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Mechanistic Studies on Pd-Catalyzed Telomerization and Co-Cyclization of Butadiene: Amphiphilicity of Bis-π-allylpalladium Intermediate in the Presence of Phosphine Ligand

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Pd-catalyzed reactions of butadiene, which proceed through a bis-π-allylpalladium intermediate, (η^3,η^3-C_8H_{12})Pd (**2**), were performed in the presence of both a pronucleophile (aceto- or cyanoacetate) and an electrophile (benzaldehyde). Methyl aceto- or cyanoacetate and benzaldehyde reacted independently with **2** to give telomers **8** and the divinyl-substituted pyranes **9**, respectively. In the case of methyl cyanoacetate, the co-cyclization of **2** with 2-cyano-3-phenylpropenoate (**11**) formed in situ also took place to afford the cyclohexane derivative **10**. Namely, three kinds of amphiphilic additions of the C_8-chain of **2** occurred to $^{\delta+}$H–Nu$^{\delta-}$, $^{\delta+}$C=C$^{\delta-}$, and $^{\delta+}$C=O$^{\delta-}$ simultaneously in a one-pot reaction. The Pd-catalyzed reaction of allyl chloride, allyltributylstannane, methyl cyanoacetate, and benzaldehyde was undertaken under neutral conditions, expecting the amphiphilic reactions by the intermediacy of (η^3-C_3H_5)$_2$Pd (**6**) formed in situ. Allylation of both benzaldehyde and methyl cyanoacetate took place. Competitively amphiphilic bis-allylation of the polar double bond of **11** also occurred to form the 1,7-octadiene derivative **18**. The mechanisms of both reactions can be explainable in terms of the amphiphilicity of the intermediates (**2** and **6**) in the presence of a phosphine ligand.

Ligand-modified palladium complexes are the most versatile catalysts for C–C bond formations.[1,2] Among them, the catalytic allylation of pronucleophiles (HNu) (Chart 1),[3,4] and telomerization (Chart 2, route a)[5–10] and co-cyclization (Chart 2, route b)[11–15] of butadiene are the typical reactions. These reactions proceed via π-allylpalladium intermediates **1** and **2**.

In the reaction of Chart 1, it is important to notice that π-allylpalladium halide **1** reacts with soft carbon nucleophiles,[16] while other allylmetals, such as allylmagnesium and -nickel, react with electrophiles, e.g., aldehydes. Therefore, the reaction pathway of the intermediate **1** is in marked contrast to that of other allyl metals. The Pd-catalyzed allylation of pronucleophiles takes place smoothly under basic conditions with a variety of allylic compounds, such as halides and esters. On the other hand, allylation with allyl carbonates,[17] vinyloxiranes,[18,19] and acetates[20] occurs even under neutral conditions.

The Pd-catalyzed reactions of butadiene (Chart 2) are different from those catalyzed by nickel catalysts.[21] Unlike nickel catalysts, neither cyclodimerization nor trimerization to form cyclooctadiene or cyclododecatriene, respectively, takes place with palladium catalysts. Palladium complexes catalyze two important reactions of butadiene. One is linear dimerization with the incorporation of pronucleophiles, namely the telomerization to form **3** (Chart 2, a route), which proceeds readily under neutral conditions. The other reaction is co-cyclization with C=O or C=N bonds to form the six-membered heterocyclic compounds **4** with two vinyl groups (Chart 2, b route). For example, co-cyclization with aldehydes affords divinyltetrahydropyranes. This co-cyclization was reported in the early 1970's,[11–15] soon after discovering the telomerization of butadiene with pronucleophiles, such as active methylene compounds.

