Effects of Bidentate Phosphine Ligands on *syn*−*anti* Isomerization in π-Allylpalladium Complexes

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The rates of *syn*−*anti* isomerization in a series of cationic π-allylpalladium complexes [Pd(η^3-$Me_2CCHCHD$)(bisphosphine)]BAr^F_4 [Ar^F = 3,5-$(CF_3)_2C_6H_3$] were measured by ^{1}H NMR spin-saturation transfer techniques. For the complexes with α,ω-bis(diphenylphosphino)-alkanes ($Ph_2P(CH_2)_nPPh_2$, n = 2−4), a correlation between the bisphosphine's bite angles and the *syn*−*anti* isomerization rates was observed, the bisphosphine with smaller bite angle accelerating the *syn*−*anti* isomerization. The isomerization rate was also dependent on the electronic characteristics of the bisphosphine ligands. Of the substituted dppf ligands (Fe(η^5-$C_5H_4PAr_2)_2$, Ar = 4-$CF_3C_6H_4$, Ph, 4-$MeOC_6H_4$), it was fastest with the electron-withdrawing 4-$CF_3C_6H_4$ group and slowest with the electron-releasing 4-$MeOC_6H_4$ group on the phosphorus atoms. These bisphosphines were used as supporting ligands for the palladium-catalyzed allylic alkylation of (*Z*)-cinnamyl acetate and (*Z*)-2-hexenyl acetate with the sodium salt of dimethyl methylmalonate. The alkylation products with *E*-geometry, which result from the isomerization of π-allylpalladium intermediates from *anti* to *syn*, were formed more with the bisphosphines of faster *syn*−*anti* isomerization.

Introduction

Palladium-catalyzed allylic alkylation is one of the most widely and the most frequently used carbon−carbon bond forming reactions catalyzed by transition metal complexes because of its wide range of reactivity, high catalytic activity, and easy manipulation,[1] and the allylic alkylation reaction has been successfully extended to catalytic asymmetric synthesis by use of chiral ligands.[2] The reaction proceeds via a π-allylpalladium(II) intermediate, and the stereochemical outcome of the catalytic reaction is highly dependent on the stereochemical structure of the π-allylpalladium(II) intermediate.[3] The π-allylpalladium complex is well known to undergo isomerization via a so-called π−σ−π process, and the isomerization plays a decisive role in the reactions that involve the π-allylpalladium intermediate in the catalytic cycle.[1−4] Thus, for example, the allylic alkylation of (*Z*)-allyl esters is usually accompanied by isomerization of the olefin geometry from *Z* to *E*, which is caused by *anti*−*syn* isomerization in the π-allylpalladium intermediates[5,6] (Scheme 1). In the asymmetric substitution reactions of racemic allylic esters using chiral ligands, epimerization is required in the π-allylpalladium intermediates, for which the π−σ−π process is responsible[7] (Scheme 2). In these reactions, the relative rate between the isomerization of the π-allylpalladium intermediates and the nucleophilic attack giving the final products is a key factor determining the stereochemical outcome.

When a palladium complex coordinated with a phosphine ligand is used as a catalyst, the influence of the phosphine ligand on stereoselectivity in the catalytic allylic substitution reactions is very large,[8] although the effect is not yet fully established. Thus, it is expected

(1) For reviews: (a) Tsuji, J. *Acc. Chem. Res.* **1969**, *2*, 144. (b) Tsuji, J. *Pure Appl. Chem.* **1982**, *54*, 197. (c) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry, Vol. 8*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; pp 799−938. (d) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985. (e) Tsuji, J. *J. Organomet. Chem.* **1986**, *300*, 281. (f) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140. (g) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1990. (h) Godleski, S. In *Comprehensive Organic Synthesis, Vol. 4*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon: Oxford, 1991; pp 585−659. (i) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley and Sons: Chichester, 1995.

(2) For reviews: (a) Trost, B. M.; Chulbom, L. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; VCH: New York, 2000; p 593. (b) Pfaltz, A.; Lautens, M. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. 2, Chapter 24. (c) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (d) Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; p 325. (e) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron Asymmetry* **1992**, *3*, 1089.

(3) For reviews: (a) Consiglio, G.; Waymouth, M. *Chem. Rev.* **1989**, *89*, 257. (b) Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev.* **1996**, *155*, 35.

(4) (a) Cuvigny, T.; Julia, M. Rolande, C. *J. Organomet. Chem.* **1985**, *285*, 395. (b) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620. (c) Åkermark, B.; Zetterberg, K.; Hansson, S.; Krakenberger, B.; Vitagliano, A. *J. Organomet. Chem.* **1987**, *335*, 133. (d) Åkermark, B.; Hansson, S.; Vigagliano, A. *J. Am. Chem. Soc.* **1990**, *112*, 4587. (e) Sjögren, M.; Hansson, S.; Norrby, P.-O.; Åkermark, B.; Cucciolito, M. E.; Vitagliano, A. *Organometallics* **1992**, *11*, 3954. (f) Sjögren, M. P. T.; Hansson, S.; Åkermark, B.; Vitagliano, A. *Organometallics* **1994**, *13*, 1963.

(5) As an example of the palladium-catalyzed allylic alkylation of (*Z*)-allyl acetates giving *E*-products: Hayashi, T,; Yamamoto, A.; Hagihara, T. *J. Org. Chem.* **1986**, *51*, 723.

(6) As an example of the nucleophilic attack before the isomerization: Kazmaier, U.; Zumpe, F. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 802.

(7)) (a) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033. (b) MacKenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046. (c) Hayashi, T.; Kishi, K.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 1743. (d) Dawson, G. J.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Asymmetry* **1995**, *6*, 2535. (e) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *Chem. Commun.* **1997**, 561. (f) Prétot, R.; Pfaltz, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 323.

(8) For recent examples: (a) Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1998**, 25. (b) van Haaren, R. J.; van Strijdonck, G. P. F.; Oevering, H.; Reek, J. N. H.; Kramer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **2001**, 837.

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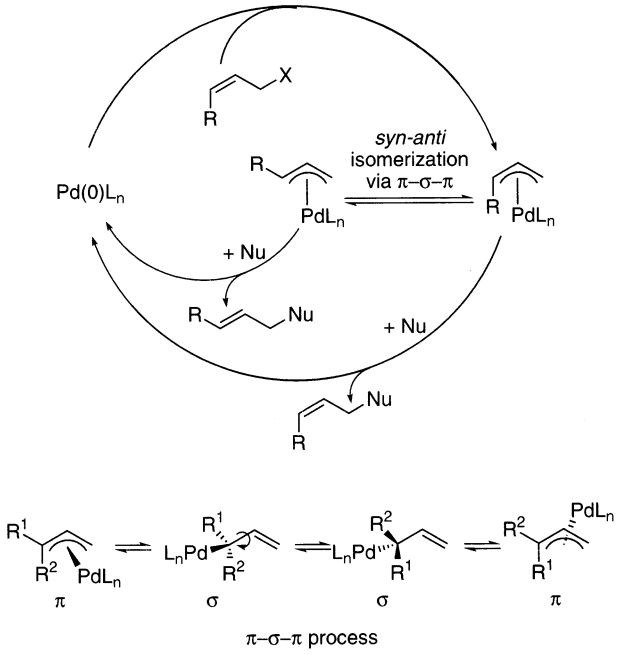
Scheme 1 *anti*−*syn* Isomerization in the Allylic Alkylation of (*Z*)-Allyl Esters

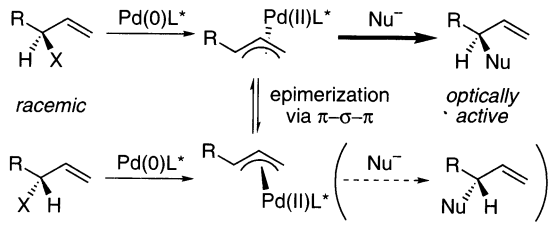


that the rate of the isomerization via the $\pi-\sigma-\pi$ process in π-allylpalladium complexes can be controlled by proper choice of the phosphine ligand. To the best of our knowledge, however, there have been only a few reports on the measurements of the absolute values of the *syn*−*anti* isomerization rates, which is in particular palladium complexes coordinated with chiral phosphine ligands.[9−11] We have measured absolute values of the isomerization rates in a series of cationic π-allylpalladium-bisphosphine complexes [Pd(η^3-$Me_2CCHCHD$)(bisphosphine)]BAr^F_4 using NMR techniques, where bisphosphine is dppe,[12] dppp,[12] dppb,[12] dppf,[12] MeO-dppf,[12] or CF_3-dppf.[12] This study has clarified the effects of the bidentate phosphines on the isomerization that proceeds through the $\pi-\sigma-\pi$ process in the π-allylpalladium complexes. These π-allylpalladium complexes have been used for the catalytic allylic alkylation of (*Z*)-allyl acetates[5] and showed a good correlation between the *E*/*Z*-selectivity in the catalytic reactions and the rates of the *syn*−*anti* isomerization in the complexes. Here we report our observations.

