Retention of Regiochemistry of Allylic Esters in Palladium-Catalyzed Allylic Alkylation in the Presence of a MOP Ligand

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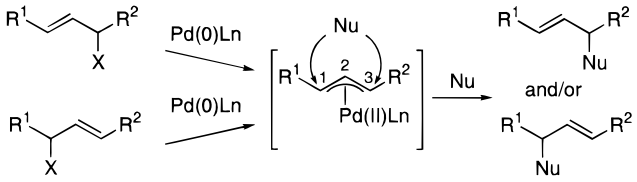
Abstract: In the palladium-catalyzed allylic alkylation of (*E*)-3-substituted-2-propenyl acetates (**1**), 1-substituted-2-propenyl acetates (**2**), and 1- or 3-deuterio-2-cyclohexenyl acetate (**5**), which proceeds through 1,3-unsymmetrically substituted π-allylpalladium intermediates, selective substitution at the position originally substituted with acetate was observed by use of a sterically bulky monodentate phosphine ligand, 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MeO-MOP). Studies of the structure of π-allylpalladium complexes generated by mixing $[PdCl(\pi\text{-cyclohexenyl})]_2$ with 1 or 2 equiv of MeO-MOP (L*) revealed that cationic bisphosphine complex $[Pd(L^*)_2(\pi\text{-cyclohexenyl})]^+Cl^-$ is not formed even in the presence of excess ligand but neutral monophosphine complex $PdCl(L^*)(\pi\text{-cyclohexenyl})$ (**11**) is formed, leaving excess ligand free, and that the exchange of the coordination site of Cl and L* in **11** is much slower than that in triphenylphosphine complex $PdCl(PPh_3)(\pi\text{-cyclohexenyl})$ (**13**). The slow exchange can rationalize the retention of regiochemistry in the allylic alkylation catalyzed by palladium/MeO-MOP complex.

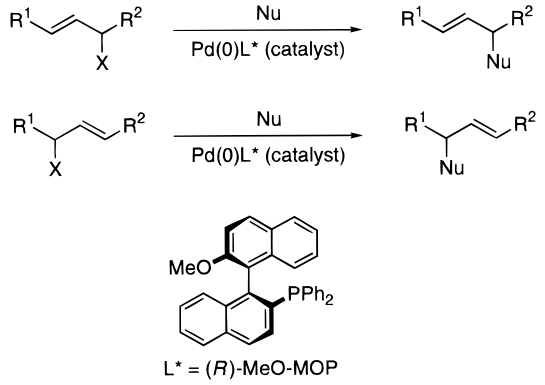
Introduction

Palladium-catalyzed allylic substitution reactions including catalytic asymmetric reactions have attracted considerable attention owing to their synthetic utility and mechanistic interest.[1] The allylic substitutions proceed by way of a π-allylpalladium(II) intermediate which is formed by oxidative addition of an allylic ester to a palladium(0) species. It has been generally accepted that, in the allylic substitution which proceeds through 1,3-unsymmetrically substituted π-allylpalladium(II) intermediate, the regiochemistry of starting allylic ester is lost at the formation of the π-allylpalladium(II) intermediate and the regiochemistry in the substitution product is determined at the attack of nucleophile on the π-allylpalladium (Scheme 1). Similarly, in the asymmetric allylic substitution which proceeds through a meso type π-allylpalladium(II) intermediate, the enantioselectivity is usually determined at the nucleophilic attack on either of diastereotopic π-allyl carbons on the π-allylpalladium(II) intermediate which is not concerned with the absolute configuration of starting allylic ester any more. Recently, Trost found[2] an interesting phenomenon that the absolute configuration of a starting allyl ester has an effect on the structure of π-allylpalladium intermediate in his asymmetric alkylation, though the effect is modest. We report here a new type of palladium-catalyzed allylic alkylation where the regiochemistry of the starting allyl esters is retained in the alkylation products (Scheme 2). The retention of the regiochemistry is observed with a sterically bulky monodentate phosphine ligand, 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MeO-MOP).[3]

Scheme 1



Scheme 2



Results

Palladium-Catalyzed Allylic Alkylation. In the presence of 2 mol % palladium catalyst generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ with 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MeO-MOP)[3], γ-substituted allyl acetates **1** and

(1) For a review on catalytic allylic substitutions, see: Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley: Chichester, 1995. For reviews on catalytic asymmetric allylic substitutions, see: (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; p 325. (c) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (d) Consiglio, G.; Waymouth, M. *Chem. Rev.* **1989**, *89*, 257.

(2) (a) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 235. See also: (b) Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* **1981**, *22*, 1399. (c) Trost, B. M.; Schmuff, N. R. *Tetrahedron Lett.* **1981**, *22*, 2999.

(3) (a) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887. (b) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945. (c) Uozumi, Y.; Suzuki, N.; Ogiwara, A.; Hayashi, T. *Tetrahedron* **1994**, *50*, 4293.

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Scheme 3

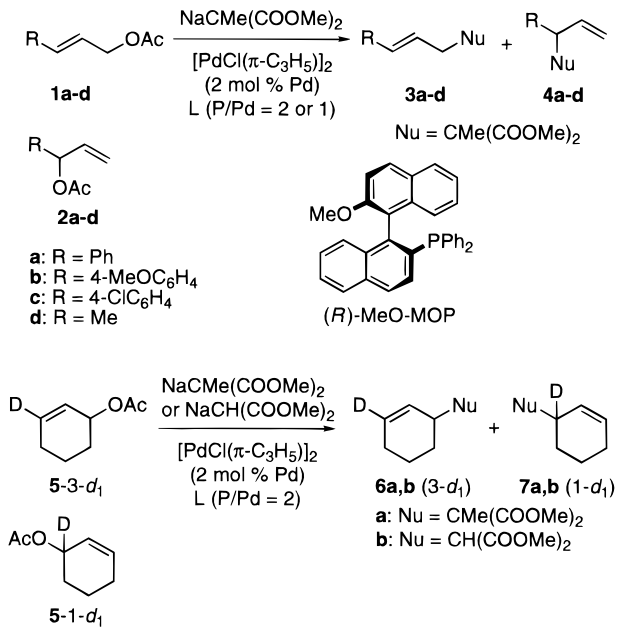


Table 1. Allylic Alkylation of Acetates **1** and **2** with $NaCMe(COOMe)_2$ Catalyzed by Palladium−Phosphine Complexes[a]