The formation of **3** and **4** is quite interesting, because the reaction pathways of bis(π- allyl)palladium intermediate **2** are in contrast to that of **1**, which reacts only with nucleophiles. It should be recognized that **2** can react with both electrophiles (aldehydes) as well as nucleophiles. Yamamoto and coworkers[22] reported on the amphiphilic nature of a simple bis(π-allyl)palladium (**6**), which is formed in situ from **1** and allyltributylstannane (**5**) (Chart 3). Recently, the application of the amphiphilic reaction to the synthesis of medium-sized carbocycles has also been reported.[23] They have shown that one allyl group reacts with a nucleophile, and the other with an electrophile. Consequently, there is a possibility that one allyl unit of **2** reacts with a nucleophile, and the other with an electrophile independently of each other to form **7**, as shown in Chart 4(a route).

To obtain a consistent mechanistic explanation concerning the reaction of the π-allylpalladium intermediates **1**, **2**, and **6**, we attempted a Pd-catalyzed reaction of butadiene, which proceeds via intermediate **2**, in the presence of both electrophiles and pronucleophiles. In addition, this paper considers the allylation of pronucleophiles through **6**.

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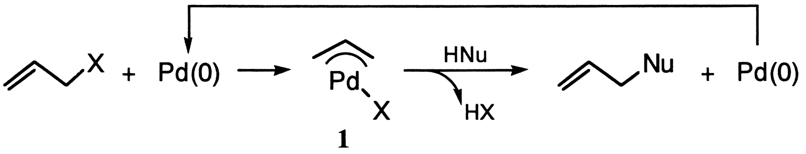


Chart 1.

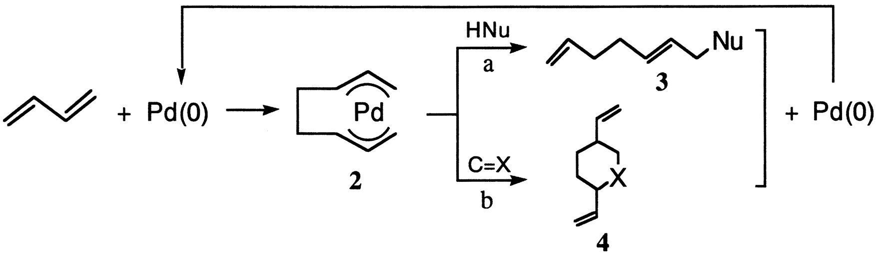


Chart 2.

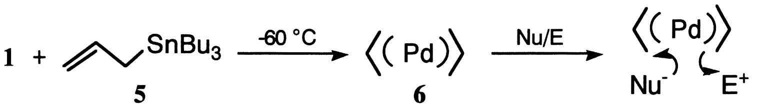


Chart 3.

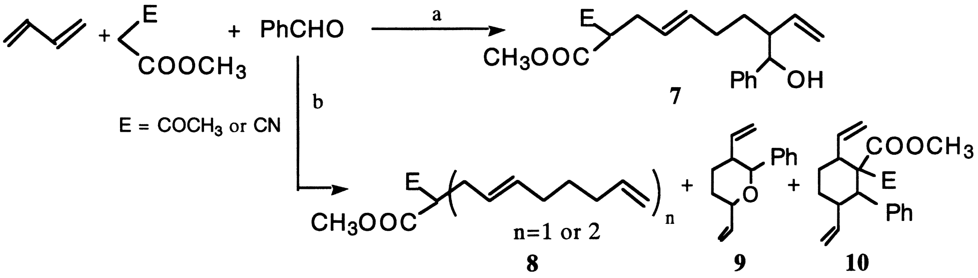


Chart 4.

Results and Discussion

Catalytic Reaction of Butadiene in the Presence of Aldehyde and Aceto- or Cyanoacetate. The reaction of butadiene in the presence of both benzaldehyde and methyl aceto- or cyanoacetate was studied with the expectation that the one allyl unit of the C$_8$-Pd intermediate **2** reacts with methyl aceto- or cyanoacetate and the other with benzaldehyde to form **7** (Chart 4a). Palladium(II) acetate combined with triphenylphosphine was used as the catalyst.