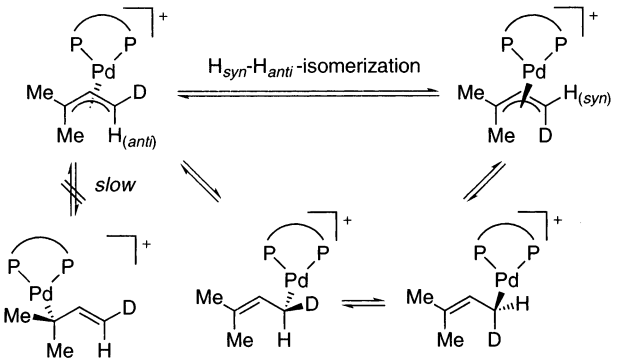
Results and Discussion

Phosphine Ligands. Two main factors characterizing the nature of bidentate phosphine ligands are their bite angles and electronic effects based on the substituents on the phosphorus atoms.[13] These two factors are fundamentally different; thus, two series of bisphosphine ligands were used in the present studies. The first series is α,ω-bis(diphenylphosphino)alkanes, where the number of methylene units between the two phosphorus atoms is two (dppe), three (dppp), or four (dppb). These three bisphosphines have different bite angles, while their electronic characteristics can be assumed to be almost the same. The second series is 1,1′-bis(diarylphosphino)ferrocenes, where the aryl substituents are phenyl (dppf), 4-$MeOC_6H_4$ (MeO-dppf), or 4-$CF_3C_6H_4$ (CF_3-dppf). The electron-releasing MeO groups or the electron-withdrawing CF_3 groups are introduced at the *p*-position of the phenyl groups. They can alter only the electronic characteristics of the phosphines without changing the steric environment around the phosphorus atoms. All of the bisphosphine ligands chosen above are highly symmetric. They are at least C_2 symmetric, the two phosphino groups being equivalent, which will not increase the number of the isomers of π-allylpalladium complexes.

Scheme 2. Epimerization via the $\pi-\sigma-\pi$ Process in Asymmetric Allylic Alkylation of Racemic Allyl Esters



Scheme 3

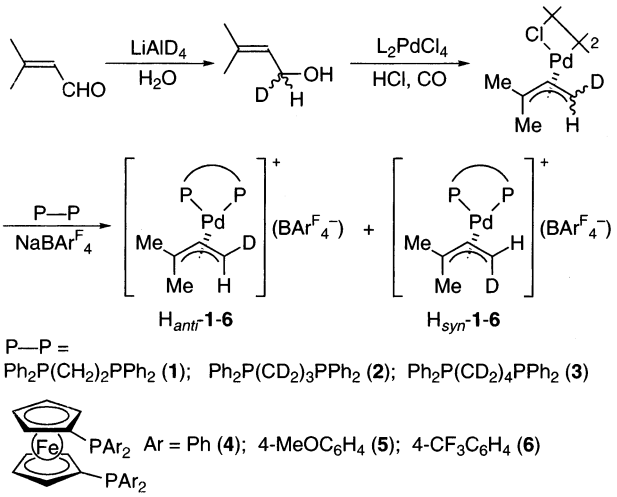


Design of Complexes. For the accurate measurement of the rates of the *syn*−*anti* isomerization, we designed a π-allylpalladium system shown in Scheme 3, which should show simple fluxional behavior as described below.

First, two methyl groups were introduced at one end of the π-allyl moiety, which is expected to make the isomerization through a σ-allyl intermediate containing a tertiary alkyl−palladium bond negligibly slow.[3,14,15] Actually, the 1,1-dimethyl-π-allyl ligand showed the

(9) Breutel, C.; Pregosin, P.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067.
(10) Kawatsura, M.; Uozumi, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron* **2000**, *56*, 2247.
(11) For the isomerization related to a memory effect in a π-allylpalladium intermediate: Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681.
(12) Abbreviations of bisphosphines: dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, dppf = 1,1′-bis(diphenylphosphino)-ferrocene, MeO-dppf = 1,1′-bis[di(4-methoxyphenyl)phosphino]ferrocene, CF_3-dppf = 1,1′-bis[bis(4-trifluoromethylphenyl)phosphino]ferrocene.
(13) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(14) During the studies on palladium-catalyzed asymmetric reduction of allylic esters with formic acid, it was observed that this type of $\pi-\sigma-\pi$ isomerization is very slow: (a) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775. (b) Hayashi, T.; Iwamura, H.; Uozumi, Y.; Matsumoto, Y.; Ozawa, F. *Synthesis* **1994**, 526. (c) Hayashi, T.; Kawatsura, M.; Iwamura, H.; Yamaura, Y.; Uozumi, Y. *Chem. Commun.* **1996**, 1767.
(15) The alkyl substituent effects on the $\pi-\sigma-\pi$ isomerization have been studied by applying a density functional theory: Solin, N.; Szabó. *Organometallics* **2001**, *20*, 5464.

Scheme 4



syn−*anti* isomerization only at the nonsubstituted CH_2 terminus. The selective isomerization is demonstrated by the NOESY spectrum of the complex where the exchange is observed between the two terminal hydrogens, but not between the two methyl groups. Second, the monodeuterated π-allyl ligand was used for the following reasons. The exchange rates between the two hydrogen nuclei were calculated from the T_1 values of the hydrogen resonances and the magnitude of the spin-saturation transfer between the two resonances (see Experimental Section). With a standard pulse sequence for the spin-saturation transfer measurement, the nuclear Overhauser effect is also induced in addition to the spin-saturation transfer effect. Thus, the intensity change is always observed as an aggregate of the two fundamentally different phenomena. In our system, the two hydrogens investigated are located on the same carbon; therefore, the NOE might not be negligible. Our strategy to solve this problem is deuterium labeling of one of the terminal hydrogens, as shown in Scheme 3. With the monodeuterated π-allyl complex, the *syn*−*anti* isomerization is observed as an intermolecular process by NMR, and thus NOE should not be induced. The third device in the design of the palladium complex is partial deuterium labeling of the bisphosphine ligands. For the dppp and dppb complexes, ^{1}H NMR signals from the alkylene backbone of the phosphines are overlapped with the resonances from the π-allyl ligand. Therefore, the partially deuterated phosphines $Ph_2P(CD_2)_nPPh_2$ (n = 3 (dppp-d_6) and 4 (dppb-d_8)) were synthesized from the corresponding deuterated α,ω-diols.[16]

Preparation of Complexes. Preparation of the deuterium-labeled π-allylpalladium complexes are shown in Scheme 4. Reduction of 3-methyl-2-butenal with $LiAlD_4$ gave a quantitative yield of 1-deuterio-3-methyl-2-butenol, which was treated with Li_2PdCl_4 and carbon monoxide in hydrochloric acid according to the standard procedure[7a] to give a dichloro-bridged dimeric π-allylpalladium complex. Treatment of the dimer with 2 equiv of the bidentate phosphines (1 equiv to Pd) followed by anion exchange with $NaB[3,5\text{-}(CF_3)_2C_6H_3]_4$[17] gave a series of cationic palladium complexes **1**−**6**. The cationic complexes are air stable and can be purified by recrystallization or column chromatography over silica gel (with chloroform). All the complexes **1**−**6** exist as a mixture of two isotopomers in solution. In any case, the two isotopomers, the H_{syn}-D_{anti} isomer and the H_{anti}-D_{syn} isomer, exist with equal abundance in solution and show no thermodynamic preference for one of the two isomers.

