# Iridium Complex-Catalyzed Allylic Alkylation of Allylic Esters and Allylic Alcohols: Unique Regio- and Stereoselectivity

**Ryo Takeuchi* and Mikihiro Kashio**

*Contribution from the Department of Environmental Science, Faculty of Science and Graduate School of Integrated Science, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236-0027, Japan*

*Received May 5, 1998*

**Abstract:** An iridium complex was found to be an efficient catalyst for allylic alkylation of allylic esters with a stabilized carbon nucleophile. Highly regioselective alkylation at the substituted allylic terminus was achieved. The catalytic activity and regioselectivity were affected by the ligand used. The reaction of (*E*)-2-alkenyl acetates or 1-substituted 2-propeny acetates with dialkyl sodiomalonate in the presence of a catalytic amount of $[Ir(COD)Cl]_2/P(OPh)_3$ (P/Ir = 1−2) gave a product alkylated at the substituted allylic terminus in 95−99% selectivity. Construction of a quaternary carbon center is possible by this methodology. The reaction of 1,1-dialkyl-2-propenyl acetates gave a product alkylated at the disubstituted allylic terminus exclusively. (*E*)-2-Alken-1-ol could be successfully used as a substrate. The products alkylated at the substituted allylic terminus were obtained in 93−99% selectivity. A $^{31}P$ NMR study of the reaction of $[Ir(COD)Cl]_2$ with $P(OPh)_3$ revealed that a catalytically active species is a monophosphite species. The $\pi$-acceptor property of $P(OPh)_3$ promotes a carbonium ion character at the substituted allylic terminus and directs the nucleophilic attack to this position. The stereochemistry of the allyl system affected the regioselectivity. In contrast to the reaction of (*E*)-2-alkenyl acetates, the reaction of (*Z*)-2-alkenyl acetates gave a product alkylated at the unsubstituted allylic terminus predominantly. This shows that the regioselectivity of the alkylation of the syn $\pi$-allyl iridium intermediate is different from that of the anti $\pi$-allyl iridium intermediate. (*Z*)-Selective allylic alkylation of (*Z*)-2-alkenyl esters is also possible by iridium catalysis.

## Introduction

Transition metal complexes are indispensable tools for organic synthesis. Many useful organic transformations have been achieved. A wide variety of transition metal complexes are extensively studied as reagents or catalysts for organic synthesis.[1] The use of iridium complexes for organic synthesis is relatively unexplored. Since Crabtree reported that a cationic iridium complex is a highly active catalyst for hydrogenation of highly hindered alkenes such as 2,3-dimethyl-2-butene[2] iridium complexes have received much attention as efficient hydrogenation catalysts.[3] Iridium complex-catalyzed hydrosilylations have also been reported.[4] On the other hand, the development of iridium complex-catalyzed carbon−carbon bond forming reactions lags far behind.[5] A limited number of synthetically useful stereo- and regiocontrolled carbon−carbon bond forming reactions are reported.[6]

One of the important carbon−carbon bond forming reactions catalyzed by a transition metal complex is allylic alkylation via a $\pi$-allyl complex, which is widely used for constructing complex organic molecules.[7] Palladium,[8] nickel,[9] molybdenum,[10] iron,[11] tungsten,[12] and ruthenium[13] complexes are used as catalysts or reagents for allylic alkylation. The control of regioselectivity in allylic alkylation is important. The selectivity depends on many factors, for example, the central metal, ligand, nucleophile, and substituent on the $\pi$-allyl system. Terminally monosubstituted palladium complexes generally lead to preferential alkylation at the unsubstituted allylic terminus[14] while such molybdenum,[10a,b,f,g,i−k,m] tungsten,[12a−c,f,g] and ruthenium[13b] complexes tend to lead to preferential alkylation at the substituted allylic terminus. Gaining complete regiocontrol of alkylation at the substituted allylic terminus is a challenging problem. We wish to report herein iridium complex-catalyzed highly

(1) (a) Gibson, S. E. *Transition Metals in Organic Synthesis: A Practical Approach*; Oxford University Press: Oxford, 1997. (b) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12. (c) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, 1994. (d) McQuillin, F. J.; Parker, D. G.; Stephenson, G. R. *Transition Metal Organometallics for Organic Synthesis*; Cambridge University Press: Cambridge, 1991. (e) Harrington, P. J. *Transition Metals in Total Synthesis*: John Wiley & Sons: New York, 1990.

(2) (a) Crabtree, R. H. *Acc. Chem. Res*. **1979**, *12*, 331. (b) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem*. **1977**, *141*, 205.

(3) (a) Schnider, P.; Koch, G.; Pretot, R.; Wang, G.; Bohnen, F. M.; Kruger, C.; Pfaltz, A. *Chem.—Eur. J*. **1997**, *3*, 887. (b) Bedford, R. B.; Castillon, S.; Chaloner, P. A.; Claver, C.; Fernandez, E.; Hitchcock, P. B.; Ruiz, A. *Organometallics* **1996**, *15*, 3990. (c) Tani, K.; Onouchi, J.; Yamagata, T.; Kataoka, Y. *Chem. Lett*. **1995**, 955. (d) Zhang, X.; Taketomi, T.; Yoshizumi, T.; Kumobayashi, H.; Akutagawa, S.; Mashima, K.; Takaya, H. *J. Am. Chem. Soc*. **1993**, *115*, 3318. (e) Esteruelas, M. A.; Lopez, A. M.; Oro, L. A.; Perez, A.; Schultz, M.; Werner, H. *Organometallics* **1993**, *12*, 1823. (f) Mashima, K.; Akutagawa, T.; Zhang, X.; Takaya, H. *J. Organomet. Chem*. **1992**, *428*, 213. (g) Chan, Y. Ng. C.; Osborn, J. A. *J. Am. Chem. Soc*. **1990**, *112*, 9400. (h) Spindler, F.; Pugin, B.; Blaser, H. U. *Angew. Chem., Int. Ed. Engl*. **1990**, *29*, 558. (i) Oro, L. A.; Cabeza, J. A.; Cativiela, C.; Diaz de Villegas, M. D.; Malendez, E. *J. Chem. Soc., Chem. Commun*. **1983**, 1383. (j) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc*. **1983**, *105*, 1072. (k) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc*. **1982**, *104*, 6994.

(4) (a) Esteruelas, M. A.; Olivan, M.; Oro, L. A.; Tolosa, J. I. *J. Organomet. Chem*. **1995**, *487*, 143. (b) Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem*. **1993**, *447*, 177. (c) Esteruelas, M. A.; Nurnberg, O.; Olivan, M.; Oro, L. A.; Werner, H. *Organometallics* **1993**, *12*, 3264. (d) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415. (e) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc*. **1990**, *112*, 7984. (f) Fernandez, M. J.; Esteruelas, M. A.; Jimenez, M. S.; Oro, L. A. *Organometallics* **1986**, *5*, 1519.

S0002-7863(98)01560-1 CCC: $15.00 
Published on Web 08/15/1998

**Table 1.** Effect of Ligand on Allylic Alkylation of **1** with **2a**[a]

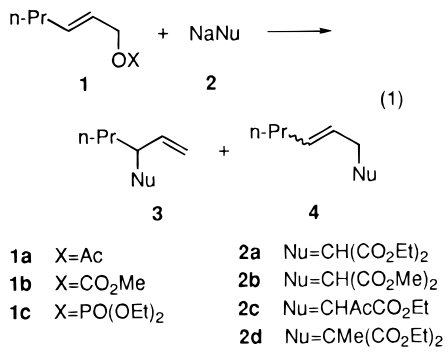
| entry | substrate | ligand | P/Ir | conditions | yield/%[b] | ratio **3**/**4** (E/Z)[c] |
|---|---|---|---|---|---|---|
| 1 | **1a** | | 0 | reflux 19 h | 66 | 12/88 (97/3) |
| 2 | **1a** | $P(OPh)_3$ | 1 | room temp 3 h | 90 | 96/4 (78/22) |
| 3 | **1a** | $P(OPh)_3$ | 2 | room temp 3 h | 89 | 96/4 (81/19) |
| 4 | **1a** | $P(OPh)_3$ | 3 | reflux 24 h | 29 | 76/24 (96/4) |
| 5 | **1b** | $P(OPh)_3$ | 2 | room temp 1 h | 94 | 97/3 (77/23) |
| 6 | **1c** | $P(OPh)_3$ | 2 | room temp 4 h | 85 | 89/11 (90/10) |
| 7 | **1a** | $P(O4-MeC_6H_4)_3$ | 2 | room temp 8 h | 81 | 95/5 (73/27) |
| 8 | **1a** | $P(O4-FC_6H_4)_3$ | 2 | room temp 23 h | 55 | 94/6 (94/6) |
| 9 | **1a** | $P(O2-Naph)_3$ | 2 | room temp 18 h | 64 | 96/4 (92/8) |
| 10 | **1a** | $PPh(OPh)_2$ | 2 | room temp 16 h | 52 | 98/2 (75/25) |
| 11 | **1a** | $P(OEt)_3$ | 2 | reflux 3 h | 81 | 59/41 (90/10) |
| 12 | **1a** | $P(O\textit{i}\text{-}Pr)_3$ | 2 | reflux 3 h | 44 | 53/47 (91/9) |
| 13 | **1a** | $PPh_3$ | 2 | reflux 16 h | 6 | 24/76 (63/37) |
| 14 | **1a** | $P(\textit{n}\text{-}Bu)_3$ | 2 | reflux 16 h | 0 | |
| 15 | **1a** | dppe | 2 | reflux 16 h | 18 | 39/61 (94/6) |

[a] A mixture of **1** (2 mmol), **2** (4 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), ligand, and THF (10 mL) was stirred under argon. [b] Isolated yield. [c] Determined by GLC.

regioselective allylic alkylation at the substituted allylic terminus with a stabilized carbon nucleophile.[15]

## Results

**Allylic Alkylation of (*E*)-Allylic Esters and 1-Substituted 2-Propenyl Esters.** The reaction of (*E*)-2-hexenyl acetate (**1a**) with diethyl sodiomalonate (**2a**) in the presence of a catalytic amount of $[Ir(COD)Cl]_2$ and ligand gave **3a**, (*E*)-**4a**, and (*Z*)-**4a**. Product **3a** arose from alkylation at the substituted allylic terminus, and **4a** arose from alkylation at the unsubstituted allylic terminus (eq 1). The phosphorus ligand that was added




had a substantial effect on the selectivity and the yield of the products. The results are summarized in Table 1. $P(OPh)_3$ was the most efficient ligand (entries 2 and 3). The reaction was completed in 3 h at room temperature to give an excellent yield of the products. Product **3a** was obtained in 96% selectivity (entry 3). The alkylation was highly selective at the substituted allylic terminus. The ratio of $P(OPh)_3$ to Ir was also important. When using 1 equiv of $P(OPh)_3$ to each equivalent of Ir, **3a** was obtained in 96% selectivity and the reaction proceeded at

(5) (a) Maitlis, P. M.; Haynes, A.; Sunley, G. J.; Howard, M. J. *J. Chem. Soc., Dalton Trans*. **1996**, 2187. (b) Patil, R. P.; Kelkar, A. A.; Chaudhari, R. V. *J. Mol. Catal*. **1992**, *72*, 153. (c) Behr, A.; Herdtweck, E.; Herrmann, W. A.; Keim, W.; Kipshagen, W. *Organometallics* **1987**, *6*, 2307. (d) Kunin, A. J.; Eisenberg, R. *J. Am. Chem. Soc*. **1986**, *108*, 535. (e) Pruett, R. L.; Kacmarcik, R. T. *Organometallics* **1982**, *1*, 1693.