Gas chromatography/mass spectrometry (GC/MS) of the reaction mixture revealed that a variety of compounds were formed. However, the expected product **7** was not obtained at all. Instead, methyl aceto- or cyanoacetate and benzaldehyde reacted independently to give telomers **8** and pyranes **9**, respectively. In addition, the cyclohexane derivatives **10** were obtained. All of these products (**8**, **9**, and **10**) were a mixture of their isomers. Two isomers of **10** were detected by GC.[24] The results are summarized in Table 1. All of the experiments were performed in the presence of an excess amount of butadiene. Therefore, the dimers of butadiene (1,3,7-octatriene and 4-vinyl-1- cyclohexene) were formed in all cases. Their yields are not included in Table 1. The yields of **8**, **9**, and **10** varied from reaction to reaction. However, three kinds of products (**8**, **9**, and **10**) were always formed when both benzaldehyde and methyl cyanoacetate were present in the reaction system. The expected product **7** was not formed even in the presence of triethylamine or DBU. When methyl acetoacetate was used instead of cyanoacetate, the cyclic product **10** was not formed. The formation of **10** can be explained by the following reaction pathway. Firstly, 2-cyano-3-phenylpropenoate (**11**) is formed in situ by aldol condensation of methyl cyanoacetate with benzaldehyde, followed by dehydration (Chart 5). This polar olefin then undergoes double allylation in a similar manner as the co-cyclization with benzaldehyde. There are only few examples of the co-cyclization of **2** with C=C double bonds,[23] though extensive work on reactions of this type has been done using nickel catalysts.[21]

In the reactions of butadiene described above, the catalyst containing the phosphine ligand seems to be a favorable choice. In the presence of the phosphine ligand, however, **2** is converted into a σ-allyl-π-allylpalladium intermediate **12**.

Table 1. Reaction of Butadiene with Benzaldehyde and Pronucleophiles (HNu) in One-Pot (Chart 4)[a]

PhCHO	HNu	$Pd(OAc)_2/PPh_3$	Solvent	Temp	Yield/%		
mmol	E, mmol			°C	**8**	**9**	**10**
20	—	1/2	*i*-PrOH	80	—	86	—
—	CN, 20	1/2	*i*-PrOH	80	95	—	—
20	CN, 20	1/2	*i*-PrOH	80	63	73	6
10	CN, 10	1/6	*i*-PrOH	80	25	48	30
10	CN, 10	1/6	THF	reflux	15	33	24
20	CH_3CO, 20	1/2	*i*-PrOH	80	89	54	—
20	CH_3CO, 20	1/4	*i*-PrOH	80	93	44	—
20	CH_3CO, 20	1/2	THF	reflux	82	16	—

a) butadiene, 10 mL; solvent, 5 mL; $Pd(OAc)_2$, 0.5 mmol; time, 20 h.

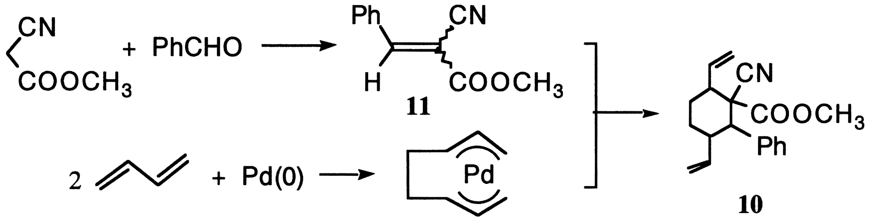


Chart 5.

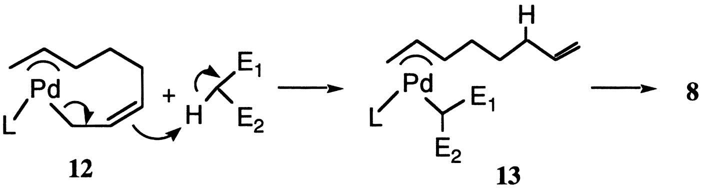


Chart 6.