entry	substrate	ligand (ratio P/Pd)	yield[b] (%) of **3** and **4**	ratio[c] **3**/**4**
1	**1a** (R = Ph)	(*R*)-MeO-MOP (2/1)	99	79/21
2	**2a** (R = Ph)	(*R*)-MeO-MOP (2/1)	96	23/77
3	**2a** (R = Ph)	(*R*)-MeO-MOP (1/1)	95	23/77
4	**1a** (R = Ph)	dppe (2/1)	99	89/11
5	**2a** (R = Ph)	dppe (2/1)	94	89/11
6	**1a** (R = Ph)	PPh_3 (2/1)	99	91/9
7	**2a** (R = Ph)	PPh_3 (2/1)	99	92/8
8	**2a** (R = Ph)	PPh_3 (1/1)	66	91/9
9	**1b** (R = 4-$MeOC_6H_4$)	(*R*)-MeO-MOP (2/1)	99	71/29
10	**2b** (R = 4-$MeOC_6H_4$)	(*R*)-MeO-MOP (2/1)	93	16/84
11	**1b** (R = 4-$MeOC_6H_4$)	PPh_3 (2/1)	99	75/25
12	**2b** (R = 4-$MeOC_6H_4$)	PPh_3 (2/1)	99	76/24
13	**1c** (R = 4-ClC_6H_4)	(*R*)-MeO-MOP (2/1)	89	81/11
14	**2c** (R = 4-ClC_6H_4)	(*R*)-MeO-MOP (2/1)	99	35/65
15	**1c** (R = 4-ClC_6H_4)	PPh_3 (2/1)	88	93/7
16	**2c** (R = 4-ClC_6H_4)	PPh_3 (2/1)	93	94/6
17	**1d** (R = Me)	(*R*)-MeO-MOP (2/1)	92	95/5
18	**2d** (R = Me)	(*R*)-MeO-MOP (2/1)	94	38/62
19	**1d** (R = Me)	dppe (2/1)	92	78/22
20	**2d** (R = Me)	dppe (2/1)	94	76/24
21	**1d** (R = Me)	PPh_3 (2/1)	91	81/19
22	**2d** (R = Me)	PPh_3 (2/1)	93	82/18

[a] All reactions were carried out in THF at 20 °C for 12 h under nitrogen: THF (1.0 mL), allylic acetate (0.20 mmol), $NaCMe(COOMe)_2$ (0.40 mmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.002 mmol), and phosphine ligand. [b] Isolated yield by silica gel column chromatography. [c] The ratio was determined by ^1H NMR analysis of the products.

α-substituted allyl acetates **2** were allowed to react with sodium salt of dimethyl methylmalonate in THF at 20 °C for 20 h (Scheme 3). The results are summarized in Table 1, which also contains the data obtained with some other phosphine ligands for comparison. An interesting new regiochemistry, which has not been observed before in allylic substitution reactions by way of 1,3-unsymmetrically substituted π-allylpalladium intermediates, was found in the allylic alkylation catalyzed by a palladium complex coordinated with MeO-MOP. Thus, the alkylation of (*E*)-3-phenyl-2-propenyl acetate (**1a**) in the presence of palladium/MeO-MOP catalyst (P/Pd = 2/1) gave linear product, dimethyl ((*E*)-3-phenyl-2-propenyl)methylmalonate (**3a**), as a major product. The ratio of **3a** to branch isomer, dimethyl (1-phenyl-2-propenyl)methylmalonate (**4a**), was 79/21 (entry 1). On the other hand, the alkylation of 1-phenyl-2-propenyl acetate (**2a**), which is a regioisomeric allyl ester of **1a**, catalyzed by the palladium/MeO-MOP complex under the same reaction conditions, gave branch isomer **4a** preferentially, the ratio of **3a** to **4a** being 23/77 (entry 2). The same catalytic activity and regioselectivity were observed in the reaction of **2a** catalyzed by a palladium catalyst consisting of MeO-MOP and palladium in a ratio of 1/1 (entry 3). The results obtained above for the reaction of **1a** and **2a** clearly show that the alkylation took place preferentially at the position originally substituted with the leaving acetate. The regiochemistry of starting allyl ester is retained in the product in the palladium-catalyzed alkylation in the presence of MeO-MOP ligand.

The retention of regiochemistry observed here is quite unusual in the palladium-catalyzed allylic substitution reactions. The allylic substitution of γ-substituted allyl acetates **1** and α-substituted allyl acetates **2** usually gives products consisting of the regioisomers in the same ratio, because the π-allylpalladium intermediate formed by the oxidative addition of **1** and **2** is considered to be the same. Actually, the alkylation of **1a** and **2a** in the presence of palladium catalyst coordinated with 1,2-bis(diphenylphosphino)ethane (dppe) or triphenylphosphine (P/Pd = 2/1) gave the alkylation products in the same ratio irrespective of the regiochemistry of the starting allylic esters (entries 4−7). It is noteworthy that the reaction catalyzed by palladium/PPh_3 requires 2 equiv (to Pd) of phosphine ligand. With 1 equiv of phosphine ligand, a deposit of palladium black was observed and the reaction stops at 66% conversion (entry 8), though the regioselectivity is the same. Similar regiochemical results were obtained in the allylic alkylation of allyl acetates substituted at the α or γ position with aryl groups, 4-methoxyphenyl (**1b** and **2b**) and 4-chlorophenyl (**1c** and **2c**) (entries 9−16). The palladium/MeO-MOP catalyst gave the alkylation products in a different ratio of regioisomers while palladium/PPh_3 catalyst gave the products of the same ratio starting from a pair of regioisomeric allyl acetates, irrespective of the electron-donating or -withdrawing characters of the aryl substituents. The retention of regiochemistry was also observed in the alkylation of methyl-substituted allyl esters **1d** and **2d** in the presence of palladium/MeO-MOP catalyst, linear ester **1d** giving linear product **3d** with high selectivity and branch ester **2d** giving branch product **4d** as a major product (entries 17 and 18). Here again, the regiochemistry was lost in the reaction catalyzed by palladium complexes of dppe and triphenylphosphine (entries 19−22).

