0.491 mmol) at −20 °C. Silver formate (112.6 mg, 0.736 mmol) was added to the solution at −40 °C, and the mixture was stirred at −30 °C for 2 h in the dark. Styrene (563 μL, 4.91 mmol) was added, and the solid of silver salts in the system was removed by filtration. The sample solution thus prepared was placed in a water bath controlled to 10 °C, and the thermolysis products (1-butene, 2-butene, and butadiene) were analyzed by means of GLC using pentane (56 μL, 0.491 mmol) as an internal standard. The results are given in Table 2 (Entries 1—4).

The time-course of thermolysis of **1d** (Fig. 1) was followed by ^{1}H NMR spectroscopy. To a solution of (1-methylallyl)palladium chloride dimer (26.1 mg, 66.3 μmol) and tri-*o*-tolylphosphine (40.3 mg, 132.5 μmol) in toluene-d_8 (1.0 mL) was added silver formate (25.3 mg, 0.166 mmol) at −30 °C. The mixture was stirred at −30 °C for 4 h in the dark. Styrene (15.2 μL, 0.133 mmol) was added, and the resulting heterogeneous mixture was filtered through a filter-paper-tipped cannula and transferred directly into an NMR sample tube equipped with a rubber septum cap. The sample tube was placed in an NMR sample probe controlled to 10.0±0.1°C. The amounts of thermolysis products (1-butene, 2-butene, and butadiene) and the starting complex **1d** in the system at intervals were determined based on the relative peak integration of the following proton signals: δ = 8.98 (s, OCHO in **1d**), 6.20 (dddd, H^2 in butadiene), 5.85 (dtd, H^2 in 1-butene), 5.33 (qq, H^2 in 2-butene). The results are shown in Fig. 1. The first-order rate constant for the thermolysis (k_{obsd} = 3.1×10^{-4} s^{-1}) was obtained by a least-squares calculation for the first-order plot for the time-conversion curve in the figure (r = 0.996).

Thermolysis of the P2-Type Formate Complexes 4a—4c. Complex **4a** (10.3 mg, 17.9 μmol) was placed in a Schlenk tube and dissolved in THF (0.6 mL) at −50 °C. Styrene (20.5 μL, 0.179 mmol) was added and the resulting yellow solution was placed in a water bath controlled to 10 °C. The thermolysis products were analyzed by GLC using pentane as an internal standard. The results of thermolysis of **4a**—**4c** are reported in Table 2.

Thermolysis of **4a** was also followed by ^{1}H NMR spectroscopy using toluene-d_8 as a solvent. The amount of **4a** remaining in the system at intervals was determined based on the relative peak integration of the following signals: δ = 8.80 (s, OCHO in **4a**), 6.20 (dddd, H^2 in butadiene), 5.85 (dtd, H^2 in 1-butene), 5.33 (qq, H^2 in 2-butene). The first-order plot for the time-conversion curve gave a good straight line with the slope of 3.10×10^{-4} s^{-1} (r = 0.991).

Catalytic Decarboxylation of (*E*)-2-Butenyl Formate. A typical procedure (Entry 1, Table 3) is as follows. To a solution of complex **1d** (0.133 mmol) in toluene (2 mL) were added (*E*)-2-butenyl formate (0.548 mL, 5.31 mmol) and pentane (0.152 mL, 1.33 mmol; GLC standard) at −20 °C. The system was placed in

a water bath controlled to 10 °C, and the reaction products formed at intervals were analyzed by GLC using pentane as an internal standard. The other reactions listed in Table 3 were similarly examined.

Catalytic Decarboxylation of 2,7-Octadienyl Formate. A typical procedure (Entry 2, Table 4) is as follows. The complex $[Pd_2(dba)_3]\cdot CHCl_3$ (16.8 mg, 16.2 μmol) and PPh_3 (17.0 mg, 64.8 μmol) were dissolved in THF (10 mL) at room temperature. 2,7-Octadienyl formate (200 mg, 1.30 mmol) and tetradecane (50 mg, GLC standard) were added, and the mixture was heated under reflux for 1 h. GLC analysis revealed the formation of 1,7-octadiene (**7**) and 1,6-octadiene (**8**) in a 96 : 4 ratio.

Reaction of (1-Methylallyl)palladium Chloride with Li[BEt_3H]. (η^3-1-Methylallyl)palladium chloride dimer (19.0 mg, 48.2 μmol) was dissolved in THF (1.0 mL) at room temperature and $PMePh_2$ (18.1 μL, 96.4 μmol) was added to the solution. The solution was stirred for 15 min, and styrene (0.110 mL, 0.965 mmol) and pentane (11 mL, 96.4 μmol; GLC standard) were added. The resulting pale-yellow solution was cooled to −60 °C, and a THF solution of Li[BEt_3H] (96.4 μL, 96.4 μmol) was added. The mixture was stirred at 0 °C for 5 min and organic products formed in the reaction system were analyzed by means of GLC. The reaction of the P2-type chloride complex was carried out similarly using 2 equivalents of $PMePh_2$. The results are shown in Eqs. 7 and 8.

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