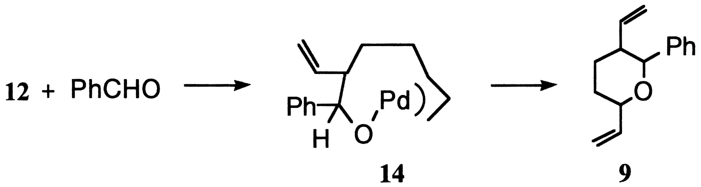


Chart 7.

Complex **12** was isolated and its reaction with cyanoacetate was studied in detail by Jolly and co-workers using NMR spectoscopy.[25] According to their results, the first step of the telomerization with cyanoacetate is abstraction of the proton from the cyanoacetate by one of the nucleophilic allyl units, while the other allyl unit remains as a π-allyl form **13**. Then, the electrophilic addition of the π-allyl unit to the coordinated soft carbon nucleophile affords the telomers **8** (Chart 6). In this way, even in the absence of a base, proton abstraction from pronucleophile occurs by one of the allyl units of the C_8-Pd intermediate. This explanation indicates that one of the allyl units acts as a base, in other words, as a nucleophile, and the other as an electrophile. That is to say, in the presence of the phosphine ligand, intermediate **2** is converted into **12**, which then shows amphiphilic reactivity.

Co-cyclization with benzaldehyde is explained by double allylation of the C=O double bond with amphiphilic **2** after conversion into **12** in the presence of phosphine ligand. Namely, while π-allylpalladium **1**, even in the presence of triphenylphosphine, does not attack the positive carbon atom of the carbonyl group at all, the one allyl unit of **2** attacks the positive carbon atom and the other the negative oxygen atom to form **9** (Chart 7).

Reaction of Allyl Chloride, Allyltributylstannane, Methyl Cyanoacetate, and Benzaldehyde in One-Pot. The simplest member of the bis(π-allyl)palladium system is $(\eta^3\text{-}C_3H_5)_2Pd$ (**6**). A traditional synthetic method of **6** is the reaction of **1** with allylmagnesium halide at low temperature.[25–27] Yamamoto and co-workers[28] have shown that **6** is also formed by the reaction of **1** with allyltributylstannane (**5**). Following their method (Chart 3), we prepared bis(π-allyl)palladium (**6**) in situ and allowed it to react with methyl cyanoacetate in the presence of triphenylphosphine (Chart 8).

Allylated products (**15** and **16**) were formed (Table 2). Without the phosphine ligand, allylation did not occur. Neither **1** nor allyltributylstannane (**5**) by itself reacted with methyl cyanoacetate. Consequently, the formation of allylated products means the intermediacy of bis(π-allyl)palladium formed in situ. The reaction of Chart 8 can be explained as follows. The coordinating and basic alkoxide anion of π-allyl(homoallyloxy)palladium, the same type of intermediate as **14** formed by the reaction of **6** with benzaldehyde, deprotonates methyl cyanoacetate to form the homoallyl alcohol **17**, while the remaining allyl group reacts as an electrophile with carboanion to form **15** and/or **16**. The formation of the homoallyl alcohol **17** is in contrast to that of the pyranes **9** in the reaction of butadiene (Chart 4), where the alkoxide anion of the intermediate **14** reacts with the remaining allyl unit before deprotonation by reductive elimination.

In this stoichiometric reaction of Chart 8, palladium was reduced to a zero-valent species. π-Allylpalladium chloride (**1**) is formed by the oxidative addition of allyl chloride to the Pd(0) complex and gives **6** in the presence of allyltributylstannane. In this way, if allyl chloride and allyltributylstannane are still present in the reaction solution, **6** is regenerated; thus, the catalytic reaction is possible.