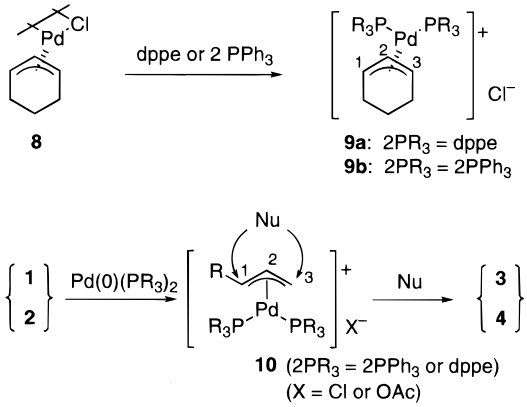
The substitution at the carbon originally substituted with acetate was also observed in the reaction of specifically deuterated cyclohexenyl acetates **5** (Scheme 3). Thus, the alkylation of 3-deuterated acetate **5**-3-d_1 and 1-deuterated acetate **5**-1-d_1 with sodium salt of dimethyl methylmalonate in the presence of palladium/MeO-MOP catalyst took place with high selectivity (83% at 20 °C) at the position originally substituted with acetate, giving **6a** and **7a**, respectively (entries 1 and 2 in Table 2). Deuterium isotope effects were not observed in the present alkylation. The reaction carried out at 0 °C in the presence of 0.5 equiv of lithium chloride increased the regioselectivity up to 88% (entries 3 and 4). Use of dppe or triphenylphosphine ligand in place of MeO-MOP gave a 1/1 mixture of **6a** and **7a**, starting with either **5**-3-d_1 or **5**-1-d_1 (entries 5−8), indicating that the regiochemical integrity of cyclohexenyl acetates **5**-3-d_1 and **5**-1-d_1 is lost before the nucleophilic attack in the case of dppe or PPh_3 as a ligand. In the allylic alkylation with dimethyl malonate catalyzed by

Table 2. Allylic Alkylation of 2-Cyclohexenyl Acetates **5** with Nucleophiles, $NaCMeE_2$ and $NaCHE_2$ (E = COOMe), Catalyzed by Palladium−Phosphine Complexes[a]

entry	acetate	Nu	ligand (ratio P/Pd)	yield[b] (%) of **6** and **7**	ratio[c] **6**/**7**
1	**5**-3-d_1	$CMeE_2$	(*R*)-MeO-MOP (2/1)	95	83/17
2	**5**-1-d_1	$CMeE_2$	(*R*)-MeO-MOP (2/1)	85	17/83
3[d]	**5**-3-d_1	$CMeE_2$	(*R*)-MeO-MOP (2/1)	90	88/12
4[d]	**5**-1-d_1	$CMeE_2$	(*R*)-MeO-MOP (2/1)	93	12/88
5	**5**-3-d_1	$CMeE_2$	dppe (2/1)	80	49/51
6	**5**-1-d_1	$CMeE_2$	dppe (2/1)	94	53/47
7	**5**-3-d_1	$CMeE_2$	PPh_3 (2/1)	91	51/49
8	**5**-1-d_1	$CMeE_2$	PPh_3 (2/1)	91	50/50
9	**5**-1-d_1	CHE_2	(*R*)-MeO-MOP (2/1)	87	18/82
10	**5**-1-d_1	CHE_2	PPh_3 (2/1)	89	45/55

[a] All reactions were carried out in THF at 20 °C for 12 h under nitrogen unless otherwise noted: THF (1.0 mL), allylic acetate (0.20 mmol), $NaCMe(COOMe)_2$ or $NaCH(COOMe)_2$ (0.40 mmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.002 mmol), and phosphine ligand. [b] Isolated yield by silica gel column chromatography. [c] The ratio was determined by ^1H NMR analysis of the products. [d] Carried out at 0 °C in the presence of 0.5 equiv of LiCl.

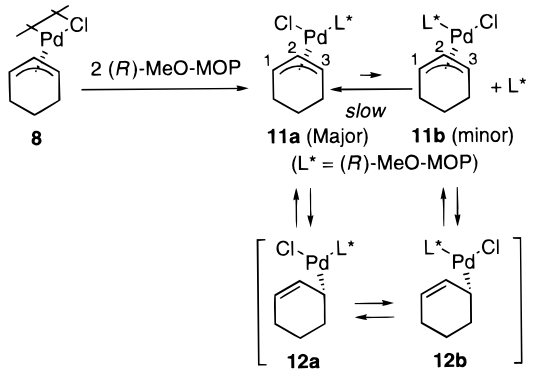
Scheme 4



palladium/MeO-MOP, the alkylation also took place at the carbon substituted with acetate (entry 9).

Structure and Isomerization of π-Allylpalladium−Phosphine Complexes. It has been reported that π-allylpalladium(II) complexes adopt cationic square planar structure on coordination with a chelating bisphosphine ligand or two molecules of monophosphine ligand.[4] We have examined the coordination number of the phosphine ligand for the (π-cyclohexenyl)palladium system (Scheme 4). Addition of 1 equiv of dppe (P/Pd = 2/1) to $[PdCl(\pi\text{-cyclohexenyl})]_2$ (**8**) in THF or $CDCl_3$ gave cationic bisphosphine complex $[Pd(\pi\text{-cyclohexenyl})(dppe)]^+Cl^-$ (**9a**) in a quantitative yield. Similarly, a cationic bisphosphine complex, $[Pd(\pi\text{-cyclohexenyl})(PPh_3)_2]^+Cl^-$ (**9b**), was formed selectively on addition of 2 equiv of PPh_3 (P/Pd = 2/1) to **8**. The formation of the cationic bisphosphine complexes was readily assigned by ^1H and ^{31}P NMR spectroscopic studies.[5] ^1H NMR for the π-cyclohexenyl moiety showed a symmetric structure in both **9a** and **9b** (see the Experimental Section). The palladium-catalyzed allylic substitution in the presence of dppe or 2 equiv of triphenylphosphine should contain cationic π-allylpalladium complex **10** which is a common intermediate formed by the oxidative addition of either allylic ester **1** or **2**. It is likely that the π-allylpalladium intermediate **10** does not have the original regiochemical characteristics of allylic esters any more. Hence, it is reasonable that allyl esters **1** and **2** gave the alkylation products **3** and **4** with the same regioselectivity (see Scheme 1).

Scheme 5



On the other hand, the reaction of **8** with 2 equiv (to Pd) of (*R*)-MeO-MOP gave neutral monophosphine complex [PdCl(π-cyclohexenyl)(MeO-MOP)] (**11**), leaving one molecule of MeO-MOP ligand free from palladium (Scheme 5). The same neutral monophosphine complex **11** was formed by mixing **8** with 1 equiv (to Pd) of MeO-MOP. With MeO-MOP ligand, the π-allylpalladium cannot accommodate two molecules of phosphine ligand because of the steric bulkiness of the MeO-MOP ligand.[6] The complex **11** consists of a pair of diastereoisomers **11a** and **11b** in a ratio of 6/1 at 20 °C in $CDCl_3$. π-Allyl protons were fully assigned by ^{31}P,^1H-correlation spectroscopy (Supporting Information). The protons which have correlation peaks with ^{31}P signals are assigned as those on the π-allyl carbons trans to phosphorus (H^1 proton of the major isomer and H^3 proton in the minor isomer). The major isomer is tentatively assigned to be **11a**, which has axial chirality *R* around the π-allyl−palladium bond axis,[7] on the basis of our structural studies of related PdCl(π-allyl)((*R*)-MeO-MOP) complexes.[8] The unusual high field shift (δ 3.15 ppm) of the H^2 proton of the major isomer supports the structure **11a**.[8] In the ^1H 2-D NOESY spectrum of **11** (Figure 1) obtained by mixing **8** with 1 equiv (to Pd) of MeO-MOP in $CDCl_3$ at 20 °C, cross-peaks arising from exchange were observed between isomers **11a** and **11b** for allylic protons, H^1, H^2, and H^3, and methoxy groups on the MeO-MOP ligand. The allylic proton trans to phosphorus in the major isomer (H^1 in **11a**: δ 5.02) found a cross-peak for the allylic proton cis to phosphorus in the minor isomer (H^1 in **11b**: δ 4.26), and that cis to phosphorus in the major isomer (H^3 in **11a**: δ 3.98) found a cross-peak for that trans to phosphorus in the minor isomer (H^3 in **11b**: δ 5.61). Thus, the isomerization between **11a** and **11b** is formally recognized to be trans−cis isomerization, exchange of the coordination site of the phosphine ligand and chloride. The rate of isomerization between **11a** and **11b** was measured by a

(4) For a review on π-allylpalladium complexes, see: Davies, J. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 9, Chapter 6.