Recrystallization of the dppb-d_8[16] complex **3** from dichloromethane/pentane gave prismatic crystals, and the solid state structure was determined by single-crystal X-ray crystallography (Figure 1). The overall molecular structure of the complex can be seen as distorted four-coordinate square planar. Pd(1), P(1), P(2), C(1), and C(3) atoms are located on the same plane: the sum of the four angles at the Pd center involving the other four atoms is 359.9°. The Pd(1)−C(3) bond is longer (i.e., weaker) than the Pd(1)−C(1) bond, which is consistent with formation of the σ-allyl intermediate at the C(1) center (vide supra). An expected outcome from these is a stronger *trans* influence from C(1) than that from C(3). Indeed the Pd(1)−P(1) bond is longer than the Pd(1)−P(2) bond. No bonding interactions were observed between the cationic palladium moiety and the BAr^F_4 anion.

Measurement of *syn*−*anti* Isomerization Rate. The *syn*−*anti* isomerization shown in Scheme 3 was so slow that no line broadening of the H_{syn} and H_{anti} signals was detected in the ^{1}H NMR spectra in $CDCl_3$ in the temperature up to 55 °C for all the complexes. However, in the ^{1}H−^{1}H NOESY spectra of the deuterium-labeled complexes, cross-peaks were observed between the H_{syn} and H_{anti} resonances as expected, which is direct evidence for the relatively slow exchange between the two nuclei; thus, the measurement of the exchange rates was carried out by a spin-saturation transfer technique using the Forsén−Hoffman method.[18] We have examined several solvents and observed that the exchange rates in less polar solvents such as $CDCl_3$ and CD_2Cl_2 are highly dependent on a small amount of impurities such as acetone or ether, which was brought to the samples during the purification processes. We found that acetone-d_6 is the solvent of choice for the rate measurement because the results are most reproducible and reliable. Thus, the spin-saturation transfer experiments were performed in acetone-d_6 by irradiating either of the H_{syn} and H_{anti} signals of the π-allyl complexes. For example, in the dppb-d_8[16] complex **3**, saturation of the H_{syn} resonance at δ 3.75 led to a considerable decrease in the intensity of the H_{anti} resonance at δ 2.83 (see Figure 2). The results obtained for the π-allylpalladium complexes **1**−**6** are summarized in Table 1. The exchange rates from H_{syn} to H_{anti} and those of reverse directions were determined for all the complexes; that is, two exchange rates were measured for each complex. As described above, all the complexes exist as a 1:1 mixture of the two isotopomers (H_{syn}-D_{anti} isomer and H_{anti}-D_{syn} isomer) in solution; thus the two exchange rates obtained for each complex should be identical. The inequality of the two values in Table 1

(16) Ogasawara, M.; Saburi, M. *Organometallics* **1994**, *13*, 1911.
(17) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.
(18) (a) Forsén, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2892. (b) Forsén, S.; Hoffman, R. A. *J. Chem. Phys.* **1964,** *40*, 1189. (c) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982.

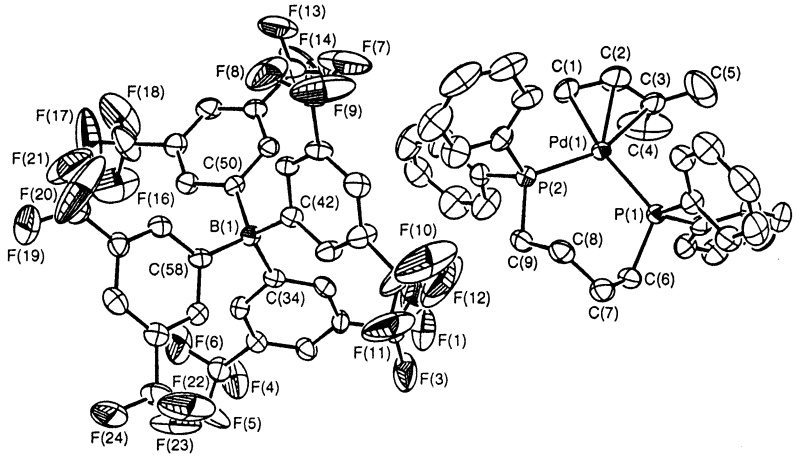


Figure 1. Molecular structure of [Pd(η^3-CMe_2CHCHD)(dppb-d_8)][$B(C_6H_3$-3,5-$(CF_3)_2)_4$] (**3**). Displacement ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd(1)−P(1) = 2.331(3), Pd(1)−P(2) = 2.287(3), Pd(1)−C(1) = 2.12(1), Pd(1)−C(2) = 2.15(1), Pd(1)−C(3) = 2.36(1), P(1)−Pd(1)−P(2) = 103.5(1), P(1)−Pd(1)−C(3) = 101.0(3), P(2)−Pd(1)−C(1) = 89.5(4), C(1)−Pd(1)−C(3) = 65.9(5).

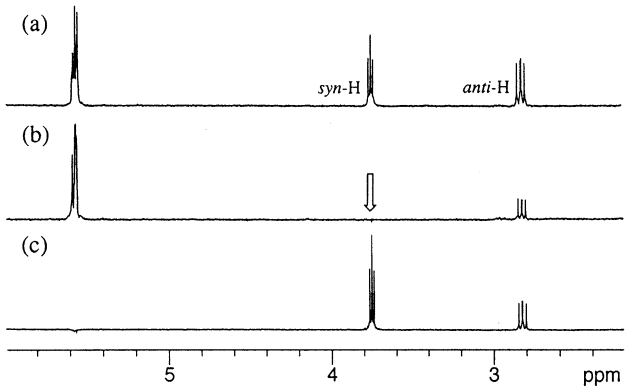


Figure 2. ^{1}H NMR (500 MHz) spectra of the complex **3** in the π-allyl region at 50 °C in acetone-d_6: (a) normal spectrum; (b) spin-saturation transfer experiment with saturation of the *syn*-H resonance at δ 3.75; (c) difference spectrum between (a) and (b).

Table 1. T_1 Values and Rate Constants, k, for *syn*−*anti* Isomerization in [Pd(η^3-$Me_2CCHCHD$)(diphosphine)]BAr^F_4 in Acetone-d_6 at 50 °C

entry	complex[a]	$T_{1(syn)}$/s[b]	$T_{1(anti)}$/s[b]	$k_{s\rightarrow a}$/s^{-1}	$k_{a\rightarrow s}$/s^{-1}
1	**1** (85.8°)[c]	3.02	3.04	3.8	3.8
2	**2** (90.6°)[c]	2.93	2.67	0.39	0.42
3	**3** (94.5°)[d]	2.58	2.56	0.37	0.38
4	**4** (99.1°)[e]	2.34	2.31	1.2	1.2
5	**5**	1.84	1.77	0.26	0.27
6	**6**	1.73	1.76	4.3	4.6

[a] Bite angles of the diphosphine ligands in $PdCl_2$(diphosphine) in parentheses. [b] Measured by an inversion−recovery method. [c] Taken from ref 19a. [d] Taken from ref 19b. [e] Taken from ref 19c.

(up to 8% difference in entry 2) can be attributed to technical errors during the experiments.

As the representative bite angles of the bisphosphines, the ∠P−Pd−P values in palladium complexes $PdCl_2$(bisphosphine),[19] which have been reported for dppe,[19a] dppp,[19a] dppb,[19b] and dppf,[19c] are also listed in Table 1. It was found that there is a good correlation between the bisphosphine's bite angles and the *syn*−*anti* isomerization rates obtained here in the π-allylpalladium complexes. Thus, the exchange rates from H_{anti} complex to H_{syn} complex in complexes **1**, **2**, and **3** were determined to be 3.8, 0.42, and 0.38 s^{-1}, respectively (entries 1−3). The order of the exchange rates in the complexes **1**−**3** is as follows.