Table 2. Stoichiometric Reaction of (η^3-C_3H_5)$_2$Pd Formed in situ with Benzaldehyde and Methyl Cyanoacetate (Chart 8)[a)]

$CNCH_2COOCH_3$	PhCHO	Temp	Yield/%		
mmol	mmol	°C	**15**	**16**	**17**
1.0	—	−20	22	12	—
—	1.0	−20	—	—	22
0.5	0.5	−40	—	58	30

a) (η^3-C_3H_5PdCl)$_2$/$C_3H_5SnBu_3$/PPh_3 = 0.5/1.0/2.0 (mmol); solvent, THF 30 mL.

Then, the reaction of allyl chloride, allyltributylstannane, methyl cyanoacetate, and benzaldehyde was undertaken in the presence of a catalytic amount of $Pd(OAc)_2$ and triphenylphosphine, expecting the amphiphilic reactions of **6** formed in situ with the liberation of tributylchlorostannane (Chart 9).

The reaction mixture was hydrolyzed and analyzed by GC. The products were homoallylic alcohol **17** and the allylated product **16** of cyanoacetate and 1,2-diallylated product **18** of the polar olefin formed from cyanoacetate and benzaldehyde. The results are given in Table 3. The formation of the diallylated product (**18**) has already been discussed as the amphiphilic reaction of bis-π-allylpalladium **6** by Yamamoto et al.[22]

When either allyl chloride or allyltributylstannane was absent, the allylations did not occur at all. In contrast to the reaction of butadiene, the co-cyclization-type reaction, namely the addition of the two allyl units of **6** to both carbon and oxygen atoms of benzaldehyde to afford an allylic ether **19** did not take place. According to a mechanistic study done by Yamamoto,[28] the formation of homoallylic alcohol **17** proceeds via a π-allyl(homoallyloxy)palladium intermediate, which reacts with allyltributylstannane to regenerate **6** along with the liberation of the alkoxystannane. This is the reason why allylic ether **19** is not formed.

In this catalytic reaction it is evident that the one allyl unit

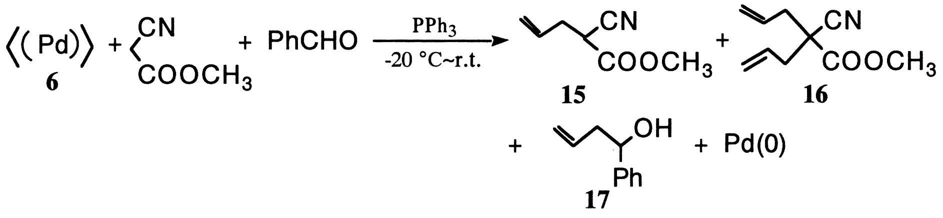


Chart 8.

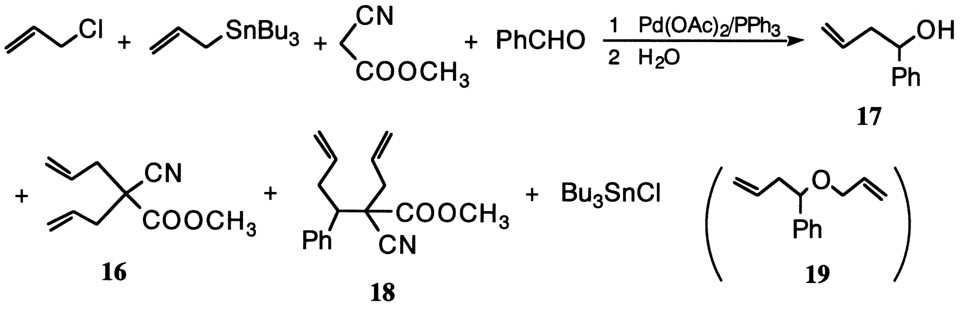
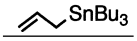


Chart 9.