(5) For recent relevant papers on NMR studies of π-allylpalladium complexes, see: (a) Pregosin, P. S.; Salzmann, R.; Togni, A. *Organometallics* **1995**, *14*, 842. (b) Trabesinger, G.; Albinati, A.; Feiken, N.; Kunz, R. W.; Pregosin, P. S.; Tschoerner, M. *J. Am. Chem. Soc.* **1997**, *119*, 6315.

(6) The cone angle of the MeO-MOP ligand is calculated to be larger than 200°. The structure of MeO-MOP on coordination to palladium has been studied; see: Uozumi, Y.; Kitayama, K.; Hayashi, T.; Yanagi, K.; Fukuyo, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 713. See also ref 8.

(7) We propose this nomenclature of absolute configuration for square planar π-allylmetal complexes containing meso type π-allyl and two different ligands.

(8) 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.

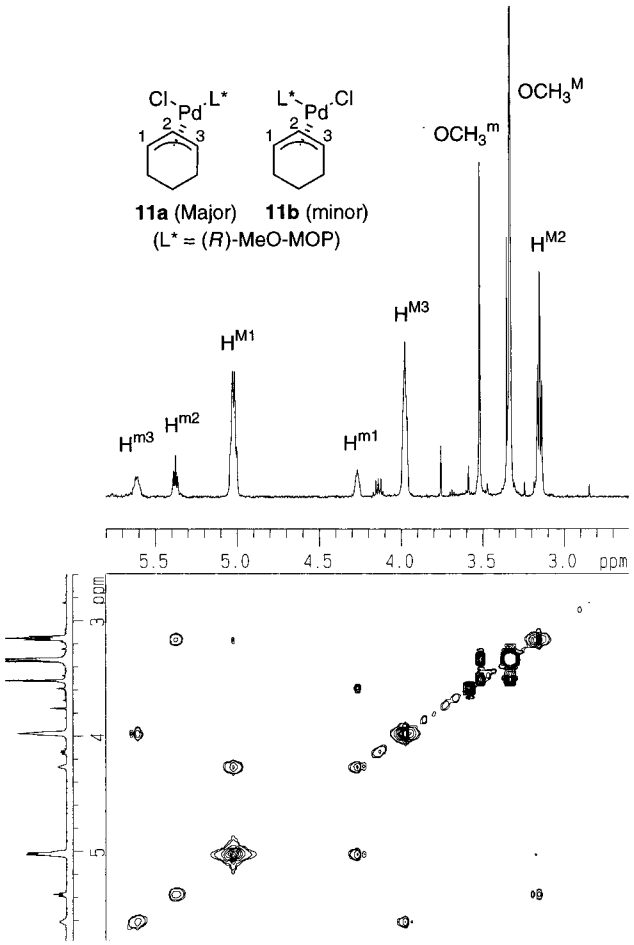


Figure 1. 2-D NOESY spectrum of PdCl(π-cyclohexenyl)((*R*)-MeO-MOP) (**11**) in $CDCl_3$ at 20 °C showing the π-allyl region. Strong correlation peaks are observed between H^{M1} and H^{m1}, between H^{M2} and H^{m2}, and between H^{M3} and H^{m3} (M = major isomer **11a**; (m = minor isomer **11b**).

magnetization saturation transfer technique in ^1H NMR.[9] The rate constant, $k_{(\mathbf{11a}\rightarrow\mathbf{11b})}$, obtained by saturation of the H^1 proton in **11b** at 20 °C in $CDCl_3$ was 0.5 s^{-1} and the rate constant, $k_{(\mathbf{11b}\rightarrow\mathbf{11a})}$, obtained by saturation of the H^1 proton in **11a** was 3.2 s^{-1}. The isomerization rate in THF-d_8 was a little slower than that in $CDCl_3$, $k_{(\mathbf{11b}\rightarrow\mathbf{11a})}$ being 2.8 s^{-1}. At −15 °C, the rate constant $k_{(\mathbf{11a}\rightarrow\mathbf{11b})}$ was decreased to 0.08 s^{-1}. The isomerization rate was not affected by addition of an excess of MOP ligand, with MOP/Pd = 2/1, $k_{(\mathbf{11a}\rightarrow\mathbf{11b})}$ being 0.6 s^{-1} at 20 °C in $CDCl_3$, which indicates that the isomerization is taking place intramolecularly, probably by way of σ-allylpalladium intermediates **12** which can undergo the trans−cis isomerization by bond rotation around the palladium carbon bond axis.

Addition of 0.9 equiv (to Pd) of triphenylphosphine to [PdCl(π-cyclohexenyl)]$_2$ (**8**) gave monophosphine complex [PdCl(π-cyclohexenyl)(PPh_3)] (**13**) and a small amount (0.1 equiv) of starting **8**. The isomerization of **13** is as slow as that of MeO-MOP analogue **11** in the absence of an excess of PPh_3 (Scheme 6). The rate constants for the isomerization, which were measured by the saturation transfer technique using exchange between H^1 (δ 5.81 in **13a**) and H^3 (δ 4.14 in **13a**) protons, were 1.4 and 0.08 s^{-1} at 20 and −15 °C, respectively. The isomerization was found to be greatly accelerated by addition of an excess of triphenylphosphine. In the presence of 0.1 equiv excess of triphenylphosphine, the rate of isomerization was 3.4 s^{-1} at −15 °C, 40 times faster than that in the absence of excess triphenylphosphine. At 20 °C, the isomerization is so fast on the NMR time scale that nonequivalent allylic protons H^1 and H^3 in **13** appear as very broad signals (Figure 2). The signal broadening was also observed for the protons on C^4 and C^6 carbons of complex **13**. At lower

(9) For examples, see: (a) Cho, H.; Iwashita, T.; Ueda, M.; Mizuno, A.; Mizukawa, K.; Hamaguchi, M. *J. Am. Chem. Soc.* **1988**, *110*, 4832. (b) Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067.