(6) For a catalytic reaction see: (a) Takaya, H.; Naota, T.; Murahashi, S.-I. *J. Am. Chem. Soc*. **1998**, *120*, 4244. (b) Murakami, M.; Itami, K.; Ubukata, M.; Tsuji, I.; Ito, Y. *J. Org. Chem*. **1998**, *63*, 4. (c) Chatani, N.; Yamaguchi, S.; Fukumoto, Y.; Murai, S. *Organometallics* **1995**, *14*, 4418. (d) Chatani, N.; Ikeda, S.; Ohe, K.; Murai, S. *J. Am. Chem. Soc*. **1992**, *114*, 9710. (e) Jun, C.-H.; Crabtree, R. H. *Tetrahedron Lett*. **1992**, *33*, 7119. (f) Rappoli, B. J.; Churchill, M. R.; Janik, T. S.; Rees, W. M.; Atwood, J. D. *J. Am. Chem. Soc*. **1987**, *109*, 5145. For a stoichiometric reaction see: (g) Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc*. **1995**, *117*, 8275. (h) Wakefield, J. B.; Stryker, J. M. *J. Am. Chem. Soc*. **1991**, *113*, 7057.

(7) See ref 1e, p 25.

(8) For review see: (a) Trost, B. M.; Varanken, D. L. V. *Chem. Rev*. **1996**, *96*, 395. (b) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: New York, 1995; p 290. (c) Harrington, P. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 797. (d) Godleski, S. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, p 585.

(9) (a) Nomura, N.; RajanBabu, T. V. *Tetrahedron Lett*. **1997**, *38*, 1713. (b) Kobayashi, Y.; Mizojiri, R.; Ikeda, E. *J. Org. Chem*. **1996**, *61*, 5391. (c) Bricout, H.; Carpentier, J. F.; Mortreux, A. *Tetrahedron Lett*. **1996**, *37*, 6105. (d) Mizoziri, R.; Kobayashi, Y. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2073. (e) Bricout, H.; Carpentier, J. F.; Mortreux, A. *J. Chem. Soc., Chem. Commun*. **1995**, 1863. (f) Trost, B. M.; Spagnol, M. D. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2083. (g) Consiglio, G.; Indolese, A. *Organometallics* **1994**, *13*, 2230. (h) Consiglio, G.; Indolese, A. *Organometallics* **1991**, *10*, 3425. (i) Alvarez, E.; Cuvigny, T.; Julia, M. *J. Organomet. Chem*. **1988**, *339*, 199. (j) Cuvigny, T.; Julia, M. *J. Organomet. Chem*. **1986**, *317*, 383. (k) Minami, I.; Shimizu, I.; Tsuji, J. *J. Organomet. Chem*. **1985**, *296*, 269.

(10) (a) Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc*. **1998**, *120*, 1104. (b) Sjogren, M. P. T.; Frisell, H.; Akermark, B.; Norrby, P.-O.; Eriksson, L.; Vintagliano, A. *Organometallics* **1997**, *16*, 942. (c) Dvorak, D.; Stary, I.; Kocovsky, P. *J. Am. Chem. Soc*. **1995**, *117*, 6130. (d) Dvorakova, H.; Dovorak, D.; Srogl, J.; Kocovsky, P. *Tetrahedron Lett*. **1995**, *36*, 6351. (e) Yu, R. H.; McCallum, J. S.; Liebeskind, L. S. *Organometallics* **1994**, *13*, 1476. (f) Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc*. **1990**, *112*, 9590. (g) Trost, B. M.; Merlic, C. A. *J. Org. Chem*. **1990**, *55*, 1127. (h) Faller, J. W.; Linebarrier, D. *Organometallics* **1988**, *7*, 1670. (i) Trost, B. M.; Lautens, M. *Tetrahedron* **1987**, *43*, 4817. (j) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc*. **1987**, *109*, 1469. (k) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc*. **1983**, *105*, 3343. (l) Trost, B. M.; Lautens, M. *Organometallics* **1983**, *2*, 1687. (m) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc*. **1982**, *104*, 5543.

(11) (a) Enders, D.; Jandeleit, B.; Raabe, G. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 1949. (b) Green, J. R.; Carroll, M. K. *Tetrahedron Lett*. **1991**, *32*, 1141. (c) Xu, Y.; Zhou, B. *J. Org. Chem*. **1987**, *52*, 974. (d) Silverman, G. S.; Strickland, S.; Nicholas, K. M. *Organometallics* **1986**, *5*, 2117. (e) Roustan, J. L.; Merour, J. Y.; Houlihan, F. *Tetrahedron Lett*. **1979**, 3721. (f) Roustan, J. L.; Houlihan, F. *Can. J. Chem*. **1979**, *57*, 2790.

(12) (a) Lloyd-Jones, G. C.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 462. (b) Lloyd-Jones, G. C.; Pfaltz, A. *Z. Naturforsch*. **1995**, *50b*, 361. (c) Lehman, J.; Lloyd-Jones, G. C. *Tetrahedron* **1995**, *51*, 8863. (d) Frisell, H.; Akermark, B. *Organometallics* **1995**, *14*, 561. (e) Trost, B. M.; Tometzki, G. B.; Hung, M.-H. *J. Am. Chem. Soc*. **1987**, *109*, 2176. (f) Trost, B. M.; Hung, M.-H. *J. Am. Chem. Soc*. **1984**, *106*, 6837. (g) Trost, B. M.; Hung, M.-H. *J. Am. Chem. Soc*. **1983**, *105*, 7757.

(13) (a) Kondo, T.; Ono, H.; Satake, N.; Mitsudo, T.; Watanabe, Y. *Organometallics* **1995**, *14*, 1945. (b) Zhang, S.; Mitsudo, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem*. **1993**, *450*, 197.

(14) For examples of allylic alkylation of a terminaly substituted $\pi$-allyl palladium intermediate, see: (a) Sjogren, M. P. T.; Hansson, S.; Akermark, B.; Vitagliano, A. *Organometallics* **1994**, *13*, 1963. (b) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc*. **1980**, *102*, 4730. (c) Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett*. **1980**, *21*, 4437. (d) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc*. **1978**, *100*, 3416. (e) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc*. **1978**, *100*, 3426.

(15) For a preliminary report of the work described here, see: Takeuchi, R.; Kashio, M. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 263.

**Table 2.** Effect of Catalyst Precursor on Allylic Alkylation of **1a** with **2a**[a]

| entry | Ir complex | conditions | yield/%[b] | ratio **3a**/**4a** (E/Z)[c] |
|---|---|---|---|---|
| 1[d] | $[Ir(COD)Cl]_2$ | room temp 3 h | 89 | 96/4 (81/19) |
| 2 | $[Ir(COD)_2]BF_4$ | THF reflux 9 h | 90 | 95/5 (90/10) |
| 3 | Ir(COD)(acac) | THF reflux 5 h | 84 | 78/22 (82/18) |
| 4 | $IrH(CO)(PPh_3)_3$ | THF reflux 28 h | 64 | 60/40 (99/1) |
| 5[e] | $Ir_4(CO)_{12}$ | THF reflux 9 h | 0 | |

[a] A mixture of **1a** (2 mmol), **2a** (4 mmol), Ir complex (008 mmol), $P(OPh)_3$ (0.16 mmol), and THF (10 mL) was stirred under argon. [b] Isolated yield. [c] Determined by GLC. [d] $[Ir(COD)Cl]_2$ (0.04 mmol). [e] $Ir_4(CO)_{12}$ (0.02 mmol).

**Table 3.** Allylic Alkylation of **1a** with **2**[a]

| entry | nucleophile | conditions | yield/%[b] | ratio **3**/**4** (E/Z)[c] |
|---|---|---|---|---|
| 1 | **2a** | room temp 3 h | 89 | 96/4 (81/19) |
| 2 | **2b** | room temp 3 h | 90 | 97/3 (79/21) |
| 3 | **2c** | reflux 7 h | 85 | 93/7 (80/20) |
| 4 | **2d** | reflux 1 h | 87 | 29/71 (90/10) |

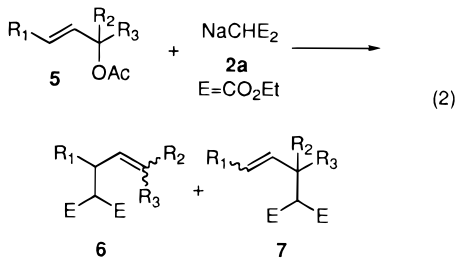
[a] A mixture of **1a** (2 mmol), **2** (4 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$ (0.16 mmol), and THF (10 mL) was stirred under argon. [b] Isolated yield. [c] Determined by GLC.

room temperature (entry 2). The reaction using 3 equiv of $P(OPh)_3$ to each equivalent of Ir did not go to completion (entry 4). The yield of products and the selectivity of **3a** were decreased. The use of $P(O4-MeC_6H_4)_3$, $P(O4-FC_6H_4)_3$, P(O-2-naph)$_3$, and $PPh(OPh)_2$ as ligands gave an excellent selectivity of **3a**, but the reactions required a longer reaction time compared to that needed when using $P(OPh)_3$ (entries 7−10). With $P(OEt)_3$ or P(O*i*-Pr)$_3$, the reaction gave **3a** in a much decreased selectivity (entries 11 and 12). Reactions in which a more electron-donating phosphorus ligand such as $PPh_3$, P(*n*-Bu)$_3$, or dppe was used gave products in poor yields (entries 13−15). Carbonate **1b** and phosphate **1c** could be used as substrates successfully. The reaction of carbonate **1b** gave **3a** in 97% selectivity (entry 5), but the reaction of phosphate **1c** decreased the selectivity of **3a** slightly (entry 6). It is well-known that the palladium complex-catalyzed reaction of allylic carbonates with dialkyl malonate proceeds under neutral conditions.[16] The reaction of **1b** with diethyl malonate under refluxing THF in the presence of $[Ir(COD)Cl]_2/P(OPh)_3$ for 24 h gave no corresponding products. The starting materials were recovered.

The catalytic activity of several iridium complexes combined with $P(OPh)_3$ ($P(OPh)_3$/Ir = 2) was examined in the reaction of **1a** with diethyl sodiomalonate (**2a**) (Table 2). $[Ir(COD)Cl]_2$ gave the best result (entry 1). The reaction using a cationic iridium complex required heating, but the yield of products and the selectivity of **3a** were the same as in the reaction using $[Ir(COD)Cl]_2$ (entry 2). Use of Ir(COD)(acac) decreased the selectivity of **3a** (entry 3). $IrH(CO)(PPh_3)_3$ alone was totally ineffective as a catalyst. $IrH(CO)(PPh_3)_3/P(OPh)_3$ showed some catalytic activity (entry 4). $Ir_4(CO)_{12}/P(OPh)_3$ was totally ineffective as a catalyst (entry 5).

Reaction of **1a** with various stabilized carbon nucleophiles was examined. The results are summarized in Table 3. The reaction of **1a** with **2a**−**c** gave products **3a**−**c**, resulting from alkylation at the substituted allylic terminus, in 93−97% selectivity (entries 1−3). Nucleophiles **2a** and **2b** were more reactive than **2c**. Reaction of **1a** with **2a** and **2b** was completed in 3 h at room temperature, while the reaction with **2c** required heating for 7 h to go to completion. Increasing the steric bulk of carbon nucleophile reversed the regioselectivity.[17] The reaction with diethyl sodiomethylmalonate (**2d**) gave product **4d**, resulting from alkylation at the unsubstituted allylic terminus, in 71% selectivity (entry 4).