1 (dppe) > **2** (dppp) ≥ **3** (dppb)

Although the difference of the exchange rates between those in **2** and **3** is not large, the *syn*−*anti* isomerization in **1** is much faster than in **2** or **3**, **1** having the bisphosphine with the smallest bite angle. As a general trend, it can be seen that bisphosphine with a smaller bite angle accelerates the *syn*−*anti* isomerization in the π-allylpalladium complex.

The electronic effect of the phosphine ligands on the *syn*−*anti* isomerization is distinct. Comparison of the complexes **4**−**6**, which are the series of dppf derivatives, clarified that the *syn*−*anti* isomerization in the π-allylpalladium species is faster with the electron-withdrawing phosphine ligands. Introduction of the electron-withdrawing CF_3 group on the diphenylphosphino group of dppf accelerates the isomerization 3−4 times faster, while the electron-releasing OMe group decelerates the isomerization 4−5 times slower.

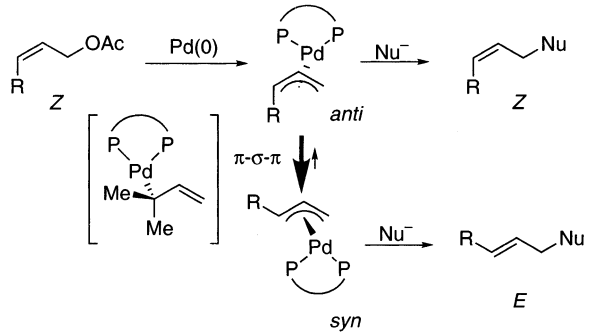
6 (CF_3-dppf) > **4** (dppf) > **5** (MeO-dppf)

Effects of *syn*−*anti* Isomerization Rate on Palladium-Catalyzed Allylic Alkylation. The results described in the previous section suggest that the choice of a phosphine ligand should have a great influence on catalyst behavior in the palladium-catalyzed allylic substitution reactions where the *syn*−*anti* isomerization of the π-allylpalladium intermediates is a crucial factor determining the selectivity. As a model reaction demonstrating the influence of the phosphine ligands, we chose a palladium-catalyzed allylic alkylation of (*Z*)-allyl acetates. The outline of the system is illustrated in Scheme 5.

The oxidative addition of (*Z*)-allyl acetate ((*Z*)-RCH═$CHCH_2OAc$) to a palladium(0) species forms a π-allylpalladium intermediate where the R substituent is

(19) (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432. (b) Makhaev, V. D.; Dzhabieva, Z. M.; Konovalikhin, S. V.; D'yachenko, O. A.; Belov, G. P. *Russ. J. Coord. Chem.* **1996**, *22*, 563. (c) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

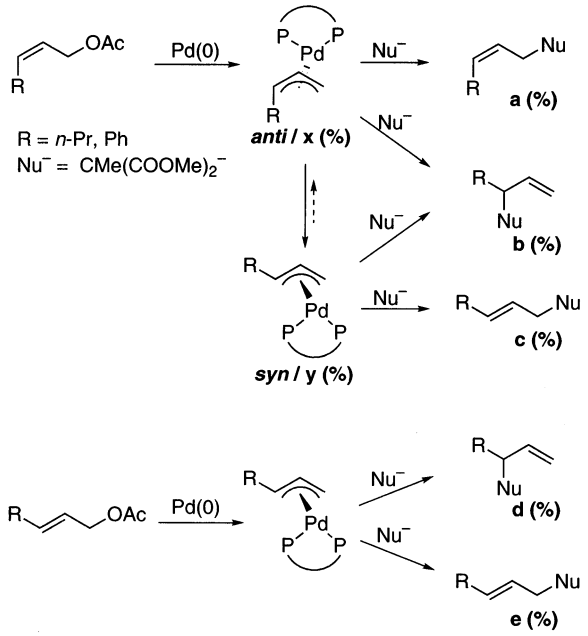
Scheme 5



located *anti* with respect to the central hydrogen. The *anti*-π-allylpalladium possibly undergoes isomerization into a *syn*-π-allylpalladium by the $\pi-\sigma-\pi$ process, because this type of *syn*-isomer which does not have a sterically bulky substituent at the central position is usually much more thermodynamically stable than the *anti*-isomer.[20] The nucleophilic attack on the nonsubstituted terminus of the *anti*-π-allylpalladium and *syn*-π-allylpalladium gives the corresponding *Z*-product and *E*-product, respectively. It follows that the *E*/*Z* ratio of the final product in the palladium-catalyzed allylic alkylation of (*Z*)-allyl acetate is dependent on the rate of *syn*−*anti* isomerization (*anti* to *syn* isomerization). Thus, the reaction of (*Z*)-allyl acetate gives the *Z*-product if the isomerization is slow compared with the nucleophilic attack, while it gives the *E*-product if the isomerization is fast. Another important factor determining the *E*/*Z* ratio of the product is lifetime of the π-allylpalladium intermediates, which is related to the relative rate of the oxidative addition forming the π-allylpalladium intermediate and the nucleophilic attack,[21] the longer lifetime offering the opportunity of more isomerization. Although we do not have a quantitative measurement of the lifetime, we do have the absolute rate of the *syn*−*anti* isomerization of a series of π-allylpalladium complexes $[(\pi\text{-allyl})Pd(P-P)]^+$. We found that the isomerization rate is a decisive factor for the *E*/*Z* ratio of the products in the palladium-catalyzed allylic alkylation of (*Z*)-allyl acetates (Scheme 6).

The allylic alkylation of (*Z*)-cinnamyl acetate and (*Z*)-2-hexenyl acetate was carried out with a large excess (5 equiv to the allyl esters) of the sodium salt of dimethyl methylmalonate in the presence of 2 mol % (Pd) of a catalyst generated in situ from $[PdCl(\pi\text{-}C_3H_5)]_2$ and one of the bisphosphines in acetone, which is the solvent used for the measurement of the *syn*−*anti* isomerization. The catalytic reactions at 20 °C for 1 h gave a high (>91%) yield of a mixture of isomeric allylation products consisting of the *Z*-isomer, branch isomer, and *E*-isomer. The ratios of the isomers are shown as *a*%, *b*%, and *c*%, respectively in Table 2. The formation of the branch isomer makes it difficult to see the ratio of an *anti*-π-allylpalladium intermediate to a *syn*-π-allylpalladium intermediate at the moment of the nucleophilic attack by the malonate, because the branch isomer can be produced from both of the π-allylpalladium intermediates.[22] The *anti*/*syn* ratio was conveniently estimated by use of the results obtained for the allylic alkylation of (*E*)-allyl acetates under the same conditions (Table 3). The (*E*)-acetates gave the *E*-isomer (*d*%) and the branched isomer (*e*%), and only a trace amount of the *Z*-products was detected, indicating that the reaction starting from (*E*)-acetates proceeded via the *syn*-intermediate almost exclusively. This is as expected because the *syn*-isomer which does not have a sterically bulky substituent at the central position is usually much more thermodynamically stable than the *anti*-isomer.[20] The higher stability of the *syn*-isomer was confirmed by the ^1H NMR analysis of the (1-phenyl-π-allyl)-palladium complex coordinated with dppb **7**, where the *syn*-species is the sole observable species in acetone-d_6 and the corresponding *anti*-species was not detected at all (Scheme 7).

Scheme 6



Assuming that the *syn*-intermediate always gives the corresponding *E* and branched products with a fixed ratio, a distribution between the *anti*-intermediate (*x*%) and the *syn*-intermediate (*y*%) at the nucleophilic attack can be estimated from the following equations.

$$x + y = 100$$

$$a + b + c = 100$$

$$d + e = 100$$

$$y = c(1 + d/e) = 100c/e$$

As shown in Table 2, the ratio of the *anti*-intermediate to *syn*-intermediate (*x*% to *y*%) at the nucleophilic attack was strongly dependent on the bisphosphine ligand on the palladium catalyst. General trends are similar for the two (*Z*)-allyl acetates. In the reaction with the α,ω-bis(diphenylphosphino)alkanes (dppe, dppp, and dppb), the ratio of the *syn*-intermediate decreased as the length

(20) Cotton, F. A.; Faller, J. W.; Musco, A. *Inorg. Chem.* **1967**, *6*, 179.