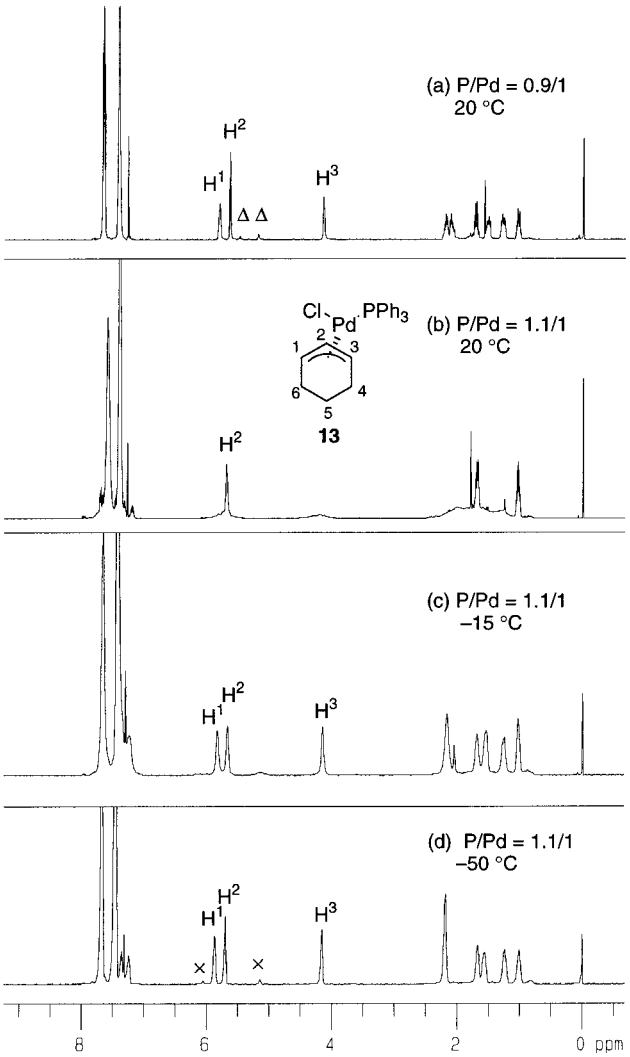
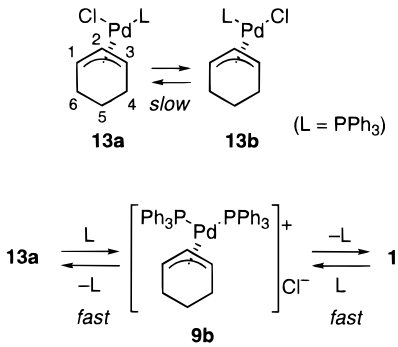
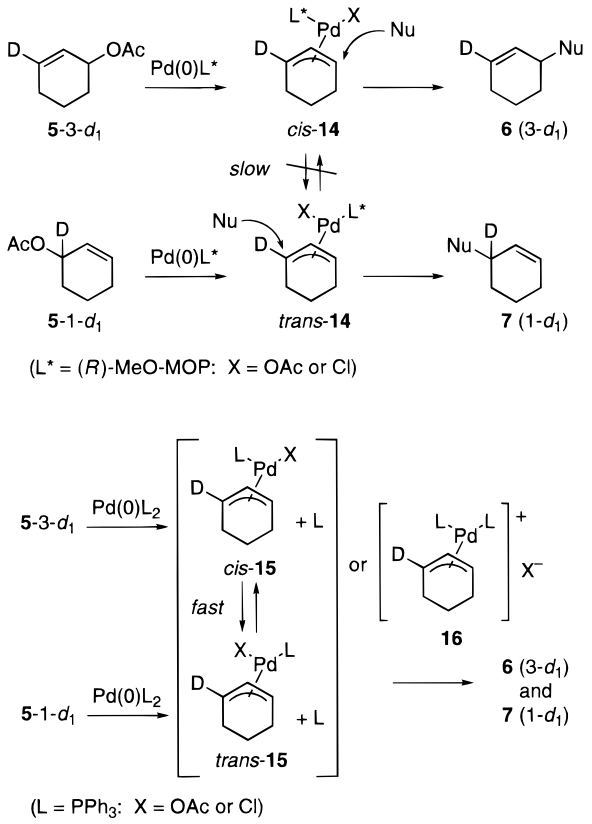


Figure 2. ^1H NMR spectra for PdCl(π-cyclohexenyl)(PPh_3) (**13**) generated by mixing [PdCl(π-cyclohexyenyl)]$_2$ (**8**) with triphenylphosphine in $CDCl_3$. The ratios of PPh_3 to Pd are 0.9/1 in (a) and 1.1/1 in (b), (c), and (d). Peaks indicated by Δ are for π-allyl protons of **8**, and those indicated by × are for π-allyl protons of cationic bisphosphine complex [Pd(π-cyclohexenyl)(PPh_3)$_2$]$^+$Cl$^-$ (**9b**).

Scheme 6



Scheme 7



temperature, the isomerization is slower, and the ^{1}H NMR spectrum in the presence of 10% excess triphenylphosphine ligand showed formation of monophosphine complex **13** and 0.1 equiv of cationic bisphosphine complex **9b**. The great acceleration of the isomerization by the addition of triphenylphosphine demonstrates that the fast isomerization of PPh_3 complex **13** takes place by an associative mechanism via cationic bisphosphine complex **9b** or a five-coordinated species. Thus, the difference between MeO-MOP complex **11** and triphenylphosphine complex **13** is that the trans−cis isomerization of **11** is much slower than that of **13** in the presence of an excess of the phosphine ligand.