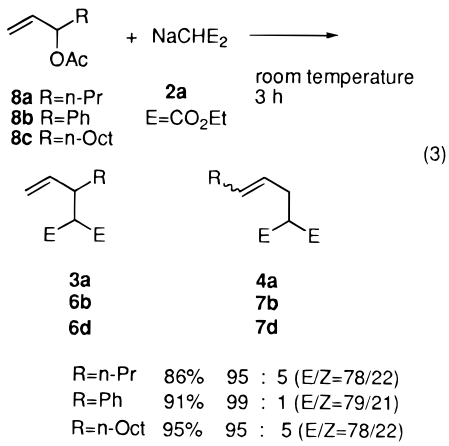
We examined the reaction of a series of acyclic allylic acetates with diethyl sodiomalonate (**2a**) in the presence of a catalytic amount of $[Ir(COD)_2Cl]_2/P(OPh)_3$ (P/Ir = 2) (eq 2). The results



(2)

are summarized in Table 4. As shown in Table 4, highly regioselective alkylation at the substituted allylic terminus was achieved. All reactions proceeded at room temperature to give products in an excellent yield. The reaction of cinnamyl acetate (**5b**) gave **6b**, resulting from alkylation at the substituted allylic terminus, in 99% selectivity (entry 2). The regioselectivity of **5b** was the same as that of **1a**. The phenyl substituent on the allylic terminus did not alter the regioselectivity as the alkyl substituent did. With (*E*)-crotyl acetate (**5a**), (*E*)-2-nonenyl acetate (**5c**), and (*E*)-2-undecenyl acetate (**5d**), the product from the alkylation at the substituted allylic terminus was obtained in 95−97% selectivity (entries 1, 3, and 4). The most unique feature of iridium complex catalysis was demonstrated for the reactions of **5e**−**g**. The reactions were regiospecific at the tertiary allylic terminus to give a product bearing a quaternary carbon center exclusively (entries 5−9). Iridium complex-catalyzed allylic alkylation provides an efficient method for the construction of a quaternary carbon center,[18] which is a feature of a broad range of natural products. Several transition metal complex-catalyzed reactions of **5g** with **2a** or **2b** have been reported. The iridium complex only led to exclusive formation of a product bearing a quaternary carbon center. A $Pd(PPh_3)_4$-catalyzed reaction[19] and a $NiCl_2$(dppe)-catalyzed reaction[9j] gave **7g** in 38% and 10% selectivity, respectively. A $Mo(CO)_6$-catalyzed reaction[10f] gave **7gb** in 85% selectivity.

Regioisomeric acetates of **1a**, **5b**, and **5d** were used as substrates (eq 3). Reactions with **2a** gave the same product



(3)

distributions as those given by **1a**, **5b**, and **5d**. The selectivity

(16) (a) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140. (b) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (c) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523. (d) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* **1982**, *23*, 4809.

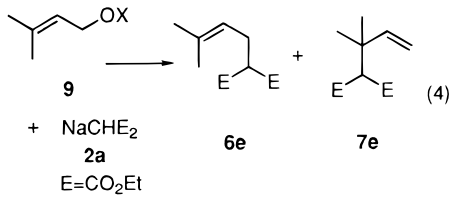
**Table 4.** Allylic Alkylation of **5**[a]

| entry | substrate | nucleophile | product | conditions | yield/%[b] | ratio **6**/**7**[c] |
|---|---|---|---|---|---|---|
| 1 | **5a** $R_1 = Me$, $R_2 = R_3 = H$ | **2a** | **6a**, **7a** | room temp 2 h | 77 | 97/3[d] |
| 2 | **5b** $R_1 = Ph$, $R_2 = R_3 = H$ | **2a** | **6b**, **7b** | room temp 3 h | 98 | 99/1[e] |
| 3 | **5c** $R_1 = n$-Hex, $R_2 = R_3 = H$ | **2a** | **6c**, **7c** | room temp 5 h | 99 | 95/5[f] |
| 4 | **5d** $R_1 = n$-Oct, $R_2 = R_3 = H$ | **2a** | **6d**, **7d** | room temp 5 h | 95 | 95/5[g] |
| 5[h] | **5e** $R_1 = H$, $R_2 = R_3 = Me$ | **2a** | **6e**, **7e** | room temp 2 h | 80 | 0/100 |
| 6[h] | **5f** $R_1 = H$, $R_2 = Me$, $R_3 = n$-Bu | **2a** | **6f**, **7f** | room temp 16 h | 80 | 0/100 |
| 7[h] | **5g** $R_1 = H$, $R_2 = Me$, $R_3 = CH_2CH_2C = CMe_2$ | **2a** | **6g**, **7g** | room temp 16 h | 85 | 0/100 |
| 8 | **5e** $R_1 = H$, $R_2 = R_3 = Me$ | **2b** | **6eb**, **7eb** | room temp 2 h | 70 | 0/100 |
| 9[h,i] | **5g** $R_1 = H$, $R_2 = Me$, $R_3 = CH_2CH_2C = CMe_2$ | **2b** | **6gb**, **7gb** | room temp 16 h | 80 | 0/100 |

[a] A mixture of **5** (2 mmol), **2** (4 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$ (0.16 mmol), and THF (10 mL) was stirred under argon. [b] Isolated yield. [c] Determined by GLC. [d] Ratio fo E/Z was not determined. [e] E/Z = 100/0. [f] E/Z = 66/34. [g] E/Z = 69/31. [h] **2** (6 mmol). [i] $[Ir(COD)Cl]_2$ (0.08 mmol), $P(OPh)_3$ (0.32 mmol).

of the alkylation at the substituted allylic terminus was 95−99%. The result strongly suggests the intermediacy of a $\pi$-allyl iridium complex.

3-Methyl-2-butenyl acetate (**9a**) failed to react with **2a** under refluxing dioxane for 24 h. The corresponding product was not obtained at all. 3-Substituted 2-alkenyl acetate was much less reactive than 2-alkenyl acetate. Changing the leaving group enhanced the reactivity of the substrate (eq 4). The reactions




**9a** X=Ac dioxane reflux 24 h
no reaction

**9b** X=$CO_2Me$ THF reflux 8 h
no reaction

**9c** X=$COCF_3$ room temperature 3 h
70% 5 : 95

**9d** X=$PO(OEt)_2$ room temperature 4 h
81% 4 : 96

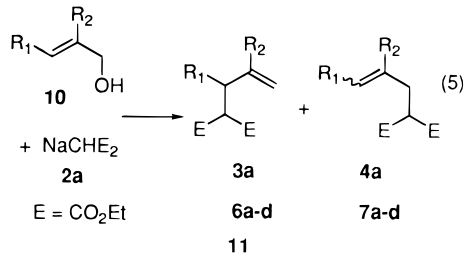
of diethyl 3-methyl-2-butenyl phosphate (**9d**) and 3-methyl-2-butenyl trifluoroacetate (**9c**) with **2a** proceeded at room temperature. Product **7e** from the alkylation at the disubstituted allylic terminus was obtained in 96% and 95% selectivity, respectively. The reactivity of leaving groups was in the order of $(EtO)_2PO_2 \sim CF_3CO_2 > MeO_2CO > AcO$. The low reactivity of 3-methyl-2-butenyl acetate compared to that of 2-alkenyl acetate is attributed to the difficulty in the coordination of the carbon−carbon double bond to an iridium complex prior to the oxidative addition. It is well-known that the coordination of an alkene to the transition metal complexes is quite sensitive to steric effects.[20]

**Allylic Alkylation of Allylic Alcohols.** Allylic esters were successfully used as substrates. If allylic alcohols can be used as substrates, the reaction might be far more beneficial. Bergbreiter reported that $Pd(PPh_3)_4$ catalyzed the reaction of allylic alcohols with α-ketoesters.[21] The reaction was nonregioselective and required extreme reaction conditions. Several allylic alcohols were smoothly alkylated at the substituted allylic terminus in high selectivities under mild conditions (eq 5).

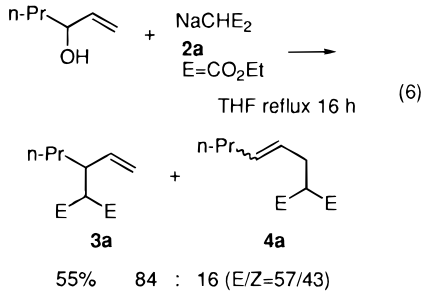
**Table 5.** Allylic Alkylation of Allylic Alcohol **10** with **2a**[a]

| entry | substrate | yield/%[b] | product | ratio[c] |
|---|---|---|---|---|
| 1 | **10a** $R_1 = n$-Pr, $R_2 = H$ | 100 | **3a**/**4a** | 96/4[d] |
| 2 | **10b** $R_1 = Me$, $R_2 = H$ | 74 | **6a**/**7a** | 96/4[e] |
| 3 | **10c** $R_1 = Ph$, $R_2 = H$ | 98 | **6b**/**7b** | 99/1[f] |
| 4 | **10d** $R_1 = n$-Hex, $R_2 = H$ | 84 | **6c**/**7c** | 95/5[g] |
| 5 | **10e** $R_1 = n$-Oct, $R_2 = H$ | 80 | **6d**/**7d** | 93/7[n] |
| 6 | **10f** $R_1 = H$, $R_2 = Me$ | 71 | **11** | |

[a] A mixture of **10** (2 mmol), **2a** (6 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$ (0.16 mmol), and THF (10 mL) was stirred under reflux for 1 h. [b] Isolated yield. [c] Determined by GLC. [d] E/Z = 68/32. [e] Ratio of E/Z was not determined. [f] E/Z = 100/0. [g] E/Z = 63/37. [h] E/Z = 71/29.




Results are summarized in Table 5. The reaction (*E*)-2-hexen-1-ol (**10a**) with **2a** under refluxing THF for 1 h gave products in a quantitative yield (entry 1). The selectivity of **3a** was 96%. (*E*)-Crotyl alcohol (**10b**), (*E*)-cinnamyl alcohol (**10c**), (*E*)-2-nonen-1-ol (**10d**), and (*E*)-2-undecen-1-ol (**10e**) reacted with **2a** similarly to give products from alkylation at the substituted allylic terminus in high selectivities (entries 2−5). 1-Alken-3-ol was less reactive than 2-alken-1-ol. The reaction of 1-hexen-3-ol with **2a** was sluggish (eq 6). The yield of products




55% 84 : 16 (E/Z=57/43)

and the selectivity of **3a** were decreased. The reaction of

(17) Use of a steric demanding nucleophile increased the selectivity of alkylation at the unsubstituted allylic terminus; see ref 14e.

(18) Martine, S. F. *Tetrahedron* **1980**, *36*, 419.

(19) Cuvigny, T.; Julia, M.; Roland, C. *J. Organomet. Chem.* **1985**, *285*, 395.

(20) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780. (b) Cramer, R. *J. Am. Chem. Soc.* **1967**, *89*, 4621.

(21) Bergbreiter, D. E.; Weatherford, D. A. *J. Chem. Soc., Chem. Commun.* **1989**, 883.