Table 3. Reaction of Allyl Chloride, Allylstannane, Cyanoacetate, and Benzaldehyde(Chart 9)[a)]

		$CNCH_2COOCH_3$	PhCHO	Solvent	Temp	Yield/%[b)]		
mmol	mmol	mmol	mmol		°C	**16**	**17**	**18**
1.1	1.0	—	0.5	DMSO	100	—	21	—
0.8	0.7	0.4	—	DMSO	100	86	—	—
1.6	1.6	1.3	1.0	DMSO	100	24	trace	47
1.7	1.9	1.1	1.0	THF	reflux	64	trace	5

a) $Pd(OAc)_2/2\ PPh_3$, 0.1/0.2 mmol; time, 20 h
b) Based on benzaldehyde.

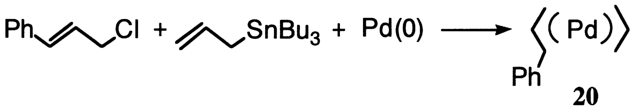


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Chart 10.

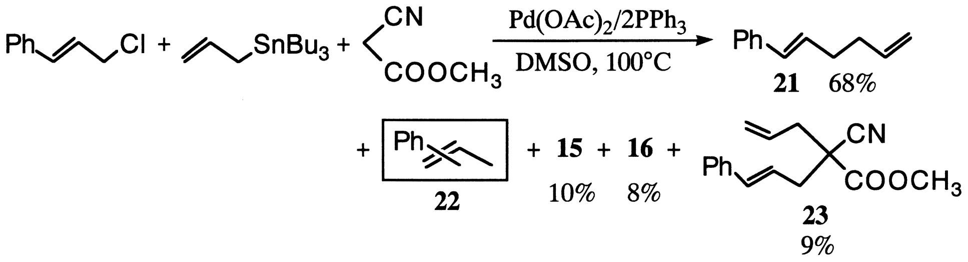


Chart 11.

of **6** formed in the catalytic cycle acts as a nucleophile abstracting the proton from the cyanoacetate in a similar manner to that of the C_8-Pd intermediate. This explanation means that propene should be evolved during allylation. At 100 °C, propene is too volatile to be detected. Therefore, to confirm the role of the allyl group as the nucleophile, cinnamyl chloride was used instead of allyl chloride, expecting the formation of the intermediate **20** (Chart 10). If the cinnamyl group of **20** acts as the nucleophile in this case, phenylpropenes **22** must be formed. Thus, a one-pot reaction of cinnamyl chloride, allyltributylstannane, and methyl cyanoacetate was carried out at 100 °C in the presence of a catalytic amount of $Pd(OAc)_2/PPh_3$ (Chart 11).