Discussion

The retention of the regiochemistry in the catalytic alkylation of cyclohexenyl acetates **5** in the presence of MeO-MOP ligand (Scheme 5) must be related to the slow isomerization of the π-allylpalladium intermediates **14** coordinated with MeO-MOP ligand (Scheme 7). It is reasonable that the nucleophilic attack takes place selectively on either of the π-allyl carbons C^1 and C^3, most probably on the carbon trans to the phosphine ligand because of its stronger trans influence than acetate or chloride.[10] Provided that the oxidative addition of **5**-3-d_1 and **5**-1-d_1 to a palladium(0) species coordinated with MeO-MOP takes place selectively in forming *cis*-**14** and *trans*-**14**, respectively, the slow isomerization between *cis*-**14** and *trans*-**14** can rationalize the retention of the regiochemistry observed in the catalytic alkylation. Attempts to isolate and characterize π-allylpalladium intermediates **14** formed by oxidative addition of **5**-3-d_1 or **5**-1-d_1 to a Pd(0)/MeO-MOP species before trans−cis isomerization are not successful because the isomerization is not so slow that they are characterized before the isomerization. It is noteworthy that the palladium(0) complex coordinated with one molecule of MeO-MOP, which was generated by addition of sodium dimethyl malonate to a mixture of [PdCl(π-cyclohexenyl)]$_2$ (**8**) and MeO-MOP (P/Pd = 1/1) in THF, is stable in solution for days at room temperature. The coordination of a naphthyl group was found in the palladium(0) complex coordinated with MeO-MOP which was demonstrated by low field shifts of the protons at the 7′ and 8′ positions of the MeO-MOP ligand in ^{1}H NMR.[11] The catalytic allylic alkylation in the presence of triphenylphosphine ligand should contain palladium(0) species coordinated with two molecules of the phosphine ligand even if the initial ratio at the generation of the catalyst was P/Pd = 1/1. A deposit of palladium black which was observed in the catalytic reaction (entry 8 in Table 1) increases the ratio of P/Pd to more than 1. Thus, the catalytic cycle of the allylic alkylation catalyzed by the palladium/triphenylphosphine system involves a cationic bisphosphine intermediate [Pd(π-allyl)$(PPh_3)_2$]$^+$ (**16**) or combination of a neutral monophosphine intermediate [PdX(π-allyl)(PPh_3)] (**15**) and an excess of the phosphine. The bisphosphine complex **16** does not have the regiochemical characteristics of the starting allylic esters, and the monophosphine complex **15** undergoes the fast isomerization in the presence of an excess of the phosphine which will lose the original regiochemistry. On the other hand, the palladium/MeO-MOP system involves only monophosphine intermediate [PdX(π-allyl)(MeO-MOP)] (**14**) which does not undergo the fast isomerization even in the presence of excess ligand.[12]

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a JEOL JNM-EX270 spectrometer (270 MHz for ^{1}H and 109 MHz for ^{31}P), JEOL JNM-AL400 spectrometer (400 MHz for ^{1}H NMR), or JEOL JNM LA500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard for ^{1}H NMR, and to an external 85% H_3PO_4 standard for ^{31}P NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as the internal reference for ^{13}C NMR. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted. Preparative medium-pressure liquid chromatography (MPLC) was performed with a silica gel prepacked column Si-10 (Kusano).

Materials. THF was dried over sodium−benzophenone ketyl and distilled prior to use. [PdCl(π-C_3H_5)]$_2$,[13] [PdCl(π-cyclohexenyl)]$_2$,[14] (*R*)-MeO-MOP,[3] 1-aryl-2-propenyl acetates,[15,16] (*E*)-3-aryl-2-propenyl

(10) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *Chem. Commun*. **1997**, 561.

(11) ^{1}H NMR for palladium(0)/MeO-MOP (THF-d_8): δ 6.00 (t, J = 7.6 Hz, 1H, H$^{7'}$), 6.22 (d, J = 7.6 Hz, 1H, H$^{8'}$), 6.65 (t, J = 7.6 Hz, 1H, H$^{6'}$). By this second coordination the unusual stability of the palladium(0)/MeO-MOP complex is rationalized. This type of coordination was not observed in the π-allyl(MeO-MOP)palladium(II) complexes, formed either by the oxidative addition of allylic esters to palladium(0) or by addition of MOP ligand to [PdX(π-allyl)]$_2$. The coordination of a biaryl double bond has been reported in a rhuthenium complex coordinated with MeO-BIPHEP: Feiken, N.; Pregosin, P. S.; Trabesinger, G.; Scalone, M. *Organometallics* **1997**, *16*, 537. The details of the palladium(0)/MeO-MOP complex will be described elsewhere.

(12) Another mechanism, for example, involving palladium−carbon bond formation by reductive elimination of σ-allyl and malonate bonded to palladium, is excluded by the net retention of stereochemistry in the catalytic allylic alkylation catalyzed by Pd/MeO-MOP as well as other palladium catalysts bearing phosphine ligands. Thus, the reaction of *cis*-3-acetoxy-5-carbomethoxy-1-cyclohexene with the sodium salt of dimethyl malonate in the presence of the palladium/MeO-MOP catalyst proceeded with net retention of configuration to give dimethyl *cis*-(5-carbomethoxy-1-cyclohexen-3-yl)malonate: Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc*. **1980**, *102*, 4730.

(13) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033.

(14) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407.

(15) Lehmann, J.; Lloyd-Jones, G. C. *Tetrahedron* **1995**, *52*, 8863.

acetates,[15,17] and 3-deuterio-2-cyclohexen-1-ol[18] were prepared according to the reported procedures.

Preparation of Allylic Acetates 5-1-d_1 and 5-3-d_1. 1-Deuterio-2-cyclohexenyl Acetate 5-1-d_1. To a solution of $LiAlD_4$ (1.12 g, 26.7 mmol) in ether (60 mL) was slowly added a solution of 2-cyclohexen-1-one (5.03 g, 52.3 mmol) in ether (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 2 h and diluted with ether. Addition of $NaSO_4 \cdot 10H_2O$ followed by filtration through a pad of Celite and evaporation of the solvent gave a quantitative yield of crude 1-deuterio-2-cyclohexen-1-ol. To a solution of this crude alcohol, pyridine (8.43 mL, 104 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in ether (50 mL) was added acetic anhydride (12.3 mL, 130 mmol). The mixture was stirred at room temperature for 12 h, quenched with water, and extracted with ether. The organic phase was washed with 10% $CuSO_4$ solution, water, and brine, dried over anhydrous magnesium sulfate, and evaporated. The residue was chromatographed on silica gel (hexane/EtOAc = 5/1) to give 5.81 g (79%) of 1-deuterio-2-cyclohexenyl acetate (**5**-1-d_1): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.62−2.03 (m, 6H), 2.05 (s, 3H), 5.23−5.27 (m, 1H), 5.70 (m, 1H); MS *m*/*z* 141 (M^+, 10), 99 (81), 79 (100).

3-Deuterio-2-cyclohexenyl Acetate (5-3-d_1). To a solution of 3-deuterio-2-cyclohexen-1-ol[18] (3.13 g, 31.9 mmol), pyridine (3.7 mL, 46 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in ether (30 mL) was added acetic anhydride (5.8 mL, 61 mmol). The mixture was stirred at room temperature for 12 h, quenched with water, and extracted with ether. The organic phase was washed with 10% $CuSO_4$ solution, water, and brine, dried over anhydrous magnesium sulfate, and evaporated. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 5/1) to give 4.46 g (99%) of 3-deuterio-2-cyclohexenyl acetate (**5**-3-d_1): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.62−2.03 (m, 6H), 2.05 (s, 3H), 5.69−5.72 (m, 1H), 5.94−5.98 (m, 1H); MS *m*/*z* 141 (M^+, 5), 99 (51), 80 (100).