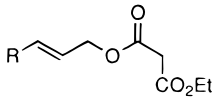
**Table 6.** Allylic Alkylation of (*Z*)-Allylic Esters (**13**) with **2a**[a]

| entry | substrate | ligand | conditions | yield/%[b] | product | ratio[c] |
|---|---|---|---|---|---|---|
| 1[d] | **13a** $R_1$ = *n*-Pr, X = Ac | $P(OPh)_3$ | room temp 2 h | 81 | **3a**/(*E*)-**4a**/(*Z*)-**4a** | 25/5/70 |
| 2 | **13a** $R_1$ = *n*-Pr, X = Ac | $P(O2-t\text{-}Bu4-MeC_6H_3)_3$ | reflux 5 h | 85 | **3a**/(*E*)-**4a**/(*Z*)-**4a** | 3/7/90 |
| 3 | **13b** $R_1$ = *n*-Pr, X = $PO(OEt)_2$ | $P(O2-t\text{-}Bu4-MeC_6H_3)_3$ | room temp 5 h | 81 | **3a**/(*E*)-**4a**/(*Z*)-**4a** | 8/5/87 |
| 4 | **13c** $R_1$ = Ph, X = Ac | $P(O2-t\text{-}Bu4-MeC_6H_3)_3$ | reflux 22 h | 72 | **6b**/(*E*)-**7b**/(*Z*)-**7b** | 55/5/40 |
| 5 | **13d** $R_1$ = *n*-Hex, X = Ac | $P(O2-t\text{-}Bu4-MeC_6H_3)_3$ | reflux 3 h | 86 | **6c**/(*E*)-**7c**/(*Z*)-**7c** | 2/9/89 |
| 6 | **13e** $R_1$ = *n*-Oct, X = Ac | $P(O2-t\text{-}Bu4-MeC_6H_3)_3$ | reflux 3 h | 84 | **6d**/(*E*)-**7d**/(*Z*)-**7d** | 2/11/87 |
| 7 | **13f** $R_1 = PhCH_2CH_2CH_2$, X = Ac | $P(O2-t\text{-}Bu4-MeC_6H_3)_3$ | reflux 4 h | 85 | **14f**/(*E*)-**15f**/(*Z*)-**15f** | 4/21/75 |

[a] A mixture of **13** (2 mmol), **2a** (4 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(O2-t\text{-}Bu4-MeC_6H_3)_3$ (0.08 mmol), and THF (10 mL) was stirred under argon. [b] Isolated yield. [c] Determined by GLC. [d] $P(OPh)_3$ (0.16 mmol).

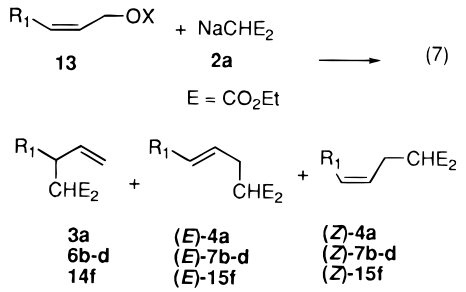
3-methyl-2-buten-1-ol and linalol with **2a** did not give the corresponding products.

Allylic alcohols were found to be good substrates for our allylic alkylation. The low reactivity of allylic alcohol toward oxidative addition is well known. Transesterification of allylic alcohol to the more reactive ester **12** prior to oxidative addition might be possible. The resulting ester **12** would oxidatively add to an iridium center to give a $\pi$-allyl iridium intermediate. We examined the possibility of formation of ester **12** during the reaction. The reaction of **12a** (R = *n*-Pr) with **2a** under refluxing THF for 1 h gave products in 99% yield. The selectivity of **3a** was 95%. Ester **12a** (R = *n*-Pr) gave the same results as alcohol **10a**. We carried out the reaction of **10a** with 1 equiv of **2a**. If transesterification occured, the yields of **3a** and **4a** should have decreased below 50%. The reaction gave products in 40% yield. Furthermore, a considerable formation of ester **12a** (R = *n*-Pr) was observed in the reaction of **10a** with **2a** under refluxing THF in the absence of catalyst. According to these results, we concluded that an initial intermediate was ester **12** formed by the transesterification. However, allylic alcohols could be practically used as a substrate for the reaction.




**12**

**Allylic Alkylation of (*Z*)-Allylic Esters.** The stereochemistry of the carbon−carbon double bond in the allyl system affected the regiochemistry of the allylic alkylation. The reaction of (*Z*)-2-hexenyl acetate (**13a**) with **2a** at room temperature gave products in 81% yield (eq 7). The major product was (*Z*)-**4a**




resulting from alkylation at the unsubstituted allylic terminus. The selectivity of **4a** was 75% (E/Z = 7/93) (Table 6 entry 1). The regioselectivity was opposite that for the reaction of (*E*)-2-hexenyl acetate (**1a**) with **2a**.

Oxidative addition of (*E*)-2-alkenyl acetate gives a syn $\pi$-allyl iridium complex as an intermediate, while oxidative addition of (*Z*)-2-alkenyl acetate gives an anti $\pi$-allyl iridium complex as an intermediate. It is well-known that $\pi$-allyl metal complexes undergo syn−anti isomerization.[22] If such isomerization occurs prior to the alkylation, the reactions of (*E*)-2-alkenyl ester and (*Z*)-2-alkenyl ester should give the same product distribution. This result showed that the alkylation occurred prior to syn−anti isomerization and the regioselectivity of the alkylation to syn $\pi$-allyl iridium complex was different from that of alkylation to the anti $\pi$-allyl iridium complex.

Palladium complex-catalyzed allylic alkylation of (*Z*)-2-alkenyl acetate resulted in a loss of the geometry of the starting material[14a,b] because the anti $\pi$-allyl palladium complex easily isomerized to the thermodynamically more stable syn $\pi$-allyl palladium complex.[23] As mentioned above, the ratio of (*Z*)-**4a**/(*E*)-**4a** was 93/7. Syn−anti isomerization of a terminally monosubstituted $\pi$-allyl iridium complex is quite slow compared to that of a terminally monosubstituted $\pi$-allyl palladium complex. Iridium catalysis provides a possibility of (*Z*)-selective allylic alkylation.[10b,12d,24] However, in the reaction of (*Z*)-2-alkenyl acetate, the regioselectivity of alkylation leading to (*Z*)-alkene is not satisfactory. To improve the selectivity of (*E*)- and (*Z*)-alkene, alkylation must be directed to the unsubstituted allylic terminus. A bulky phosphite ligand is expected to increase such selectivity. We examined the reaction of (*Z*)-2-alkenyl ester with **2a** using a bulky phosphite ligand. The results are summarized in Table 6. The reaction using 1 equiv of tris-(2-*tert*-butyl-4-methylphenyl)phosphite to each equivalent of iridium under refluxing THF for 3 h gave the product in 85% yield (entry 2). The selectivity of (*Z*)-**4a** was increased to 90%. The ratio of phosphite to iridium was critical. The same reaction using 2 equiv of tris(2-*tert*-butyl-4-methylphenyl)phosphite to each equivalent of iridium under refluxing THF for 24 h gave no product. The starting material was recovered. Phosphate was more reactive than acetate. The reaction of diethyl (*Z*)-2-hexenyl phosphate (**13b**) was completed in 3 h at room temperature, but the selectivity of (*Z*)-**4a** was not improved (entry 3). The phenyl substituent showed a preference for alkylation at the substituted allylic terminus to decrease (*Z*)-selectivity. The reaction of (*Z*)-cinnamyl acetate (**13c**) using tris(2-*tert*-butyl-4-methylphenyl)phosphite gave (*Z*)-**7b** in 40% selectivity (entry 4). Compound **6b** resulting from the alkylation at the substituted allylic terminus was obtained in 55% selectivity. The reactions of (Z)-2-nonenyl acetate (**13d**) and (Z)-2-undecenyl acetate (**13e**) with **2a** gave (*Z*)-**7c** and (*Z*)-**7d** in 89% and 87% selectivity, respectively (entries 5 and 6). The reaction

(22) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: New York, 1994; p 112. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Book: Mill Valley, 1987; p 175.

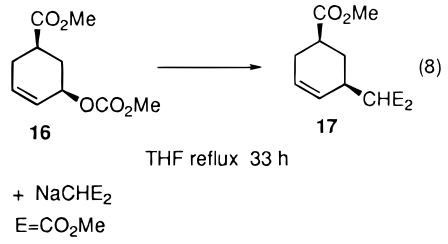
(23) (a) Sjogren, M.; Hansson, S.; Norrby, P.; Akermark, B.; Cucciolito, M. E.; Vitagliano, A. *Organometallics* **1992**, *11*, 3954. (b) Akermark, B.; Hansson, S.; Vitagliano, A. *J. Am. Chem. Soc.* **1990**, *112*, 4587.

(24) Akermark reported that 2,9-disubstituted-1,10-phenanthroline could stabilize anti $\pi$-allyl palladium complex and its use for Pd-catalyzed allylic alkylation. The reaction of (*Z*)-2-hexenyl acetate with diethyl sodiomethylmalonate gave (*Z*)-product in 72% selectivity; see ref 14a.

of **13f**, where a phenyl group is substituted away from the allylic terminus, gave (*Z*)-**15f** in 75% selectivity (entry 7).

The reaction of (*Z*)-2-alkenyl esters gave a small amount of (*E*)-product. We examined the formation of the (*E*)-product under the reaction conditions. Treatment of a 23:4:73 mixture of **3a**, (*E*)-**4a**, and (*Z*)-**4a** with 2 equiv of **2a** in the presence of a catalytic amount of $[Ir(COD)Cl]_2$ and $P(OPh)_3$ (P/Ir = 2) for 4 h at room temperature gave a 23:17:60 mixture of **3a**, (*Z*)-**4a**, and (*Z*)-**4a**. The ratio of (*Z*)-**4a** decreased, while the ratio of (*E*)-**4a** increased. Isomerization of (*Z*)-**4a** to (*E*)-**4a** occurred. According to the result, we concluded that a small amount of (*E*)-product was formed by the isomerization of an initially formed (*Z*)-product during the alkylation.

**Stereochemical Course of Allylic Alkylation.** The stereochemical course of the reaction was examined. We chose (*Z*)-5-(methoxycarbonyl)-2-cyclohexen-1-yl methyl carbonate (**16**) as a substrate because it was extensively used to examine the stereochemical course of palladium[14b] and molybdenum complex-catalyzed[10f,j] allylic alkylation. Unlike the reactions with the acyclic systems mentioned above, this reaction was quite sluggish and did not go to completion (eq 8). Product **17** was

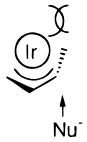



obtained in 37% yield. The starting material was recovered in 40% yield. The product of net retention of configuration was obtained exclusively. This suggests the reaction proceeds with a double inversion mechanism.[25]

## Discussion

Regioselectivity of allylic alkylation is controlled by three factors: (1) the steric interaction between the incoming nucleophile and the allylic terminus, (2) the charge distribution of the $\pi$-allyl ligand on the metal, and (3) the stability of the resulting alkene−metal complexes as an initial product. When the nucleophile is **2a**, results described here indicate factor 1 is not important. With regard to factor 3, it is clear that alkylation at the substituted allylic terminus results in the formation of the more stable terminal alkene complex as an initial product.[26] $P(OPh)_3$ plays a crucial role with regard to factor 2. We examined the reaction of $[Ir(COD)Cl]_2$ with $P(OPh)_3$ in $d_8$-THF by $^{31}P$ NMR. The $^{31}P$ NMR spectra of a mixture of $[Ir(COD)Cl]_2$ and $P(OPh)_3$ (P/Ir = 1) showed a singlet ($\delta$ 86.9). No free $P(OPh)_3$ was detected. This indicated the formation of a monophosphite species. Increasing the amount of $P(OPh)_3$ led to the appearance of a new set of signals. The $^{31}P$ NMR spectra of a mixture of $[Ir(COD)Cl]_2$ and $P(OPh)_3$ (P/Ir = 2) showed a singlet ($\delta$ 86.9), three sets of doublets of doublets ($\delta$ 71.7, 86.1, and 95.9, $J$ = 30, 24 Hz), and two sets of doublets ($\delta$ 96.3 and 101.8, $J$ = 24 Hz) in a ratio of 42:42:16. The reaction of $[Ir(COD)Cl]_2$ with 2 equiv of $P(OPh)_3$ formed three species. The $^{31}P$ NMR spectra of a mixture of $[Ir(COD)Cl]_2$ and $P(OPh)_3$ (P/Ir = 3) showed three doublets of doublets ($\delta$ 71.7, 86.1, and 95.9 $J$ = 30, 24 Hz). The singlet and two sets of doublets shown in the reaction at P/Ir = 2 disappeared. As mentioned above, the allylic alkylation was highly regioselective at the ratios of P/Ir = 1 and 2 (Table 1 entries 2−4). It is clear that the monophosphite species is catalytically active. The presence of one molecule of $P(OPh)_3$ on the $\pi$-allyl iridium intermediate is necessary for the high regioselectivity. Since $P(OPh)_3$ is a better $\pi$-acceptor,[27] it promotes a carbonium ion character at the substituted allylic terminus and directs the nucleophilic attack to this position.[28,29] In agreement with this, when a ligand with weaker acceptor properties was used such as $P(OEt)_3$ or $P(Oi\text{-}Pr)_3$, the reaction was much less selective (Table 1 entries 11 and 12).