(21) The rate constants of the reaction of π-allylpalladium-phoshine complexes with some nucleophiles have been reported. Kuhn, O.; Mayr, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 343.

(22) The *anti*-isomers of the monosubstituted π-allylpalladium species have a tendency to give relatively high degrees of the corresponding branched products by the reactions with carbon soft nucleophiles. See refs 4d and 8b.

Table 2. Allylic Alkylation of (*Z*)-Cinnamyl Acetate and (*Z*)-2-Hexenyl Acetate Catalyzed by Palladium-Bisphosphine Complexes[a]

entry	R	phosphine	*Z* a (%)	branched *b* (%)	*E* c (%)	total yield (%)	*anti x* (%)[b]	*syn y* (%)[b]
1	Ph	dppe	24	14	61	>99	32	68
2		dppp	58	30	13	97	87	13
3		dppb	51	46	3	99	97	3
4		dppf	24	75	1	>99	99	1
5		MeO-dppf	33	65	2	>99	98	2
6		CF_3-dppf	38	57	5	93	92	8
7	*n*-Pr	dppe	8	2	90	99	9[c]	91[c]
8		dppp	39	8	53	93	46	54
9		dppb	80	17	3	96	97	3
10		dppf	73	27	<1	91	>99	<1
11		MeO-dppf	72	28	<1	99	>99	<1
12		CF_3-dppf	81	18	<1	97	>99	<1

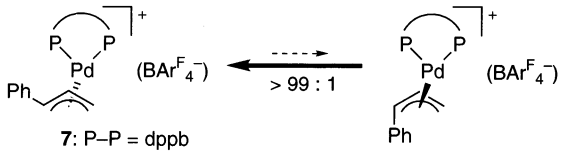
[a] The reactions were carried out with allyl acetate (0.3 mmol) and $NaCMe(COOMe)_2$ (1.5 mmol) in the presence of 2 mol % (Pd) of the catalyst generated from $[PdCl(\pi\text{-}C_3H_5)]_2$ and bisphosphine in a mixture of acetone (1 mL) and THF (1 mL) at 20 °C for 1 h. [b] The estimated ratio of the intermediates at the nucleophilic attack. [c] Estimated in disregard of the *Z*-product obtained from the *E*-substrate (see Table 3).

Table 3. Allylic Alkylation of (*E*)-Cinnamyl Acetate and (*E*)-2-Hexenyl Acetate Catalyzed by Palladium-Bisphosphine Complexes[a]

entry	R	phosphine	Z (%)	branched *d* (%)	*E* e (%)	total yield (%)
1	Ph	dppe	<1	10	90	94
2		dppp	<1	3	97	96
3		dppb	<1	8	92	97
4		dppf	<1	12	88	98
5		MeO-dppf	<1	8	92	97
6		CF_3-dppf	<1	57	43	98
7	*n*-Pr	dppe	3	2	95	>99
8		dppp	1	1	98	>99
9		dppb	<1	1	98	>99
10		dppf	<1	1	99	98
11		MeO-dppf	<1	1	99	>99
12		CF_3-dppf	<1	1	98	>99

[a] The reactions were carried out with allyl acetate (0.3 mmol) and $NaCMe(COOMe)_2$ (1.5 mmol) in the presence of 2 mol % (Pd) of the catalyst generated from $[PdCl(\pi\text{-}C_3H_5)]_2$ and bisphosphine in a mixture of acetone (1 mL) and THF (1 mL) at 20 °C for 1 h.

Scheme 7



of polymethylene chains in the bisphosphines increases (entries 1−3 and 7−9), which is in good agreement with the *syn*−*anti* isomerization rates measured in the π-allylpalladium complexes coordinated with dppe, dppp, and dppb (see Table 1). It may be regarded that the dppe-, dppp-, and dppb-palladium catalysts have similar reactivity toward the nucleophile, because their electronic characteristics are not very different. The more isomerization from *Z* to *E* with dppe than with dppb has been reported by van Leeuwen,[8b] and it is in good agreement with our present results.

In the allylic alkylation catalyzed by the dppf-palladium complex (entries 4 and 10), the contribution of the *syn*-intermediate at the nucleophilic attack is much smaller than expected from the rate of the *syn*−*anti* isomerization of the dppf complex **4**. The isomerization rate of **4** was measured to be between those of the dppe complex **1** and dppp complex **2**, but the catalytic reaction with the dppf complex gave only a trace amount of the *E*-isomers. A probable explanation for these results is an electronic effect of the dppf ligand.[23] The electronic effect of the ferrocenylbisphosphine, which is a less basic triarylphosphine,[23] decreases the reactivity at the oxidative addition forming the π-allylpalladium intermediate and enhances the reactivity of the π-allylpalladium intermediate toward the nucleophile attack. It follows that the less basic character of dppf shortens the lifetime of the π-allypalladium intermediate, and as a result, the intermediate undergoes nucleophilic attack before its isomerization from *Z* to *E*. In the reaction of (*Z*)-hexenyl acetate, almost no isomerization of the π-allypalladium intermediate was detected with either dppf, MeO-dppf, or CF_3-dppf (entries 10−12). The contribution of the *syn*-intermediate was too small to compare the influence of the dppf ligands. In the catalytic reaction of (*Z*)-cinnamyl acetate, we were able to observe the isomerization from *Z* to *E* at 8% with the CF_3-dppf ligand (entry 6), whose π-allylpalladium complex is fastest in the $\pi-\sigma-\pi$ isomerization. It is interesting that the isomerization of the π-allylpalladium intermediates was observed in the catalytic reaction with the CF_3-dppf catalyst system because the lifetime of its π-allylpalladium intermediates is considered to be shortest of the complexes examined, due to the substitution with the electron-withdrawing CF_3 groups on the diphenylphosphino groups.[21]

Conclusions

The *syn*−*anti* isomerization rates in the π-allylpalladium complexes $[Pd(\pi\text{-}Me_2CCHCHD)(bisphosphine)]\text{-}BAr^F_4$ were measured for a variety of bisphosphine ligands. It was revealed that the rates of the *syn*−*anti* isomerization are dependent on both the bite angles and electronic characteristics of the phosphine ligands. As we have demonstrated in this report, the *syn*−*anti* isomerization rate plays an important role in the catalytic allylic alkylation which proceeds through π-allylpalladium intermediates. Although the *syn*−*anti* isomerization rate is not a sole factor determining the selectivity of the reaction, it is still a decisive factor and constitutes a very important part of the π-allylpalladium chemistry. The results reported here suggest that selectivity of π-allylpalladium-mediated reactions can

(23) Gan, K.-S.; Hor, T. S. A. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; pp 3−104.

be controlled by selection of an appropriate phosphine ligand, if the *syn*−*anti* isomerization is the crucial factor determining the selectivity. This report will be a useful guideline for choice of suitable phosphine ligands in palladium-catalyzed allylic substitution reactions including asymmetric ones.

Experimental Section

General Procedures. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 Hz; ^{31}P, 202 MHz; ^{19}F, 470 MHz; ^{2}H, 76.5 MHz). ^{1}H and ^{13}C-{^{1}H} chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P{^{1}H} and ^{19}F NMR chemical shifts are externally referenced to 85% H_3PO_4 and C_6F_6 (δ −162), respectively. ^{2}D NMR chemical shifts are reported in ppm using $CDCl_3$ (δ 7.24) as an internal standard. Tetrahydrofuran, Et_2O, and toluene were distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. Methanol was dried over magnesium methoxide, distilled, and stored in a glass flask with a Teflon stopcock under nitrogen. $P(NMe_2)Cl_2$,[24] Na[$B(C_6H_3$-3,5-$(CF_3)_2)_4$],[17] $Ph_2P(CD_2)_4PPh_2$,[16] Fe[η^5-$C_5H_4P(C_6H_4$-4-$CF_3)_2]_2$,[24a,25] [PdCl(η^3-allyl)]$_2$,[26] and [PdCl(η^3-1-phenylallyl)]$_2$[7a] were synthesized as reported. Allyl acetates (*cis*- and *trans*-2-hexenyl acetates, *cis*- and *trans*-3-phenyl-2-propenyl acetates) were prepared from corresponding allyl alcohols and acetic anhydride.