Palladium-Catalyzed Allylic Alkylation of 1 and 2. The reaction conditions and results are shown in Table 1. A typical procedure is given for the reaction of 1-(4-methoxyphenyl)-2-propenyl acetate (**2b**)**.** To a solution of $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.90 mg, 0.0025 mmol) and (*R*)-MeO-MOP (5.1 mg, 0.011 mmol) in THF (0.1 mL) was added a solution of the sodium salt of dimethyl methylmalonate prepared from dimethyl methylmalonate (73 mg, 0.50 mmol) and sodium hydride in THF (1.0 mL). Allyl acetate **2b** (56 mg, 0.27 mmol) was added, and the mixture was stirred at 20 °C for 12 h. The catalyst was removed by filtration through a short silica gel pad (ether). The filtrate was evaporated, and the residue was chromatographed on silica gel (hexane/EtOAc = 6/1) to give 74 mg (99%) of a mixture of dimethyl ((*E*)-3-(4-methoxyphenyl)-2-propenyl)methylmalonate (**3b**) and dimethyl (1-(4-methoxyphenyl)-2-propenyl)methylmalonate (**4b**). The ratio of **3b** to **4b** was determined to be 16/84 by ^{1}H NMR. Analytically pure samples of **3b** and **4b** were obtained by MPLC (hexane/EtOAc = 6/1).

Dimethyl ((*E*)-3-(4-Methoxyphenyl)-2-propenyl)methylmalonate (3b): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.59 (s, 3H), 2.74 (dd, J = 7.8, 1.0 Hz, 2H), 3.73 (s, 6H), 3.80 (s, 3H), 5.93 (dt, J = 15.6, 7.8 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 6.82 (d, J = 6.4 Hz, 2H), 7.25 (d, J = 6.4 Hz, 2H). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.80; H, 7.11.

Dimethyl (1-(4-Methoxyphenyl)-2-propenyl)methylmalonate (4b): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.51 (s, 3H), 3.71 (s, 3H), 3.79 (s, 3H), 3.87 (s, 3H), 4.19 (d, J = 8.3 Hz, 1H), 5.09 (d, J = 16.8 Hz, 1H), 5.14 (d, J = 11.3, 1H), 6.32 (ddd, J = 8.3, 11.3, 16.8 Hz, 1H), 6.90 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 66.00; H, 6.85.

^{1}H NMR and analytical data for other allylic alkylation products **3** and **4** are shown below.

Dimethyl ((*E*)-3-Phenyl-2-propenyl)methylmalonate (3a): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.46 (s, 3H), 2.77 (dd, J = 7.8, 1.0 Hz, 2H), 3.73 (s, 6H), 6.08 (dt, J = 15.6, 7.8 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 7.19−7.34 (m, 5H). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.55; H, 7.01.

Dimethyl (1-Phenyl-2-propenyl)methylmalonate (4a): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.43 (s, 3H), 3.62 (s, 3H), 3.72 (s, 3H), 4.10 (d, J = 8.6 Hz, 1H), 5.11 (d, J = 16.8 Hz, 1H), 5.12 (d, J = 10.0, 1H), 6.32 (ddd, J = 8.6, 10.0, 16.8 Hz, 1H), 7.18−7.34 (m, 5H). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.70; H, 6.95.

Dimethyl ((*E*)-3-(4-Chlorophenyl)-2-propenyl)methylmalonate (3c): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.45 (s, 3H), 2.75 (d, J = 7.3 Hz, 2H), 3.73 (s, 6H), 6.07 (dt, J = 15.6, 7.3 Hz, 1H), 6.39 (d, J = 15.6 Hz, 1H), 7.25 (s, 4H). Anal. Calcd for $C_{15}H_{17}O_4Cl$: C, 60.71; H, 5.77. Found: C, 60.57; H, 5.93.

Dimethyl (1-(4-Chlorophenyl)-2-propenyl)methylmalonate (4c): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.42 (s, 3H), 3.63 (s, 3H), 3.70 (s, 3H), 4.11 (d, J = 8.8 Hz, 1H), 5.09 (d, J = 17.1 Hz, 1H), 5.15 (d, J = 10.3, 1H), 6.26 (ddd, J = 8.8, 10.3, 17.1 Hz, 1H), 7.22 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H). Anal. Calcd for $C_{15}H_{17}O_4Cl$: C, 60.71; H, 5.77. Found: C, 60.57; H, 5.89.

Dimethyl ((*E*)-2-Butenyl)methylmalonate (3d): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.38 (s, 3H), 1.65 (dd, J = 1.0, 6.9 Hz, 3H), 2.54 (d, J = 7.3 Hz, 2H), 3.71 (s, 6H), 5.29 (qdt, J = 1.0, 15.1, 7.3 Hz, 1H), 5.51 (dq, J = 15.1, 6.9 Hz, 1H). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.80; H, 8.33.

Dimethyl (1-Methyl-2-propenyl)methylmalonate (4d): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.98 (d, J = 6.8 Hz, 3H), 1.29 (s, 3H), 2.93 (dq, J = 8.3, 6.8 Hz, 1H), 3.63 (s, 3H), 3.64 (s, 3H), 4.93 (d, J = 10.7 Hz, 1H), 5.00 (d, J = 18.1 Hz, 1H), 5.70 (ddd, J = 8.3, 10.7, 18.1 Hz, 1H). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.71; H, 8.00.

Palladium-Catalyzed Allylic Alkylation of 2-Cyclohexenyl Acetates 5-1-d_1 and 5-3-d_1. The reaction conditions and results are shown in Table 2. The ratio of regioisomers **6** and **7** was determined by ^{1}H NMR studies of the mixture of **6** and **7**.

Dimethyl (3-Deuterio-2-cyclohexenyl)methylmalonate (6a): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.26−1.32 (m, 1H), 1.34 (s, 3H), 1.51−1.62 (m, 2H), 1.78−1.81 (m, 1H), 1.95−1.98 (m, 2H), 3.04 (m, 1H), 3.71 (s, 3H), 3.72 (s, 3H), 5.48 (br s, 1H).

Dimethyl (1-Duterio-2-cyclohexenyl)methylmalonate (7a): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.26−1.31 (m, 1H), 1.34 (s, 3H), 1.51−1.62 (m, 2H), 1.77−1.81 (m, 1H), 1.95−1.98 (m, 2H), 3.71 (s, 3H), 3.72 (s, 3H), 5.48 (m, 1H), 5.78 (m, 1H).