The regioselectivity of the reaction of (*Z*)-2-alkenyl acetate is different from that of (*E*)-2-alkenyl acetate. The difference is explained as follows. Nucleophilic attack at the substituted allylic terminus in the anti $\pi$-allyl iridium intermediate would bring the anti substituent close to the iridium moiety. The steric interaction gives an unfavorable transition state.[30] On the other hand, such steric interaction does not occur in the alkylation at the substituted allylic terminus of the syn $\pi$-allyl iridium intermediate. Thus, alkylation at the unsubstituted allylic terminus is favored in the case of (*Z*)-2-alkenyl acetate.




## Conclusion

An iridium complex was found to be a new and efficient catalyst for allylic alkylation. The structure of the allyl system greatly affected the reaction. With (*E*)-2-alkenyl esters and 1-substituted-2-propenyl esters, highly regioselective alkylation at the substituted allylic terminus was achieved. With (*Z*)-2-alkenyl esters, the regioselectivity was opposite that of the (*E*)-2-alkenyl esters. (Z)-Selective allylic alkylation at the unsubstituted allylic terminus could be achieved. The selectivity described here complements palladium catalysis. These unique features will make iridium complexes a useful tool for the carbon−carbon bond forming reaction.

## Experimental Section

**Materials.** All reagents and solvents were dried and purified before use by the usual procedures. Allylic esters were prepared by the

(25) For a mechanism with double inversion of configuration, see: (a) Hayashi, T.; Yamamoto, A.; Hagihara, T. *J. Org. Chem.* **1986**, *51*, 723. (b) Fiaud, J. C.; Legros, J. Y. *J. Org. Chem.* **1987**, *52*, 1907. A mechanism with double retention of configuration cannot be ruled out; see ref 10h.

(26) A complex of terminal alkenes is more stable than that of internal alkenes: see ref 20b.

(27) $P(OPh)_3$ is more electron withdrawing than $PPh_3$; see Tolman, C. A. *Chem. Rev.* **1997**, *77*, 313.

(28) (a) Akermark, B.; Hansson, S.; Krankenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679. (b) Akermark, B.; Zetterberg, K.; Hansson, S.; Krankenberger, B.; Vitagliano, A. *J. Organomet. Chem.* **1987**, *335*, 133. (c) Pretot, R.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 323.

(29) The reaction of **1b** with diethyl malonate resulted in the recovery of the starting material, while the reaction of **1b** with diethyl sodiomalonate gave products in 94% yield (Table 1, entry 5). It is well-known that the formation of $MeO^-$ by the dissociation from the metal center is necessary for the reaction of allylic carbonates under neutral conditions.[16] The result indicates that dissociation of $MeO^-$ from the iridium center did not occur. The leaving group from the allylic ester coordinates on iridium. According to the result, an intermediate is presumed to be $[Ir(\pi\text{-allyl})Cl(OAc)(P(OPh)_3)]$. To avoid a steric repulsion of the substituted allylic terminus, triphenyl phosphite coordinates trans to the substituted allylic terminus.

(30) (a) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 954. (b) Similar dependency of the regioselectivity on the stereochemistry of the allyl system was observed. The $Fe_2(CO)_9$-catalyzed reaction of (*E*)-crotyl acetate with dimethyl sodiomalonate gave the product from the alkylation at the substituted allylic terminus as a major product, whereas the same reaction of (*Z*)-crotyl acetate gave the product from the alkylation at the unsubstituted allylic terminus as a major product; see ref 11d.

reaction of the corresponding alcohols with acetyl chloride, methyl chloroformate, diethyl chlorophosphate, or trifluoroacetic anhydride. Acetates **1a**, **5b**, and **5g** were purchased. Alcohols **10a**−**f**, 2-methyl-3-buten-2-ol, 1-hexen-3-ol, and (*Z*)-2-hexen-1-ol were purchased. 1-Phenyl-2-propen-1-ol was prepared by the reaction of benzaldehyde with vinylmagnesium bromide. 2-Alkyn-1-ols were prepared by the reaction of 1-alkynyllithium with paraformaldehyde.[31] (*Z*)-3-Phenyl-2-propen-1-ol, (*Z*)-2-nonen-1-ol, (*Z*)-2-undecen-1-ol, and (*Z*)-6-phenyl-2-hexen-1-ol were prepared by the hydrogenation of the corresponding 2-alkyn-1-ols. Ester **12a** was prepared by the transesterification of diethyl malonate with sodium (*E*)-2-hexenyloxide. Methyl (*Z*)-5-hydroxy-3-cyclohexenecarboxylate was prepared according to the published method.[14b] $[Ir(COD)Cl]_2$,[32] $[Ir(COD)_2]BF_4$,[33] and $IrH(CO)(PPh_3)_3$[34] were prepared according to the published methods. Ir(COD)(acac) and $Ir_4(CO)_{14}$ were purchased. $P(O\text{-}4\text{-}MeC_6H_4)_3$,[35] $P(O\text{-}4\text{-}FC_6H_4)_3$,[35] $P(O\text{-}2\text{-}Naph)_3$,[35] $P(O\text{-}2\text{-}tert\text{-}Bu\text{-}4\text{-}MeC_6H_4)_3$,[35] and $PPh(OPh)_2$[36] were prepared according to the published methods. Lindlar catalyst was purchased from Wako.

**General Methods.** $^1H$ NMR and $^{13}C$ NMR spectra were measured on a JEOL-EX-270 spectrometer using $Me_4Si$ as an internal standard. Samples were dissolved in $CDCl_3$ solutions. $^{31}P$ NMR spectra were measured on a JEOL JNM GX-400 spectrometer using $H_3PO_4$ as an external standard. GC analyses were performed on a Shimadzu GC-14A using 3 mm × 2 m glass columns packed with either 5% PEG-HT on 60/80 mesh Chromosorb w, AW-DMCS or 5% OV-17 on 60/80 mesh chromosorb w, AW-DMCS, and a Shimadzu GC-17A using 60 m × 0.25 mm SP-2331 and 30 m × 0.25 mm DB-17 columns. Column chromatography was carried out on 70/230 mesh silica gel (Merk; Silica Gel 60). Elemental analyses were performed at the Microanalytical Center of Kyoto University. Samples for elemental analysis were purified by preparative gas chromatography.

**Preparation of (*Z*)-2-Alken-1-ol.** A typical procedure is described for preparation of (*Z*)-3-phenyl-2-propen-1-ol. A mixture of 3-phenyl-2-propyn-1-ol (3.272 g, 24.4 mmol), Lindlar catalyst (1.316 g), and 3,6-dithia-1,8-octanediol (4.1 mg) was vigorously stirred in toluene (20 mL) at room temperature under a hydrogen atmosphere for 24 h. The progress of the reaction was monitored by GLC. After the 3-phenyl-2-propyn-1-ol was consumed, the reaction mixture was filtered. After toluene was removed in vacuo, distillation of the residue gave (*Z*)-3-phenyl-2-propen-1-ol (3.274 g, yield 95%).

**(*Z*)-3-Phenyl-2-propen-1-ol:** $^1H$ NMR $\delta$ 2.82 (br, 1H), 4.37 (dd, $J$ = 6.6, 2.0 Hz, 2H), 5.81 (dt, $J$ = 11.9, 6.3 Hz, 1H), 6.49 (d, $J$ = 11.9 Hz, 1H), 7.14−7.33 (m, 5H); $^{13}C$ NMR $\delta$ 59.3, 127.0, 128.1 (2C), 128.6 (2C), 130.5, 131.2, 136.4.

**(Z)-2-Nonen-1-ol:** $^1H$ NMR $\delta$ 0.88 (t, $J$ = 6.6 Hz, 3H), 1.22−1.40 (m, 8H), 2.06 (q, $J$ = 6.6 Hz, 2H), 2.32 (br, 1H), 4.17 (d, $J$ = 5.6 Hz, 2H), 5.51 (dt, $J$ = 11.2, 6.9 Hz, 1H), 5.58 (dt, $J$ = 11.2, 6.3 Hz, 1H); $^{13}C$ NMR $\delta$ 14.0, 22.5, 27.3, 28.8, 29.5, 31.6, 58.3, 128.4, 132.8.

**(*Z*)-2-Undecen-1-ol:** $^1H$ NMR $\delta$ 0.88 (t, $J$ = 6.6 Hz, 3H), 1.20−1.35 (m, 12H), 1.82 (br, 1H), 2.06 (q, $J$ = 6.3 Hz, 2H), 4.18 (d, $J$ = 5.9 Hz, 2H), 5.52 (dt, $J$ = 11.2, 6.9 Hz, 1H), 5.59 (dt, $J$ = 11.2, 5.9 Hz, 1H); $^{13}C$ NMR $\delta$ 14.0, 22.6, 27.4, 29.18, 29.22, 29.4, 29.6, 31.8, 58.4, 128.3, 133.0.

**(*Z*)-6-Phenyl-2-hexen-1-ol:** $^1H$ NMR $\delta$ 1.69 (quintet, $J$ = 7.3 Hz, 2H), 1.94 (br, 1H), 2.09 (q, $J$ = 7.3 Hz, 2H), 2.60 (t, $J$ = 7.3 Hz, 2H), 4.12 (d, $J$ = 5.9 Hz, 2H), 5.52 (dt, $J$ = 11.2, 6.9 Hz, 1H), 5.60 (dt, $J$ = 11.2, 6.3 Hz, 1H), 7.14−7.33 (m, 5H); $^{13}C$ NMR $\delta$ 26.8, 31.1, 35.2, 58.3, 125.7, 128.2 (2C), 128.3 (2C), 128.9, 132.2, 142.0.

**Allylic Alkylation of Allylic Esters.** A typical procedure is described for the reaction of **1a** with **2a**. (*E*)-2-Hexenyl acetate **1a** (284 mg, 2.0 mmol), triphenyl phosphite (49.6 mg, 0.16 mmol), and $[Ir(COD)Cl]_2$ (26.9 mg, 0.04 mmol) were stirred in 5.0 mL of THF under Ar atmosphere. In a separate flask, diethyl malonate (640 mg, 4.0 mmol) was added to a slurry of hexane-washed sodium hydride (96 mg, 4.0 mmol) in 5.0 mL of THF. The resulting clear solution was added to the former by a syringe, and the combined mixture was stirred at room temperature for 3 h. The progress of the reaction was monitored by GLC. After **1a** was consumed, the reaction mixture was partitioned between ether and water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane/ethyl acetate (98/2)) to give **3a** and **4a** as a mixture (431 mg, yield 89%).