Measurements of Exchange Rates between *syn*- and *anti*-Hydrogens in the Palladium Complexes. The solvent, acetone-d_6, was dried over activated 4 Å molecular sieves and vacuum transferred prior to use. The NMR samples for the exchange rate measurements were degassed by three freeze−pump−thaw cycles and flame-sealed in the NMR tubes. Determination of the exchange rates between the two isotopomers was carried out according to the Forsén−Hoffman method.[18] Spin-saturation transfer experiments were performed by irradiating either of the H_{syn} or H_{anti} signals of the π-allyl complexes. The exchange rates, k, were calculated from the following equation:

$$I'/I = \tau/(\tau + T_1)$$

where I and I' are the signal intensities of the nonirradiated H (*syn*-H or *anti*-H) without and with saturation of the other H resonance, respectively. T_1 is the spin−lattice relaxation time of the nonirradiated H resonance and τ (=1/k) is the pre-exchange lifetime of this exchange system. The ratio I'/I was calculated from the difference spectrum recorded by subtracting the irradiated spectrum from the reference (nonirradiated) spectrum. ^{1}H NMR T_1 determinations were performed with a standard 180°−τ−90° pulse sequence by the inversion−recovery method.

$HO(CD_2)_3OH$. Malonic acid-d_4 (5.0 g, 46 mmol) in tetrahydrofuran (50 mL) was added dropwise to a suspension of $LiAlD_4$ (5.0 g, 0.12 mol) in tetrahydrofuran (100 mL) at 0 °C by means of syringe. The reaction mixture was warmed to room temperature gradually with stirring, then refluxed for 1 h. The mixture was quenched with aqueous NaOH (5% in H_2O, 25 mL), and it was heated to reflux for 1 h. The cooled mixture was filtered through a pad of Celite, and the filter cake was rinsed with Et_2O. The filtrate was dried ($MgSO_4$), concentrated in vacuo, and then vacuum-transferred to give 1.7 g (44% yield) of propanediol-d_6. ^{1}H NMR ($CDCl_3$): δ 2.43 (br, 2H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 1.75 (br, 2D), 3.80 (br, 4D).

$TsO(CD_2)_3OTs$. To a solution of $HO(CD_2)_3OH$ (1.00 g, 12.1 mmol) in pyridine (20 mL) was added *p*-toluenesulfonyl chloride (5.03 g, 26.4 mmol). After stirring the mixture for 5 min, the cooling bath was removed and the reaction mixture was vigorously stirred for 3 h. The volume of the mixture was reduced to about half of the initial volume, and the mixture was poured into ice−water. The ditosylate, deposited as a white solid, was filtered, washed with water and hexane, and then dried under reduced pressure. The residual solid was recrystallized from $CHCl_3$/hexane to give colorless crystals (1.97 g, 42% yield). ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 6H), 7.35 (d, J = 8.3 Hz, 4H), 7.75 (d, J = 8.3 Hz, 4H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 1.97 (br, 2D), 3.65 (br, 4D). Anal. Calcd for $C_{17}H_{14}D_6O_6S_2$: C, 52.29; H+D, 6.71. Found: C, 52.09; H+D, 6.42.

$Ph_2P(CD_2)_3PPh_2$. A solution of $LiPPh_2$, which was prepared from PPh_3 (2.55 g, 9.7 mmol) and Li (182 mg, 26.2 g atom) in THF (8.3 mL) followed by *t*-BuCl (1.1 mL, 9.7 mmol) treatment, was added to a THF (5 mL) solution of $TsO(CD_2)_3OTs$ (1.89 g, 4.8 mmol) at 0 °C, and the mixture was refluxed for 1 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel with Et_2O as an eluent under nitrogen atmosphere. The NMR analysis of the product showed a small amount of impurities; however, it was sufficiently pure for the synthesis of the palladium complex. ^{1}H NMR ($CDCl_3$): δ 7.24−7.38 (m, 20H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 1.56 (br, 2D), 2,16 (br, 4D). ^{31}P{^{1}H} NMR ($CHCl_3$): δ −17.32.

$(4\text{-}MeOC_6H_4)_2PCl$. An ether solution of *p*-methoxyphenylmagnesium bromide, which was prepared from *p*-methoxybromobenzene (25.3 g, 0.14 mol) and Mg (3.6 g, 0.15 mol) in dry ether (70 mL), was added dropwise to a cold (−78 °C) solution of Me_2NPCl_2 (7.3 g, 0.050 mol) and pyridine (20 mL, 0.25 mol) in dry ether (150 mL). The reaction mixture was stirred for 2 h at room temperature and heated to reflux for a further 2 h. The solution was cooled to room temperature, and anhydrous HCl was bubbled through the reaction mixture for 1 h. The mixture consisted of two layers. The upper one was collected and concentrated under reduced pressure to give 5.2 g of the crude $(4\text{-}MeOC_6H_4)_2PCl$. This crude product was used in the next reaction without further purification.

Fe[η^5-$C_5H_4P(C_6H_4$-4-OMe$)_2]_2$. To a suspension of ferrocene (0.63 g, 3.4 mmol) in hexane (17.2 mL) were quickly added ^{n}BuLi in hexane (1.54 M, 4.8 mL, 7.4 mmol) and TMEDA (0.81 g, 7.1 mmol), and the resulting orange solution was stirred at 60 °C for 1 h. The heating bath was removed, and 6.9 mL of dry THF was added. The dark brown suspension was cooled to −50 °C, and a solution of $(4\text{-}MeOC_6H_4)_2PCl$ (2.1 g, 7.5 mmol) in THF (3.5 mL) was added dropwise over 5 min. The reaction mixture was stirred overnight at room temperature. The reaction mixture was diluted with Et_2O, and insoluble solid was removed by filtration. The filtrate was washed with dilute HCl, saturated $NaHCO_3$, and H_2O, then dried over Na_2SO_4. The resulting crude product was chromatographed on silica gel (hexane/Et_2O = 1) to give the title compound in pure form. Yield: 1.1 g (46%). ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 12H), 3.97 (dd, J = 3.8 and 1.8 Hz, 4H), 4.25 (t, J = 1.8 Hz, 4H), 6.82 (d, J = 8.8 Hz, 8H), 7.22 (d, J = 8.8 Hz, 8H). ^{31}P{^{1}H} NMR ($CHCl_3$): δ −20.2.

1-Deuterio-3-methyl-2-butenol. To a suspension of $LiAlD_4$ (5.0 g, 120 mmol) in Et_2O (160 mL) was added dropwise 3-methyl-2-butenal (13.6 g, 160 mmol) over 30 min by means of syringe. The reaction mixture was stirred at room temperature for 1 h and heated under reflux for 1.5 h. The mixture was cooled with ice−water and quenched with saturated sodium sulfate. The mixture was filtered through a pad of Celite, and the filter cake was rinsed with Et_2O. The combined organic solution was dried over $MgSO_4$ and concentrated. The

(24) (a) Unruh, J. D.; Christenson, J. R. *J. Mol. Catal.* **1982**, *14*, 19. (b) Issleib, K.; Seidel, W. *Chem. Ber.* **1959**, *92*, 2681.
(25) (a) Hamann, B. C.; Hartwing, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 3694. (b) de Lang, R.-J.; van Soolinger, J.; Verkruijsse, H. D.; Brandsma, L. *Synth. Commun.* **1995**, *25*, 2989.
(26) Tatsuno, A.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220.

residue was vacuum-transferred to give the title compound with a small amount of residual solvents. This crude material was sufficiently pure for the next step and used without further purification. Yield: 13.7 g (99%). ^{1}H NMR ($CDCl_3$): δ 1.21 (br, 1H), 1.69 (s, 3H), 1.75 (s, 3H), 4.11 (br, 1H), 5.43 (d, J = 7.1 Hz, 1H).