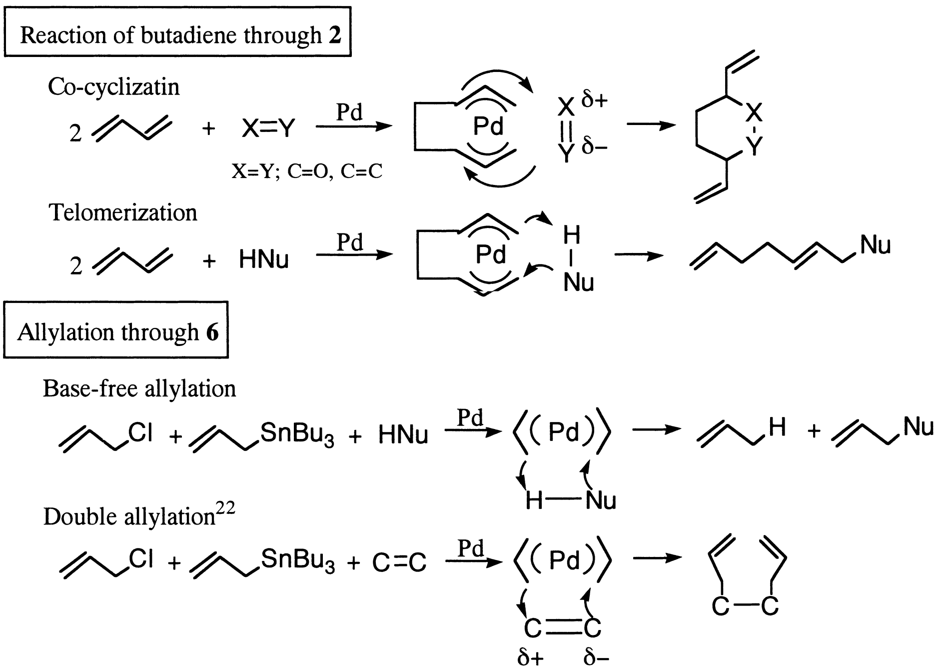
Since cinnamyl chloride readily forms a cross-coupling product with allyltributylstannane, 1-phenyl-1,5-hexadiene (**21**) was formed in 68% yield.[29] In this reaction, however, phenylpropenes **22**, which were formed from the cinnamyl group as a result of proton abstraction, were detected by GC/MS together with allylated products **15**, **16**, and **23**. Compared with the other products, phenylpropenes were still so volatile that their yields were not determined.

Conclusion

A palladium-catalyzed three-component reaction of butadiene, aldehyde (electrophile) and methyl aceto- or cyanoacetate (pronucleophile) (Chart 4) was attempted in the absence of a base; but the expected product **7**, in which the electrophile is bound to the one end and the nucleophile to the other end of the C_8-chain, was not formed. Instead, benzaldehyde and methyl cyanoacetate underwent amphiphilic reactions with butadiene separately. In parallel with the reaction of butadiene, mixtures of allyl chloride, allyltributylstannane, benzaldehyde, and methyl cyanoacetate were allowed to react in a one-pot manner (Chart 9). In this case, allylated products of cyanoacetate and benzaldehyde were formed. The formations of the products of both reactions, except for homoallylic alcohol **17**, are explained by the amphiphilic allylation through the bis(π-allyl)palladium intermediates (**2** and **6**) in the presence of the phosphine ligand. As described above, bis(π-allyl)palladium complexes **2** and **6** have a π-allyl-σ-allyl structure in the presence of the phosphine ligand. However, for simplicity and in order to emphasize their amphiphilic reactivity in consistent mechanistic explanations, we use here the bis-π-allyl structures as adopted for elucidating reaction paths everywhere. Thus, the Pd-catalyzed allylation of pronucleophiles (so-called Tsuji–Trost reaction) under neutral conditions and the reaction of butadiene are schematically expressed as in Scheme 1. It is worth noting that the three kinds of amphiphilic reactions of **2** (Chart 4) take place simultaneously in a one-pot manner.

Experimental

General. Solvents were purified by conventional methods and used under an atmosphere of argon. Liquefied butadiene was dried over Molecular Sieve 3A at room temperature. Other com-



Scheme 1. Amphiphilic reactions of bis(π-allyl)palladium.

mercially available reagents were used without further purification. A gas-chromatographic analysis was performed on a Shimadzu GC-14B (TCD). Spectral data were recorded by the following instruments: IR, Perkin Elmer 1600FT-IR; NMR, JEOL GX-200 and Varian VXR-500 (500 MHz); GC/MS, Hitachi M-4100 MS/MS system.