**Allylic Alkylation of Allylic Alcohols.** A typical procedure is described for the reaction of **10a** with **2a**. (*E*)-2-Hexen-1-ol **10a** (200 mg, 2.0 mmol), triphenyl phosphite (49.6 mg, 0.16 mmol), and $[Ir(COD)Cl]_2$ (26.9 mg, 0.04 mmol) were stirred in 5.0 mL of THF under Ar atmosphere. In a separate flask, diethyl malonate (640 mg, 4.0 mmol) was added to a slurry of hexane-washed sodium hydride (96 mg, 4.0 mmol) in 5.0 mL of THF. The resulting clear solution was added to the former by a syringe, and the combined mixture was stirred under refluxing THF for 1 h. The progress of the reaction was monitored by GLC. After **10a** was consumed, the reaction mixture was partitioned between ether and water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane/ethyl acetate (98/2)) to give **3a** and **4a** as a mixture (480 mg, yield 99%).

**Ethyl 3-Ethenyl-2-ethoxycarbonylhexanoate (3a):** $^1H$ NMR $\delta$ 0.88 (t, $J$ = 6.9 Hz, 3H), 1.25 (t, $J$ = 7.3 Hz, 3H), 1.27 (t, $J$ = 7.3 Hz, 3H), 1.33−1.45 (m, 4H), 2.78 (qd, $J$ = 8.9, 3.3 Hz, 1H), 3.33 (d, $J$ = 8.9 Hz, 1H), 4.15 (q, $J$ = 7.3 Hz, 2H), 4.20 (q, $J$ = 7.3 Hz, 2H), 5.06 (dd, $J$ = 10.2, 2.0 Hz, 1H), 5.07 (dd, $J$ = 17.5, 2.0 Hz, 1H), 5.65 (dt, $J$ = 17.5, 9.9 Hz, 1H); $^{13}C$ NMR $\delta$ 13.7, 14.0 (2C), 20.0, 34.3, 43.8, 56.9, 61.0, 61.1, 117.1, 138.1, 168,1, 168.3. Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15; O, 26.41. Found: C, 64.37; H, 9.16.

**Ethyl (*E*)-2-Ethoxycarbonyl-4-octenoate ((*E*)-4a):**[37] $^1H$ NMR $\delta$ 0.86 (t, $J$ = 7.3 Hz, 3H), 1.26 (t, $J$ = 7.3 Hz, 6H), 1.35 (sextet, $J$ = 7.6 Hz, 2H), 1.95 (q, $J$ = 6.9 Hz, 2H), 2.58 (t, $J$ = 6.9 Hz, 2H), 3.37 (t, $J$ = 6.9 Hz, 1H), 4.19 (q, $J$ = 7.3 Hz, 4H), 5.36 (dt, $J$ = 15.5, 6.9 Hz, 1H), 5.52 (dt, $J$ = 15.5, 6.9 Hz, 1H); $^{13}C$ NMR $\delta$ 13.4, 14.0 (2C), 22.3, 31.8, 34.4, 52.3, 61.2 (2C), 125.4, 133.6, 169.0 (2C).

**Ethyl (*Z*)-2-Ethoxycarbonyl-4-octenoate ((*Z*)-4a):** $^1H$ NMR $\delta$ 0.90 (t, $J$ = 7.3 Hz, 3H), 1.27 (t, $J$ = 7.3 Hz, 6H), 1.37 (sextet, $J$ = 7.3 Hz, 2H), 2.04 (q, $J$ = 7.3 Hz, 2H), 2.64 (t, $J$ = 7.3 Hz, 2H), 3.35 (t, $J$ = 7.3 Hz, 1H), 4.19 (q, $J$ = 7.3 Hz, 4H), 5.32 (dt, $J$ = 10.9, 7.3 Hz, 1H), 5.48 (dt, $J$ = 10.9, 7.3 Hz, 1H); $^{13}C$ NMR $\delta$ 13.6, 14.0 (2C), 22.5, 26.6, 29.1, 52.0, 61.2 (2C), 124.7, 132.8, 169.0 (2C). Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15; O, 26.41. Found: C, 64.64; H, 9.34.

**Methyl 3-Ethenyl-2-methoxycarbonylhexanoate (3b):**[14c] $^1H$ NMR $\delta$ 0.89 (t, 3H, $J$ = 7.3 Hz), 1.19−1.45 (m, 4H), 2.78 (qd, $J$ = 8.9, 3.3 Hz, 1H), 3.39 (d, $J$ = 8.9 Hz, 1H), 3.69 (s, 3H), 3.73 (s, 3H), 5.07 (dd, $J$ = 9.4, 1.7 Hz, 1H), 5.08 (ddd, $J$ = 17.8, 2.0, 0.7 Hz, 1H), 5.63 (dt, $J$ = 17.8, 9.7 Hz, 1H); $^{13}C$ NMR $\delta$ 13.6, 20.0, 34.3, 43.9, 52.0, 56.8 (2C), 117.2, 138.0, 168.4, 168.6.

**Methyl (*E*)-2-Methoxycarbonyl-4-octenoate ((*E*)-4b):**[38] $^1H$ NMR $\delta$ 0.86 (t, $J$ = 7.3 Hz, 3H), 1.35 (sextet, $J$ = 7.3 Hz, 2H), 1.95 (q, $J$ = 6.9 Hz, 2H), 2.58 (td, $J$ = 6.9, 1.0 Hz, 2H), 3.42 (t, $J$ = 7.6 Hz, 1H), 3.72 (s, 6H), 5.35 (dt, $J$ = 15.2, 6.6 Hz, 1H), 5.52 (dt, $J$ = 15.2, 6.6 Hz, 1H); $^{13}C$ NMR $\delta$ 13.3, 22.3, 31.8, 34.4, 51.9, 52.2 (2C), 125.2, 133.8, 169.3 (2C).

**Methyl (*Z*)-2-Methoxycarbonyl-4-octenoate ((*Z*)-4b):** $^1H$ NMR $\delta$ 0.90 (t, $J$ = 7.3 Hz, 3H), 1.37 (sextet, $J$ = 7.3 Hz, 2H), 2.04 (q, $J$ = 7.3 Hz, 2H), 2.65 (t, $J$ = 7.6 Hz, 2H), 3.40 (t, $J$ = 7.6 Hz, 1H), 3.73 (s, 6H), 5.30 (dt, $J$ = 10.9, 7.3 Hz, 1H), 5.49 (dt, $J$ = 10.9, 7.3 Hz, 1H); $^{13}C$ NMR $\delta$ 13.6, 22.5, 26.7, 29.1, 51.7, 52.3 (2C), 124.4, 133.0, 169.3 (2C). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47; O, 29.87. Found: C, 61.77; H, 8.68.

**Ethyl 3-Ethenyl-2-(1-oxoethyl)hexanoate (3c):**[13b] A mixture of 1:1 diastereomer $^1H$ NMR $\delta$ 0.86−0.90 (m, 3H × 2), 1.25 (t, $J$ = 7.3 Hz,

(31) Denis, J.-N.; Greene, A. E.; Serra, A. A.; Luche, M.-J. *J. Org. Chem.* **1986**, *51*, 46.
(32) Crabtree, R. H.; Quirk, J. M.; Felkin, H.; Fillebeen-Khan, T. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 407.
(33) Schenck, T. G.; Downs, J. M.; Milne, C. R. C.; Mackenzie, P.; Boucher, H.; Whealan, J.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2334.
(34) Wilkinson, G. *Inorg. Synth.* **1972**, *13*, 126.
(35) Van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; Van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 34.
(36) Hoffmann, F. W.; Moore, T. R. *J. Am. Chem. Soc*. **1958**, *80*, 1150.
(37) Hiyama, T.; Morizawa, Y.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn*. **1981**, *54*, 2151.
(38) Shaw, G. J. *J. Labelled Compd. Radiopharm*. **1981**, *18*, 1641.

3H), 1.27 (t, $J$ = 7.3 Hz, 3H), 1.30−1.41 (m, 4H × 2), 2.17 (s, 3H), 2.23 (s, 3H), 2.81 (q, $J$ = 9.2 Hz, 1H × 2), 3.42 (d, $J$ = 9.9 Hz, 1H), 3.43 (d, $J$ = 9.2 Hz, 1H), 4.14 (q, $J$ = 6.9 Hz, 2H), 4.20 (q, $J$ = 6.9 Hz, 2H), 5.06 (d, $J$ = 10.0 Hz, 1H × 2,), 5.07 (d, $J$ = 17.5 Hz, 1H × 2,), 5.53 (dt, $J$ = 17.5, 10.0 Hz, 1H), 5.61 (dt, $J$ = 17.5, 10.0 Hz, 1H); $^{13}$C NMR $\delta$ 13.6 (2C), 13.9 (2C), 19.8, 19.9, 29.2 (2C), 34.4 (2C), 43.6, 43.7, 61.0, 61.1, 65.0, 65.1, 117.1, 117.3, 138.0 (2C), 168.4, 168.6, 202.3 (2C).

**Ethyl (*E*)-2-(1-Oxoethyl)-4-octenoate ((*E*)-4c):**[13b] $^1$H NMR $\delta$ 0.86 (t, $J$ = 7.3 Hz, 3H), 1.26 (t, $J$ = 7.3 Hz, 3H), 1.35 (sextet, $J$ = 7.3 Hz, 2H), 1.95 (q, $J$ = 6.9 Hz, 2H), 2.21 (s, 3H), 2.53 (t, $J$ = 6.6 Hz, 2H), 3.47 (t, $J$ = 6.6 Hz, 1H), 4.19 (q, $J$ = 7.3 Hz, 2H), 5.33 (dt, $J$ = 15.5, 6.6 Hz, 1H), 5.51 (dt, $J$ = 15.5, 6.6 Hz, 1H); $^{13}$C NMR $\delta$ 13.4, 14.0, 20.0, 22.3, 31.1, 34.4, 59.8, 61.1, 125.4, 133.5, 169.3, 202.5.

**Ethyl (*Z*)-2-(1-Oxoethyl)-4-octenoate ((*Z*)-4c):** $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.3 Hz, 3H), 1.27 (t, $J$ = 7.3 Hz, 3H), 1.37 (sextet, $J$ = 7.3 Hz, 2H), 2.04 (q, $J$ = 7.3 Hz, 2H), 2.23 (s, 3H), 2.59 (t, $J$ = 7.3 Hz, 2H), 3.45 (t, $J$ = 7.3 Hz, 1H), 4.19 (q, $J$ = 7.3 Hz, 2H), 5.27 (dt, $J$ = 10.9, 7.3 Hz, 1H), 5.47 (dt, $J$ = 10.9, 7.3 Hz, 1H); $^{13}$C NMR $\delta$ 13.6, 13.9, 19.8, 22.5, 25.9, 29.0, 59.5, 61.2, 124.7, 132.7, 169.3, 202.6. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50; O, 22.61. Found: C, 67.83; H, 9.55.

**Ethyl 2-Ethoxycarbonyl-3-ethenyl-2-methylhexanoate (3d):**[14a] Compound **3d** could not be isolated in pure form. Partial $^1$H NMR spectra was obtained from the mixture of **3d** and (*E*)-**4d**. $^1$H NMR $\delta$ 5.05 (dd, $J$ = 16.8, 2.3 Hz, 1H), 5.09 (dd, $J$ = 10.2, 2.3 Hz, 1H), 5.57 (dt, $J$ = 16.8, 10.2 Hz, 1H).