[PdCl(η^3-3-deuterio-1,1-dimethylallyl)]$_2$. A mixture of palladium(II) chloride (27.7 g, 156 mmol) and lithium chloride (22.2 g, 523 mmol) was dissolved in hot water (35 mL), and to this were added ethanol (300 mL), 1-deuterio-3-methyl-2-butenol (13.7 g, 157 mmol) in tetrahydrofuran (100 mL), and concentrated hydrochloric acid (100 mL), successively. Carbon monoxide was passed through the solution for 4 h at room temperature with vigorous stirring. During this period, the solution became clear orange. After removing the solvents under reduced pressure, the residue was dissolved in $CHCl_3$ and the solution was washed with water, then dried over $MgSO_4$. Evaporation of the solvent gave a yellow solid. This crude product was purified by chromatography over alumina (with $CHCl_3$), then by recrystallization from CH_2Cl_2/hexane. Yield: 1.73 g (52%), mp 110−111 °C. ^{1}H NMR ($CDCl_3$): δ 1.25 (s, 3H), 1.44 (s, 3H), 3.08 (d, J = 12.7 Hz, 0.5H), 3.84 (d, J = 7.4 Hz, 0.5H), 5.08 (m, 1H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 3.09 (br, 0.5D), 3.85 (br, 0.5D). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.85, 21.86, 27.09, 55.57 (t, J = 24.6 Hz), 95.08, 106.27, and 106.30. Anal. Calcd for $C_{10}H_{16}D_2Cl_2Pd_2$: C, 28.33; H+D, 4.75. Found: C, 28.18; H+D, 4.61.

[Pd(η^3-3-deuterio-1,1-dimethylallyl)(bisphosphine)]-[B(C_6H_3-3,5-$(CF_3)_2$)$_4$] (1−6): General Procedure. A mixture of [PdCl(3-deuterio-1,1-dimethylallyl)]$_2$ (0.165 mmol) and the bisphosphine (0.30 mmol) was suspended in methanol (0.6 mL). The solids dissolved after 10 min to give a yellow or faintly orange solution. To the solution was added dropwise Na[B(C_6H_3-3,5-$(CF_3)_2$)$_4$] (316.9 mg, 0.33 mmol) in methanol (0.5 mL). The mixture was allowed to stand for 30 min at ambient temperature and then at 0 °C overnight. For **1**−**4**, the crude complexes were crystallized from the solution. The precipitates were collected and were washed with methanol/water (1:1) and then with hexane. These materials were further purified by recrystallization. For **5** and **6**, which were not crystalline, the reaction solutions were evaporated to dryness and the residual complexes were purified by preparative thin-layer chromatography over SiO_2 (with $CHCl_3$).

Dppe complex (1) was recrystallized from methanol (34% yield). Mp: 141−142 °C. ^{1}H NMR ($CDCl_3$): δ 1.01 (t, J = 6.3 Hz, 3H), 1.84 (dd, J = 9.8 and 8.3 Hz, 3H), 2.05−2.19 (m, 1H), 2.26−2.45 (m, 1H), 2.57−2.75 (m, 2H), 3.21 (dd, J = 14.2 and 10.4 Hz, 0.5H), 4.21 (t, J = 7.1 Hz, 0.5H), 5.30 (d, J = 7.1 Hz, 0.5H), 5.31 (d, J = 14.2 Hz, 0.5H), 7.18−7.63 (m, 20H), 7.49 (br, 4H), 7.70 (br, 8H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 3.25 (br, 0.5D), 4.27 (br, 0.5D). ^{19}F NMR ($CDCl_3$): δ −63.59. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.27 (d, J = 2.6 Hz, 1P), 51.45 (d, J = 2.6 Hz, 1P). Anal. Calcd for $C_{63}H_{44}DBF_{24}P_2Pd$: C, 52.61; H+D, 3.22. Found: C, 52.51; H+D, 3.10.

Dppp-d_6 complex (2) was recrystallized from $CHCl_3$/hexane (71% yield). Mp: 177−179 °C. ^{1}H NMR ($CDCl_3$): δ 1.04 (t, J = 6.2 Hz, 3H), 1.32 (dd, J = 10.3 and 7.9 Hz, 3H), 2.80 (dd, J = 14.2 and 10.3 Hz, 0.5H), 3.71 (t, J = 7.6 Hz, 0.5H), 5.16 (d, J = 7.6 Hz, 0.5H), 5.18 (d, J = 14.2 Hz, 0.5H), 7.15−7.54 (m, 20H), 7.51 (br, 4H), 7.71 (br, 8H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 1.74 (br, 1D), 2.06 (br, 1D) 2.58 (br, 4.5D), 3.68 (br, 0.5D). ^{19}F NMR ($CDCl_3$): δ −63.56. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 5.89 (d, J = 63.4 Hz, 1P), 10.30 (d, J = 63.4 Hz, 1P). Anal. Calcd for $C_{64}H_{40}D_7BF_{24}P_2Pd$: C, 52.71; H+D, 3.73. Found: C, 52.47; H+D, 3.80.

Dppb-d_8 complex (3) was recrystallized from CH_2Cl_2/pentane (70% yield). Mp: 189−191 °C. ^{1}H NMR ($CDCl_3$): δ 0.81 (t, J = 5.9 Hz, 3H), 1.29 (dd, J = 10.5 and 6.9 Hz, 3H), 2.73 (dd, J = 13.7 and 10.1 Hz, 0.5H), 3.55 (t, J = 7.8 Hz, 0.5H), 5.16 (d, J = 7.8 Hz, 0.5H), 5.17 (d, J = 13.7 Hz, 0.5H), 7.20−7.58 (m, 20H), 7.50 (br, 4H), 7.71 (br, 8H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 1.61 (br, 4D), 2.51 (br, 4.5D), 3.59 (br, 0.5D). ^{19}F NMR ($CDCl_3$): δ −63.57. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 20.53 (d, J = 49.1 Hz, 1P), 22.87 (d, J = 49.1 Hz, 1P). Anal. Calcd for $C_{65}H_{40}D_8BF_{24}P_2Pd$: C, 52.96; H+D, 3.96. Found: C, 52.75; H+D, 3.67.

Dppf complex (4) was recrystallized from $CHCl_3$/hexane (53% yield). Mp: 206−207 °C. ^{1}H NMR ($CDCl_3$): δ 1.07 (t, J = 6.1 Hz, 3H), 1.09 (dd, J = 10.8 and 6.1 Hz, 3H), 2.76 (dd, J = 13.7 and 10.0 Hz, 0.5H), 3.60 (t, J = 7.9 Hz, 0.5H), 3.87 (br, 1H), 4.13 (br, 1H), 4.19 (br, 1H), 4.34 (br, 1H), 4.40 (br, 1H), 4.41 (br, 1H), 4.45 (br, 1H), 4.51 (br, 1H), 5.19 (d, J = 7.9 Hz, 0.5H), 5.20 (d, J = 13.7 Hz, 0.5H), 7.34−7.63 (m, 20H), 7.50 (br, 4H), 7.71 (br, 8H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 2.76 (br, 0.5D), 3.63 (br, 0.5D). ^{19}F NMR ($CDCl_3$): δ −63.56. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 22.17 (d, J = 45.2 Hz, 0.5P), 22.19 (d, J = 45.2 Hz, 0.5P), 26.95 (d, J = 45.2 Hz, 1P). Anal. Calcd for $C_{71}H_{48}DBF_{24}FeP_2Pd$: C, 53.49; H+D, 3.16. Found: C, 53.25; H+D, 3.27.

Fe[η^5-$C_5H_4P(C_6H_4$-4-OMe)$_2$]$_2$ Complex (5) was purified by preparative TLC (94% yield). ^{1}H NMR ($CDCl_3$): δ 1.06 (t, J = 6.1 Hz, 3H), 1.09 (dd, J = 11.0 and 6.4 Hz, 3H), 2.76 (dd, J = 13.5 and 10.1 Hz, 0.5H), 3.56 (t, J = 7.6 Hz, 0.5H), 3.83 (br, 6H), 3.83 (br, 3H), 3.88 (br, 1H), 4.11 (br, 1H), 4.14 (br, 1H), 4.31 (br, 1H), 4.35 (br, 2H), 4.42 (br, 1H), 4.45 (br, 1H), 5.17 (d, J = 7.6 Hz, 0.5H), 5.18 (d, J = 13.5 Hz, 0.5H), 6.86−7.05 (m, 8H), 7.28−7.44 (m, 8H), 7.51 (br, 4H), 7.70 (br, 8H). ^{2}H-{^{1}H} NMR ($CHCl_3$): δ 2.78 (br, 0.5D), 3.60 (br, 0.5D). ^{19}F NMR ($CDCl_3$): δ −63.57. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.49 (d, J = 47.9 Hz, 0.5P), 19.51 (d, J = 47.9 Hz, 0.5P), 24.08 (d, J = 47.9 Hz, 1P). Anal. Calcd for $C_{75}H_{56}DBF_{24}FeO_4P_2Pd$: C, 52.55; H+D, 3.41. Found: C, 52.29; H+D, 3.32.