Reaction of Butadiene, Methyl Cyanoacetate, and Benzaldehyde (Chart 4). The typical procedure was as follows. In a 50 mL stainless steel autoclave, $Pd(OAc)_2$ (0.5 mmol), triphenylphosphine (1.0 mmol), and a stirring bar were placed. Then, 2-propanol (5 mL), methyl cyanoacetate (20 mmol), and benzaldehyde (20 mmol) were added by a syringe under an atmosphere of argon. The autoclave was cooled in a dry ice-methanol bath. Liquefied butadiene (10 mL) was added by syringe. The autoclave was stirred magnetically at 80 °C for 20 h. After the reaction, the solvent was removed by a rotary evaporator and the residue was distilled by a glass tube oven (Shibata GTO-350RD) under reduced pressure. The products were analyzed by GC using *o*-terphenyl as an internal standard (column, Silicon DC-560, 3 m, 250 °C). The yields were calculated by assuming that the peak area ratio of the products to that of *o*-terphenyl corresponds to the ratio of their weights. Identification of the products was done by GC/MS and ^{1}H NMR spectroscopy. The reaction conditions and the results are given in Table 1.

One of the isomers of **10**, which was eluted earlier in GC, was isolated by recycle HPLC (column, JA1GEL 1H+2H; eluent, $CHCl_3$ of a rate of 3.5 mL/min).[30] IR (neat film) 2242 ($\nu_{C=N}$), 1744 ($\nu_{C=O}$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.53 (m, 1H), 1.91 (m, 2H), 2.04 (m, 1H), 2.83 (m, 2H), 2.98 (d, J = 12 Hz, 1H), 3.44 (s, 3H), 4.83 (d, J = 10.5 Hz, 1H), 4.95 (d, J = 12 Hz, 1H), 5.13 (d, J = 10.5 Hz, 1H), 5.17 (d, J = 17 Hz, 1H), 5.40 (m, 1H), 5.78 (m, 1H), 7.26 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 27,7, 31.6, 41.4, 48.6, 52.7, 53.8, 59.0, 115.0, 116.8, 118.4, 127.9, 128.3, 128.4, 129.0, 136.4, 137.2, 139.6, 168.3; HRMS (EI) Calcd for $C_{19}H_{21}NO_2$: 295.1573, found: 295.1575.

Stoichiometric Reaction of π-Allylpalladium Chloride (1), Allyltributylstannane (5), Methyl Cyanoacetate, and Benzaldehyde (Chart 8). A typical example is the following. Complex **1** (0.5 mmol) was placed in a two-neck flask. The atmosphere was replaced with argon and THF (30 mL) was added. After the solution was cooled to ca. −60 °C, a THF solution of allyltributylstannane (1 mmol) was added. The solution was stirred between −60 and −40 °C for 1 h. Triphenylphosphine (2 mmol), methyl cyanoacetate (0.5 mmol), and benzaldehyde (0.5 mmol) were added in this order at −40 °C. While the flask was left in the bath with stirring overnight, the temperature was gradually raised to room temperature. The solution was treated with water. The products were extracted with ether and distilled under reduced pressure. The yields were determined by GC (column, Silicon DC-560, 3 m, at programmed temperature ranging from 100 to 250 °C at a rate of 5 °C/min) using 4-methylbiphenyl as an internal standard. Identification of the products was done by GC-MS; their retention times were compared with those of authentic samples prepared by the reported method.[17b] The results are given in Table 2.

Reaction of Allyl Chloride, Allyltributylstannane, Methyl Cyanoacetate, and Benzaldehyde (Chart 9). The following is a representative example. In a two-neck flask equipped with a condenser, $Pd(OAc)_2$ (0.10 mmol), triphenylphosphine (0.20 mmol), and a stirring bar were placed. The atmosphere was replaced with argon. THF (10 mL), allyl chloride (1.7 mmol), allylstannane **5** (1.9 mmol), methyl cyanoacetate (1.1 mmol), and benzaldehyde (1.0 mmol) were added by syringe in this order under an argon atmosphere. The solution was heated at 100 °C for 20 h. The isolation and analysis of the products were done as described above. The results are summarized in Table 3.

Reaction of Cinnamyl Chloride, Allyltributylstannane, and Methyl Cyanoacetate (Chart 11). The reaction was performed as described above for allyl chloride.

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