**Ethyl (*E*)-2-Ethoxycarbonyl-2-methyl-4-octenoate ((*E*)-4d):**[14a] $^1$H NMR $\delta$ 0.87 (t, $J$ = 7.3 Hz, 3H), 1.24 (t, $J$ = 7.3 Hz, 6H), 1.31−1.40 (m, 5H), 1.96 (q, $J$ = 6.9 Hz, 2H), 2.55 (d, $J$ = 6.9 Hz, 2H), 4.17 (q, $J$ = 7.3 Hz, 4H), 5.29 (dt, $J$ = 15.2, 6.9 Hz, 1H), 5.50 (dt, $J$ = 15.2, 6.9 Hz, 1H); $^{13}$C NMR $\delta$ 13.5, 14.0 (2C), 19.6, 22.4, 34.6, 38.8, 53.7, 61.0 (2C), 122.8, 135.1, 172.0 (2C).

**Ethyl (*Z*)-2-Ethoxycarbonyl-2-methyl-4-octenoate ((*Z*)-4d):**[14a] $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.3 Hz, 3H), 1.24 (t, $J$ = 7.3 Hz, 6H), 1.31−1.41 (m, 5H), 2.02 (q, $J$ = 7.6 Hz, 2H), 2.63 (d, $J$ = 7.6 Hz, 2H), 4.18 (q, $J$ = 7.3 Hz, 4H), 5.26 (dt, $J$ = 10.9, 7.6 Hz, 1H), 5.53 (dt, $J$ = 10.9, 7.6 Hz, 1H); $^{13}$C NMR $\delta$ 13.9, 14.0 (2C), 19.5, 22.6, 29.3, 33.1, 53.4, 61.0 (2C), 123.0, 133.6, 172.0 (2C).

**Ethyl 2-Ethoxycarbonyl-3-methyl-4-pentenoate (6a):**[13b] $^1$H NMR $\delta$ 1.11 (d, $J$ = 6.6 Hz, 3H), 1.25 (t, $J$ = 7.3 Hz, 3H), 1.27 (t, $J$ = 7.3 Hz, 3H), 2.95 (sextet, $J$ = 7.6 Hz, 1H), 3.27 (d, $J$ = 8.9 Hz, 1H), 4.17 (q, $J$ = 7.3 Hz, 2H), 4.20 (q, $J$ = 7.3 Hz, 2H), 5.01 (dd, $J$ = 10.2, 0.7 Hz, 1H), 5.07 (dd, $J$ = 17.5, 0.7 Hz, 1H), 5.65 (dt, $J$ = 17.2, 9.9 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (2C), 17.8, 37.8, 57.6, 61.0, 61.1, 115.2, 139.7, 168.1, 168.2.

**Ethyl (*E*)-2-Ethoxycarbonyl-4-hexenoate ((*E*)-7a):**[13b] $^1$H NMR $\delta$ 1.26 (t, $J$ = 6.9 Hz, 6H), 1.63 (dd, $J$ = 6.3, 1.0 Hz, 3H), 2.56 (t, $J$ = 6.6 Hz, 2H), 3.36 (t, $J$ = 7.6 Hz, 1H), 4.19 (q, $J$ = 6.9 Hz, 4H), 5.38 (dtq, $J$ = 15.2, 6.6, 1.3 Hz, 1H), 5.55 (dq, $J$ = 15.2, 6.3 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (2C), 17.7, 31.8, 52.1, 61.0, 61.1, 126.5, 128.1, 168.9 (2C).

**Ethyl 2-Ethoxycarbonyl-3-phenyl-4-pentenoate (6b):**[13b] $^1$H NMR $\delta$ 1.26 (t, $J$ = 7.3 Hz, 3H), 1.27 (t, $J$ = 7.3 Hz, 3H), 3.83 (d, $J$ = 11.2 Hz, 1H), 4.11 (dd, $J$ = 11.2, 8.3 Hz, 1H), 4.20 (q, $J$ = 7.3 Hz, 4H), 5.06 (d, $J$ = 9.2 Hz, 1H), 5.11 (d, $J$ = 15.8 Hz, 1H), 6.00 (ddd, $J$ = 15.8, 9.2, 8.3 Hz, 1H), 7.17−7.31 (m, 5H); $^{13}$C NMR $\delta$ 13.6 (2C), 49.5, 57.2, 61.1 (2C), 116.2, 126.9, 127.9 (2C), 128.4 (2C), 137.8, 139.9, 167.6 (2C).

**Ethyl (*E*)-2-Ethoxycarbonyl-5-phenyl-4-pentenoate ((*E*)-7b):**[13b] $^1$H NMR $\delta$ 1.25 (t, $J$ = 7.3 Hz, 3H), 1.27 (t, $J$ = 7.3 Hz, 3H), 2.80 (td, $J$ = 7.3, 1.3 Hz, 2H), 3.49 (t, $J$ = 7.3 Hz, 1H), 4.20 (q, $J$ = 7.3 Hz, 4H), 6.15 (dt, $J$ = 15.8, 7.3 Hz, 1H), 6.47 (d, $J$ = 15.8 Hz, 1H), 7.16−7.34 (m, 5H); $^{13}$C NMR $\delta$ 14.0 (2C), 32.1, 51.9, 61.3 (2C), 125.5, 126.1 (2C), 127.2, 128.4 (2C), 132.7, 137.0, 168.7 (2C).

**Ethyl (*Z*)-2-Ethoxycarbonyl-5-phenyl-4-pentenoate ((*Z*)-7b):** $^1$H NMR $\delta$ 1.22 (t, $J$ = 6.9 Hz, 3H), 1.28 (t, $J$ = 6.9 Hz, 3H), 2.94 (td, $J$ = 7.3, 1.7 Hz, 2H), 3.44 (t, $J$ = 7.3 Hz, 1H), 4.17 (q, $J$ = 6.9 Hz, 2H), 4.20 (q, $J$ = 6.9 Hz, 2H), 5.60 (dt, $J$ = 11.9, 7.3 Hz, 1H), 6.51 (d, $J$ = 11.9 Hz, 1H), 7.17−7.37 (m, 5H); $^{13}$C NMR $\delta$ 13.9 (2C), 41.5, 52.0, 61.3 (2C), 126.8, 127.9, 128.1 (2C), 128.6 (2C), 131.4, 137.9, 168.8 (2C). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.29; O, 23.16. Found: C, 69.82; H, 7.25.

**Ethyl 3-Ethenyl-2-ethoxycarbonylnonanate (6c):** $^1$H NMR $\delta$ 0.87 (t, $J$ = 6.9 Hz, 3H), 1.21−1.45 (m, 16H), 2.76 (qd, $J$ = 8.9, 3.6 Hz, 1H), 3.33 (d, $J$ = 8.9 Hz, 1H), 4.15 (q, $J$ = 6.9 Hz, 2H), 4.20 (q, $J$ = 7.3 Hz, 2H), 5.06 (d, $J$ = 10.2 Hz, 1H), 5.07 (d, $J$ = 17.5 Hz, 1H), 5.65 (dt, $J$ = 17.2, 9.6 Hz, 1H); $^{13}$C NMR $\delta$ 13.9, 14.0 (2C), 22.5, 26.8, 28.9, 31.6, 32.2, 44.0, 57.0, 61.0, 61.1, 117.1, 138.2, 168,1, 168.3. Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92; O, 22.50. Found: C, 67.36; H, 10.20.

**Ethyl (*E*)-2-Ethoxycarbonyl-4-undecenoate ((*E*)-7c):**[39] $^1$H NMR $\delta$ 0.88 (t, $J$ = 6.9 Hz, 3H), 1.22−1.45 (m, 14H), 1.96 (q, $J$ = 6.6 Hz, 2H), 2.57 (t, $J$ = 6.6 Hz, 2H), 3.36 (t, $J$ = 7.6 Hz, 1H), 4.19 (q, $J$ = 6.9 Hz, 4H), 5.36 (dt, $J$ = 15.2, 6.6 Hz, 1H), 5.52 (dt, $J$ = 15.5, 6.6 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (3C), 22.5, 28.7, 29.2, 31.6, 31.8, 32.4, 52.3, 61.2 (2C), 125.2, 133.9, 169.0 (2C).

**Ethyl (*Z*)-2-Ethoxycarbonyl-4-undecenoate ((*Z*)-7c):**[40] $^1$H NMR $\delta$ 0.88 (t, $J$ = 6.9 Hz, 3H), 1.24−1.29 (m, 14H), 2.05 (q, $J$ = 6.6 Hz, 2H), 2.64 (t, $J$ = 7.6 Hz, 2H), 3.34 (t, $J$ = 7.6 Hz, 1H), 4.19 (q, $J$ = 6.9 Hz, 4H), 5.30 (dt, $J$ = 10.9, 7.6 Hz, 1H), 5.48 (dt, $J$ = 10.9, 7.6 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (3C), 22.5, 26.6, 27.1, 28.9, 29.4, 31.7, 52.0, 61.2 (2C), 124.5, 133.1, 169.0 (2C).

**Ethyl 3-Ethenyl-2-ethoxycarbonylundecanoate (6d):** $^1$H NMR $\delta$ 0.87 (t, $J$ = 7.3 Hz, 3H), 1.21−1.45 (m, 20H), 2.76 (qd, $J$ = 9.2, 3.3 Hz, 1H), 3.33 (d, $J$ = 8.9 Hz, 1H), 4.15 (q, $J$ = 7.3 Hz, 2H), 4.19 (q, $J$ = 7.3 Hz, 2H), 5.06 (dd, $J$ = 9.6, 2.0 Hz, 1H), 5.07 (dd, $J$ = 17.8, 2.0 Hz, 1H), 5.65 (dt, $J$ = 17.8, 9.6 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (3C), 22.6, 26.9, 29.2, 29.3, 29.4, 31.8, 32.2, 44.0, 57.0, 61.0, 61.2, 117.1, 138.2, 168,1, 168.3. Anal. Calcd for $C_{18}H_{32}O_4$: C, 69.19; H, 10.32; O, 20.48. Found: C, 68.96; H, 10.38.

**Ethyl (*E*)-2-Ethoxycarbonyl-4-tridecenoate ((*E*)-7d):**[39] $^1$H NMR $\delta$ 0.88 (t, $J$ = 6.9 Hz, 3H), 1.14−1.42 (m, 18H), 1.96 (q, $J$ = 6.6 Hz, 2H), 2.57 (t, $J$ = 7.6 Hz, 2H), 3.36 (t, $J$ = 7.6 Hz, 1H), 4.19 (q, $J$ = 7.3 Hz, 4H), 5.35 (dt, $J$ = 15.2, 6.6 Hz, 1H), 5.53 (dt, $J$ = 15.2, 6.6 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (3C), 22.6, 29.0, 29.2 (2C), 29.4, 31.8 (2C), 32.4, 52.2, 61.1 (2C), 125.1, 133.9, 168.9 (2C).

**Ethyl (*Z*)-2-Ethoxycarbonyl-4-tridecenoate ((*Z*)-7d):** $^1$H NMR $\delta$ 0.88 (t, $J$ = 6.9 Hz, 3H), 1.24−1.29 (m, 18H), 2.05 (q, $J$ = 7.3 Hz, 2H), 2.64 (t, $J$ = 7.3 Hz, 2H), 3.35 (t, $J$ = 7.6 Hz, 1H), 4.19 (q, $J$ = 7.3 Hz, 4H), 5.30 (dt, $J$ = 10.9, 7.3 Hz, 1H), 5.48 (dt, $J$ = 10.9, 7.3 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (3C), 22.5, 26.6, 27.1, 29.2 (2C), 29.4, 29.5, 31.8, 52.0, 61.2 (2C), 124.5, 133.1, 169.0 (2C). Anal. Calcd for $C_{18}H_{32}O_4$: C, 69.19; H, 10.32; O, 20.48. Found: C, 69.24; H, 10.55.