Fe[η^5-$C_5H_4P(C_6H_4$-4-$CF_3)_2$]$_2$ complex (6) was purified by preparative TLC (66% yield). ^{1}H NMR ($CDCl_3$): δ 1.04 (t, J = 5.9 Hz, 3H), 1.13 (dd, J = 11.5 and 6.6 Hz, 3H), 2.79 (dd, J = 13.7 and 10.0 Hz, 0.5H), 3.66 (t, J = 7.4 Hz, 0.5H), 3.91 (br, 1H), 4.15 (br, 1H), 4.19 (br, 1H), 4.38 (br, 1H), 4.41 (br, 1H), 4.43 (br, 1H), 4.52 (br, 1H), 4.54 (br, 1H), 5.21 (d, J = 7.4 Hz, 0.5H), 5.22 (d, J = 13.7 Hz, 0.5H), 7.45−7.88 (m, 16H), 7.48 (br, 4H), 7.68 (br, 8H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 2.83 (br, 0.5D), 3.72 (br, 0.5D). ^{19}F NMR ($CDCl_3$): δ −64.68 (s, 6F), −64.66 (s, 3F), −64.61 (s, 3F), −63.55 (s, 24F). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 22.05 (d, J = 45.2 Hz, 0.5P), 22.07 (d, J = 45.2 Hz, 0.5P), 27.01 (d, J = 45.2 Hz, 1P). Anal. Calcd for $C_{75}H_{44}DBF_{36}FeP_2Pd$: C, 48.27; H+D, 2.48. Found: C, 48.04; H+D, 2.71.

General Procedures for Palladium-Catalyzed Allylic Alkylation. A typical procedure is given for the reaction of (*E*)-2-hexenyl acetate with Pd-dppe complex. To a solution of [PdCl(η^3-allyl)]$_2$ (1.1 mg, 6 μmol of Pd) and dppe (2.7 mg, 6.6 μmol) in acetone (1 mL) was added a THF solution of Na[MeC(COOMe)$_2$] (1.5 mmol), which was prepared from dimethyl methylmalonate and sodium hydride, at −78 °C. To the solution was added (*E*)-2-hexenyl acetate (42.7 mg, 0.3 mmol) at the same temperature, and the reaction mixture was stirred at 20 °C for 1 h. The mixture was quenched with water and extracted with ether. The combined organic layer was washed with saturated NaCl, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel (EtOAc/hexane, 1:5) to give a mixture of alkylated products (68.4 mg, 99.8% yield). The ratio of the isomers in the mixture was determined by a GC analysis, and the results are listed in Tables 2 and 3. ^{1}H NMR spectra of the products are shown below.

Dimethyl 2-((*Z*)-2-hexenyl)-2-methylpropane-1,3-dioate.[27] ^{1}H NMR ($CDCl_3$): δ 0.87 (t, J = 7.4 Hz, 3H), 1.38 (sext, J = 7.4 Hz, 2H), 1.40 (s, 3H), 2.02 (q, J = 7.4 Hz, 2H), 2.64 (d, J = 7.6 Hz, 2H), 3.72 (s, 6H), 5.24 (dt, J = 11.0 and 7.6 Hz, 1H), and 5.53 (dt, J = 11.0 and 7.4 Hz, 1H).

Dimethyl 2-((*E*)-2-hexenyl)-2-methylpropane-1,3-dioate.[27] ^{1}H NMR ($CDCl_3$): δ 0.87 (t, J = 7.4 Hz, 3H), 1.35 (sext, J = 7.4 Hz, 2H), 1.38 (s, 3H), 1.96 (q, J = 7.4 Hz, 2H), 2.55 (d,

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J = 6.9 Hz, 2H), 3.71 (s, 6H), 5.28 (dt, J = 15.0 and 7.4 Hz, 1H), and 5.50 (dt, J = 15.0 and 6.9 Hz, 1H).

Dimethyl 2-(1-hexen-3-yl)-2-methylpropane-1,3-dioate.[27] ^{1}H NMR ($CDCl_3$): δ 0.87 (t, J = 7.4 Hz, 3H), 1.38 (sext, J = 7.4 Hz, 2H), 1.39 (s, 3H), 2.02 (q, J = 7.6 Hz, 2H), 2.72 (t, J = 7.6 Hz, 1H), 3.68 (s, 3H), 3.71 (s, 3H), 5.05 (dd, J = 16.9 and 1.9 Hz, 1H), 5.09 (dd, J = 10.2 and 1.9 Hz, 1H), and 5.57 (dd, J = 16.9 and 10.2 Hz, 1H).

Dimethyl 2-((*Z*)-3-phenyl-2-propenyl)-2-methylpropane-1,3-dioate. ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 3H), 2.93 (d, J = 7.2 Hz, 2H), 3.68 (s, 6H), 5.53 (dt, J = 11.7 and 7.2 Hz, 1H), 6.57 (d, J = 11.7 Hz, 1H), and 7.18−7.37 (m, 5H).

Dimethyl 2-((*E*)-3-phenyl-2-propenyl)-2-methylpropane-1,3-dioate.[11] ^{1}H NMR ($CDCl_3$): δ 1.46 (s, 3H), 2.77 (d, J = 7.5 Hz, 2H), 3.73 (s, 6H), 6.08 (dt, J = 15.8 and 7.5 Hz, 1H), 6.45 (d, J = 15.8 Hz, 1H), and 7.18−7.37 (m, 5H).

Dimethyl (1-phenyl-2-propenyl)-2-methylpropane-1,3-dioate.[11] ^{1}H NMR ($CDCl_3$): δ 1.43 (s, 3H), 3.62 (s, 3H), 3.68 (s, 3H), 4.15 (d, J = 8.8 Hz, 1H), 5.11 (d, J = 16.9 Hz, 1H), 5.14 (d, J = 10.3 Hz, 1H), 6.32 (ddd, J = 16.9, 10.3, and 8.8 Hz, 1H), and 7.16−7.37 (m, 5H).

[Pd(η^3-1-phenylallyl)(dppb)][B(C_6H_3-3,5-$(CF_3)_2)_4$]. A mixture of [PdCl(1-phenylallyl)]$_2$ (30 mg, 58 mmol) and dppb (49 mg, 116 mmol) was dissolved in methanol (0.9 mL) and stirred for 10 min to give a pale orange solution. To the solution was added Na[B(C_6H_3-3,5-$(CF_3)_2)_4$] (223 mg, 251 mmol) in methanol (0.3 mL) dropwise. The mixture was stirred for 30 min at ambient temperature, then the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel with $CHCl_3$ to give the title complex in pure form. Yield: 106 mg (57%). ^{1}H NMR ($CDCl_3$): δ 1.65−2.05 (br, 4H), 2.25−2.74 (br, 4H), 2.91 (t, J = 12.5 Hz, 1H), 3.81 (t, J = 7.8 Hz, 1H), 4.84 (t, J = 12.5 Hz, 1H), 5.99 (td, J = 12.5 and 7.8 Hz, 1H), 6.64−6.77 (m, 3H), 6.82−6.96 (m, 2H), 7.03−7.60 (m, 20H), 7.51 (s, 4H), and 7.73 (s, 8H). ^{19}F NMR ($CDCl_3$): δ −63.53. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.47 (d, J = 53.1 Hz, 1P) and 25.21 (d, J = 53.1 Hz, 1P). Anal. Calcd for $C_{69}H_{49}BF_{24}P_2$-Pd: C, 52.71; H, 3.73. Found: C, 52.47; H, 3.80.

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Supporting Information Available: Tables of crystallographic data for complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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