Dimethyl (3-Deuterio-2-cyclohexenyl)malonate (6b): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.34−1.43 (m, 1H), 1.54−1.61 (m, 1H), 1.70−1.80 (m, 2H), 1.97−2.04 (m, 2H), 2.88−2.94 (m, 1H), 3.29 (m, 1H), 3.74 (s, 6H), 5.53 (br s, 1H).

Dimethyl (1-Deuterio-2-cyclohexenyl)malonate (7b): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.34−1.43 (m, 1H), 1.54−1.61 (m, 1H), 1.70−1.80 (m, 2H), 1.97−2.04 (m, 2H), 3.73 (s, 3H), 3.74 (s, 3H), 5.12 (m, 1H), 5.78 (m, 1H).

NMR Study of [Pd(π-cyclohexenyl)(dppe)]$^+$Cl$^-$ (9a). In an NMR sample tube were placed dppe (11.3 mg, 0.028 mmol) and $[PdCl(\pi\text{-cyclohexenyl})]_2$ (6.3 mg, 0.014 mmol). The tube was filled with nitrogen, and $CDCl_3$ (0.5 mL) was added. ^{1}H NMR and ^{31}P NMR spectra were measured at 25 °C: ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 1.06−1.08 (m, 1H), 1.22−1.31 (m, 3H), 2.15−2.20 (m, 2H), 2.57−2.64 (m, 2H), 3.02-3.06 (m, 2H), 5.81 (t, J = 6.8 Hz, 1H), 5.97 (br d, J_{H-P} = 4.9 Hz, 2H), 7.29−7.59 (m, 20H); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 25 °C) δ 46.7.

NMR Study of [Pd(π-cyclohexenyl)(PPh_3)$_2$]$^+$Cl$^-$ (9b). In an NMR sample tube were placed PPh_3 (11.8 mg, 0.045 mmol) and $[PdCl(\pi\text{-cyclohexenyl})]_2$ (4.9 mg, 0.011 mmol). The tube was filled with nitrogen, and $CDCl_3$ (0.5 mL) was added. ^{1}H NMR and ^{31}P NMR spectra were measured at −30 °C: ^{1}H NMR ($CDCl_3$, 500 MHz, −30 °C) δ 0.89−1.58 (m, 6H), 5.15 (br s, 2H), 6.09 (br s, 1H), 7.24−7.54 (m, 30H); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, −30 °C) δ 22.2.

Isolation of [PdCl(π-cyclohexenyl)(MeO-MOP)] (11a). A solution of (*R*)-MeO-MOP (21.2 mg, 0.045 mmol) and $[PdCl(\pi\text{-cyclohexenyl})]_2$ (10.1 mg, 0.023 mmol) in benzene (0.8 mL) was placed in a small open bottle (5 mL), and the bottle was placed in a reagent bottle (25 mL) which contained ether (3 mL). After 1 day, yellow crystals (13.5

(16) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132.

(17) Malet, R.; Moreno-Mañas, M.; Parella, T.; Pleixats, R. *Organometallics* **1995**, *14*, 2463.

(18) Kawasaki, M.; Suzuki, Y.; Terashima, S. *Chem. Pharm. Bull.* **1985**, *33*, 52.

mg, 43%) were formed owing to dispersion of the solvents. Anal. Calcd for $C_{39}H_{34}OClPPd$: C, 67.73; H, 5.86. Found: C, 68.01; H, 5.15.

NMR Study of [PdCl(π-cyclohexenyl)(MeO-MOP)] (11a + 11b). (*R*)-MeO-MOP (21.2 mg, 0.045 mmol) and [PdCl(π-cyclohexenyl)]$_2$ (10.0 mg, 0.023 mmol) were placed in an NMR sample tube. The tube was filled with nitrogen, and $CDCl_3$ (0.5 mL) was added. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were measured at 20 °C. The ratio of major isomer **11a** to minor isomer **11b** was 6/1. The rate of isomerization was measured by a saturation transfer experiment in ^{1}H NMR.

Major Isomer (11a): ^{1}H NMR ($CDCl_3$, 500 MHz, 20 °C) δ 0.20−0.25 (m, 1H), 0.63−0.71 (m, 1H), 0.87−0.94 (m, 1H), 1.28−1.33 (m, 1H), 1.57−1.63 (m, 1H), 1.75−1.81 (m, 1H), 3.15 (br t, J = 6.4 Hz, 1H), 3.33 (s, 3H), 3.98 (br s, 1H), 5.02 (br d, J_{H-P} = 5.4 Hz, 1H), 6.86−8.00 (m, 22H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 20 °C) δ 54.9 (CH_3), 75.4 (C^3), 94.4 (d, J_{C-P} = 29.0 Hz, C^1), 107.6 (d, J_{C-P} = 5.2 Hz, C^2); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 25 °C) δ 20.8.

Minor Isomer (11b): ^{1}H NMR ($CDCl_3$, 500 MHz, 20 °C) 0.86−2.03 (m, 6H), 3.52 (s, 3H), 4.26 (br s, 1H), 5.37 (br t, J = 6.8 Hz, 1H), 5.61 (br d, J_{H-P} = 5.8 Hz, 1H), 6.86−8.00 (m, 22H); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 20 °C) δ 28.7.

NMR Study and Isolation of [PdCl(π-cyclohexenyl)(PPh_3)] (13). PPh_3 (5.3 mg, 0.020 mmol) and [PdCl(π-cyclohexenyl)]$_2$ (5.0 mg, 0.011 mmol) were placed in an NMR sample tube. The tube was filled with nitrogen, and $CDCl_3$ (0.5 mL) was added. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were measured at 20 °C. The spectral data at 20 °C are shown below. The rate of isomerization was measured by a saturation transfer experiment in ^{1}H NMR. The tube was placed at −20 °C. After 7 days, yellow crystals (6.3 mg, 58%) were formed. ^{1}H NMR ($CDCl_3$, 500 MHz, 20 °C) δ 1.00−1.08 (m, 1H), 1.25−1.32 (m, 1H), 1.50−1.57 (m, 1H), 1.68−1.76 (m, 1H), 2.07−2.15 (m, 1H), 2.18−2.33 (m, 1H), 4.14 (m, 1H), 5.64 (br t, J = 6.8 Hz, 1H), 5.81 (br d, J_{H-P} = 5.4 Hz, 1H), 7.27−7.69 (m, 15H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 20 °C) δ 77.4 (C^3), 96.2 (J_{C-P} = 29.9 Hz, C^1), 108.4 (J_{C-P} = 5.3 Hz, C^2); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 20 °C) δ 23.9. Anal. Calcd for $C_{24}H_{24}ClPPd$: C, 59.40; H, 4.99. Found: C, 59.45; H, 5.28.

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Supporting Information Available: ^{1}H NMR spectrum for complex **11** and ^{31}P,^{1}H-correlation spectrum for complex **11** (2 pages). See any current masthead page for ordering information and Web access instructions.

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