**Ethyl 2-Ethoxycarbonyl-5-methyl-4-hexenoate (6e):**[19] $^1$H NMR $\delta$ 1.26 (t, $J$ = 7.3 Hz, 6H), 1.64 (s, 3H), 1.68 (s, 3H), 2.59 (t, $J$ = 7.6 Hz, 2H), 3.32 (t, $J$ = 7.6 Hz, 1H), 4.19 (q, $J$ = 7.3 Hz, 4H), 5.07 (tq, $J$ = 7.3, 1.7 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (2C), 17.6, 25.6, 27.5, 52.1, 61.1 (2C), 119.7, 134.7, 169.1 (2C).

**Ethyl 2-Ethoxycarbonyl-3,3-dimethyl-4-pentenoate (7e):**[19] $^1$H NMR $\delta$ 1.24 (s, 6H), 1.26 (t, $J$ = 7.3 Hz, 6H), 3.32 (s, 1H), 4.17 (q, $J$ = 7.3 Hz, 4H), 5.01 (dd, $J$ = 10.6, 1.0 Hz, 1H), 5.03 (dd, $J$ = 17.5, 1.0 Hz, 1H), 6.06 (dd, $J$ = 17.5, 10.6 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (4C), 25.0, 38.7, 60.8 (2C), 112.0, 144.8, 167.8 (2C).

**Methyl 2-Methoxycarbonyl-3,3-dimethyl-4-pentenoate (7eb):**[19] $^1$H NMR $\delta$ 1.24 (s, 6H), 3.38 (s, 1H), 3.70 (s, 6H), 5.01 (dd, $J$ = 10.1, 1.0 Hz, 1H), 5.03 (dd, $J$ = 18.3, 1.0 Hz, 1H), 6.04 (dd, $J$ = 18.3, 10.1 Hz, 1H); $^{13}$C NMR $\delta$ 24.9 (2C), 38.8, 51.9 (2C), 60.5, 112.2, 144.6, 168.2 (2C).

**Ethyl 3-Ethenyl-2-ethoxycarbonyl-3-methylheptanoate (7f):** $^1$H NMR $\delta$ 0.88 (t, $J$ = 6.9 Hz, 3H), 1.17−1.31 (m, 13H), 1.47−1.60 (m, 2H), 3.41 (s, 1H), 4.15 (q, $J$ = 6.9 Hz, 2H), 4.17 (q, $J$ = 6.9 Hz, 2H), 4.99 (dd, $J$ = 17.5, 1.0 Hz, 1H), 5.08 (dd, $J$ = 10.9, 1.0 Hz, 1H), 5.99 (dd, $J$ = 17.5, 10.9 Hz, 1H); $^{13}$C NMR $\delta$ 13.9, 14.0 (2C), 19.8, 23.1, 26.0, 38.8, 42.0, 60.0, 60.7, 60.8, 113.3, 143.3, 167.8 (2C). Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69; O, 23.67. Found: C, 66.40; H, 9.88.

**Ethyl 3-Ethenyl-2-ethoxycarbonyl-3,7-dimethyl-6-octenoate (7g):**[19] $^1$H NMR $\delta$ 1.24 (t, $J$ = 6.9 Hz, 3H), 1.26 (t, $J$ = 6.9 Hz, 3H), 1.27

(39) Nii, H.; Furukawa, K.; Iwakiri, M. *Nippon Kagaku Zasshi* **1971**, *92*, 1214.

(40) Vig, O. P.; Sharma, M. L.; Taneja, K. C.; Malik, N. *Indian J. Chem.* **1981**, *20B*, 863.

(s, 3H), 1.50−1.61 (m, 5H), 1.66 (s, 3H), 1.90 (q, $J$ = 7.6 Hz, 2H), 3.41 (s, 1H), 4.15 (q, $J$ = 6.9 Hz, 2H), 4.17 (q, $J$ = 6.9 Hz, 2H), 5.01 (dd, $J$ = 17.5, 1.0 Hz, 1H), 5.03 (m, 1H), 5.10 (dd, $J$ = 10.9, 1.0 Hz, 1H), 6.00 (dd, $J$ = 17.5, 10.9 Hz, 1H); $^{13}$C NMR $\delta$ 14.0 (2C), 17.5, 19.7, 22.6, 25.6, 39.0, 42.0, 59.9, 60.8, 60.9, 113.3, 124.1, 131.4, 143.1, 167.8 (2C).

**Methyl 3-Ethenyl-2-methoxycarbonyl-3,7-dimethyl-6-octenoate (7gb):**[10f] $^1$H NMR $\delta$ 1.27 (s, 3H), 1.49−1.59 (m, 5H), 1.66 (s, 3H), 1.90 (q, $J$ = 7.3 Hz, 2H), 3.46 (s, 1H), 3.68 (s, 3H), 3.70 (s, 3H), 5.01 (dd, $J$ = 17.5, 1.0 Hz, 1H), 5.03 (m, 1H), 5.11 (dd, $J$ = 10.9, 1.0 Hz, 1H), 5.98 (dd, $J$ = 17.5, 10.9 Hz, 1H); $^{13}$C NMR $\delta$ 17.5, 19.6, 22.6, 25.6, 39.0, 42.1, 51.9, 52.0, 59.8, 113.8, 124.0, 131.5, 142.9, 168.1, 168.2.

**Ethyl 2-Ethoxycarbonyl-4-methyl-4-pentenoate (11):**[9i] $^1$H NMR $\delta$ 1.26 (t, $J$ = 7.3 Hz, 6H), 1.74 (s, 3H), 2.61 (d, $J$ = 7.9 Hz, 2H), 3.57 (t, $J$ = 7.9 Hz, 1H), 4.19 (q, $J$ = 7.3 Hz, 4H), 4.73 (s, 1H), 4.78 (s, 1H); $^{13}$C NMR $\delta$ 13.9 (2C), 22.1, 36.4, 50.4, 61.2 (2C), 112.1, 141.6, 168.9 (2C).

**Ethyl 2-Ethenyl-2-ethoxycarbonyl-6-phenylhexanoate (14f):** $^1$H NMR $\delta$ 1.22 (t, $J$ = 7.3 Hz, 3H), 1.23 (t, $J$ = 7.3 Hz, 3H), 1.32−1.76 (m, 4H), 2.48−2.68 (m, 2H), 2.80 (qd, $J$ = 9.6, 3.3 Hz, 1H), 3.33 (d, $J$ = 8.9 Hz, 1H), 4.14 (q, $J$ = 7.3 Hz, 2H), 4.17 (q, $J$ = 7.3 Hz, 2H), 5.07 (dd, $J$ = 9.6, 2.0 Hz, 1H), 5.08 (d, 1H, $J$ = 17.2 Hz, 1H), 5.63 (dt, 1H, $J$ = 17.2, 9.6 Hz, 1H), 7.13−7.28 (m, 5H); $^{13}$C NMR $\delta$ 13.9 (2C), 28.8, 31.8, 35.5, 43.9, 56.9, 61.2 (2C), 61.3, 117.4, 125.6, 128.1 (2C), 128.2 (2C), 137.9, 142.2, 168.0, 168.2. Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23; O, 20.10. Found: C, 71.85; H, 8.18.

**Ethyl (*E*)-2-Ethoxycarbonyl-8-phenyl-4-octenoate ((*E*)-15f):**[41] $^1$H NMR $\delta$ 1.25 (t, $J$ = 6.9 Hz, 3H), 1.27 (t, $J$ = 6.9 Hz, 3H), 1.65 (quintet, $J$ = 7.6 Hz, 2H), 2.01 (q, $J$ = 6.9 Hz, 2H), 2.54−2.60 (m, 4H), 3.37 (t, $J$ = 7.6 Hz, 1H), 4.17 (q, $J$ = 7.3 Hz, 2H), 4.18 (q, $J$ = 7.3 Hz, 2H), 5.38 (dt, $J$ = 15.2, 6.9 Hz, 1H), 5.55 (dt, $J$ = 15.2, 6.6 Hz, 1H), 7.14−7.29 (m, 5H); $^{13}$C NMR $\delta$ 13.9, 14.0, 30.9 (2C), 31.8, 35.1, 52.2, 61.2 (2C), 125.6, 125.8, 128.2 (2C), 128.3 (2C), 133.3, 142.3, 168.9 (2C).

**Ethyl (*Z*)-2-Ethoxycarbonyl-8-phenyl-4-octenoate ((*Z*)-15f):** $^1$H NMR $\delta$ 1.25 (t, $J$ = 6.9 Hz, 3H), 1.27 (t, $J$ = 6.9 Hz, 3H), 1.67 (quintet, $J$ = 7.6 Hz, 2H), 2.11 (q, $J$ = 7.3 Hz, 2H), 2.58−2.65 (m, 4H), 3.34 (t, $J$ = 7.6 Hz, 1H), 4.18 (q, $J$ = 6.9 Hz, 4H), 5.34 (dt, $J$ = 10.9, 7.3 Hz, 1H), 5.50 (dt, $J$ = 10.9, 7.3 Hz, 1H), 7.13−7.29 (m, 5H); $^{13}$C NMR $\delta$ 13.9 (2C), 26.6, 26.7, 31.1, 35.3, 51.9, 61.2, 61.3, 125.0, 125.6, 128.2 (2C), 128.3 (2C), 132.4, 142.2, 166.5, 168.9. Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23; O, 20.10. Found: C, 71.78; H, 8.43.

**Dimethyl (*Z*)-(5-Carbomethoxy-1-cyclohexen-3-yl)malonate (17):**[14b] $^1$H NMR $\delta$ 1.46 (q, $J$ = 12.5 Hz, 1H), 2.09−2.18 (m, 1H), 2.20−2.33 (m, 2H), 2.61−2.70 (m, 1H), 2.99−3.03 (m, 1H), 3.30 (d, $J$ = 8.9 Hz, 1H), 3.69 (s, 3H), 3.75 (s, 6H), 5.53 (d, $J$ = 9.6 Hz, 1H), 5.78 (ddt, $J$ = 10.2, 5.0, 2.3 Hz, 1H); $^{13}$C NMR $\delta$ 27.5, 29.3, 35.9, 39.3, 51.6, 52.3 (2C), 56.3, 127.2 (2C), 168.4 (2C), 175.3.

**Isomerization of (*Z*)-4a in the Presence of Diethyl Sodiomalonate (2a) and an Ir Catalyst.** A 23:4:73 mixture of **3a**, (*E*)-**4a**, (*Z*)-**4a** (485 mg, 2.0 mmol), triphenyl phosphite (49.6 mg, 0.16 mmol), and $[Ir(COD)Cl]_2$ (26.9 mg, 0.04 mmol) was stirred in 5.0 mL of THF under Ar atmosphere. In a separate flask, diethyl malonate (640 mg, 4.0 mmol) was added to a slurry of hexane-washed sodium hydride (96 mg, 4.0 mmol) in 5.0 mL of THF. The resulting clear solution was added to the former by a syringe, and the combined mixture was stirred for 4 h. The reaction mixture was partitioned between ether and water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was analyzed by GLC. The ratio of **3a** to (*E*)-**4a** to (*Z*)-**4a** was 23:17:60.

**Acknowledgment.** This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 283, "Innovative Synthetic Reactions") from the Ministry of Education, Science, Sports and Culture, Government of Japan. We thank Kuraray Company Ltd. for financial support. We thank Prof. T. Ohta for measuring the $^{31}$P-NMR spectra.

**Supporting Information Available:** $^{31}$P NMR spectra of the reaction of $[Ir(COD)Cl]_2$ with $P(OPh)_3$ in $d_8$-THF (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA981560P

(41) Larock, R. C.; Lu, Y.; Bain, A. C.; Russell, C. E. *J. Org. Chem.* **1991**, *56*, 4589.