

Amphiphilic Catalytic Allylating Reagent, Bis- π -allylpalladium Complex

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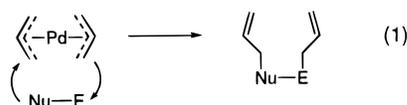
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π -Allylpalladium complexes **1** react with various nucleophiles to construct carbon–carbon or carbon–heteroatom bond, and the so-called Tsuji–Trost type reaction via **1** is well recognized as a very important modern organic transformation.¹ We previously found that bis- π -allylpalladium complex **2** reacts with



electrophiles such as aldehydes and imines to produce carbon–carbon bond in a manner different from the reaction via **1**.^{2,3} Herein we wish to report that bis- π -allylpalladium complex acts as the first amphiphilic catalytic allylating agent; it reacts with both nucleophilic and electrophilic carbons at once to produce double allylation products in high to good yields (eq 1).⁴



The reaction of phenylethylidene malononitrile **3a** (1 equiv), allyltributylstannane **4** (1.2 equiv), and allyl chloride **5** (1.2 equiv) in THF was carried out in the presence of PdCl₂(PPh₃)₂ (3 mol %) under Ar atmosphere, and the results are shown in eq 2 and Table 1 (entry 1). NMR yield of **6a** was 99% yield, and it was isolated in 91% yield (entry 1). The use of 5 mol % and 1.5 mol % of the catalyst also gave **6a** in 99% and 98% NMR yields, respectively. The use of allyl chloride gave higher yields in comparison with that of allyl bromide. Although tetrakis(triphenylphosphine)palladium was as an efficient catalyst as dichlorobis(triphenylphosphine)palladium,⁵ other catalysts such as Pd(dba)₂, or its diphosphine complexes, Pd(OAc)₂, and PdCl₂(PBU₃)₂, gave **6a** in lower yields. Acetonitrile or *N,N*-dimethylformamide was an equally effective solvent as THF for the double allylation reaction. In all cases, monoallylated

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(2) Nakamura, H.; Asao, N.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1273. Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 1459. Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641, and references cited therein.

(3) Although π -allylpalladium-X complexes **1** in which X is an electron withdrawing group react with nucleophiles, it is also known that certain π -allyltransition metal complexes react with electrophiles. π -Allylmolybdenum complexes: Faller, J. W.; Nguyen, J. T.; Ellis, W.; Mazzieri, M. R. *Organometallics* **1993**, *12*, 1434. Faller, J. W.; DiVerdi, M. J.; John, J. A. *Tetrahedron Lett.* **1991**, *32*, 1271. Faller, J. W.; Linebarrier, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937. π -Allylnickel complexes: Hegedus, L. S.; Wagner, S. D.; Waterman, E. L.; Siirala-Hansen, K. *J. Org. Chem.* **1975**, *40*, 593. π -Allyltitanium complexes: Sato, F.; Iijima, S.; Sato, M. *Tetrahedron Lett.* **1981**, *22*, 243. Collins, S.; Kuntz, B. A.; Hong, Y. *J. Org. Chem.* **1989**, *54*, 4154.

(4) Ohno, K.; Mitsuyasu, T.; Tsuji, J. *Tetrahedron Lett.* **1972**, *28*, 3705.

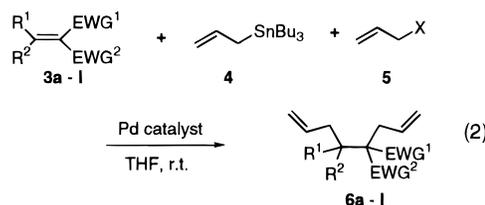
(5) The use of tetrakis(triphenylphosphine)palladium gave **6a** in 99% yield under the same conditions.

Table 1. Palladium Catalyzed Double Allylation of Activated Olefins **3** with Allyltributylstannane **4** and Allyl Chloride **5**

entry	olefin 3	reaction time	yield of 6 (%) ^a
1		13 h	91 ^b
2		17 h	91
3		1.5 d	81
4		1 d	82
5		1 w	trace
6		2.5 d	63 (77 / 23)
7		2.5 d	59 (55 / 45)
8		2.5 d	49 (58 / 42)
9		2.5 h	64 (51 / 49)
10		2.5 d	43 (67 / 33)
11		3 d	80 (51 / 49)
12 ^c		2.5 d	46 (80 / 20)

^a Isolated yields based on **3**. Diastereomer ratios were indicated in the parentheses and the stereochemistries of those diastereomers were not determined. ^b ¹H NMR yield was 99%. ^c 10 mol % of the catalyst was used.

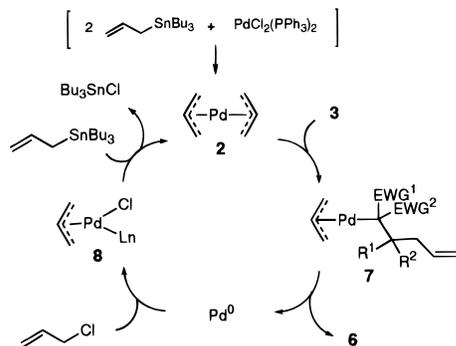
products were not obtained.⁶



The activated olefins (**3b–d**) underwent the double allylation very smoothly to give the corresponding 1,7-octadienes (**6b–d**) in high yields (entries 2–4). However, only trace amounts of desired compound **6e** were obtained in the reaction of tetrasubstituted olefin **3e**. Not only the activated olefins having two CN groups (**3a–d**) but also those bearing CN and CO₂Et (**3f–i**) or CN and SO₂Ph (**3j–k**) underwent the double allylation

(6) The use of Ni(PPh₃)₄ as a catalyst in THF gave a monoallylated product (Michael type product) in 70% yield along with small amounts (~9%) of **6a**.

Scheme 1



reaction, giving the corresponding octadienes (**6f–k**) in good yields (entries 6–11), although the diastereoselectivities of the reactions were not high. Even an olefin **3l**, activated by a single CN group, gave the double allylation product **6l** in an allowable yield (entry 12).

A mechanistic rationale which accounts for the unprecedented double allylation of activated olefins is shown in Scheme 1. The transmetalation of allyltributylstannane to palladium would produce bis- π -allylpalladium complex **2**,⁷ which would react with activated olefins **3** to give the π -allylpalladium intermediate

7. The reductive coupling from **7** would give the corresponding 1,7-octadienes **6** and palladium(0) species. At this stage, π -allyl group of **7** reacts with a nucleophilic carbon center. The oxidative insertion of Pd(0) into allyl chloride would produce the π -allylpalladium complex **8**. When Pd(PPh₃)₄ was used as a catalyst instead of PdCl₂(PPh₃)₂, the catalytic cycle would start from the Pd(0) species. The reaction of **8** with allylstannane would produce **2** and Bu₃SnCl.

In organic chemistry, a few amphiphilic reagents are known,^{8,9} but we believe that *catalytic* amphiphilic reagents and reactions are unprecedented.¹⁰ Further extension of the double catalytic allylation is now in progress.

Supporting Information Available: Experimental data for **6a–d** and **6f–l** (6 pages). See any current masthead page for ordering and Internet access instructions.

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(7) It has been confirmed that the reaction between allyltributylstannane and PdCl₂(PPh₃)₂ produces bis- π -allylpalladium complex. See ref 2.

(8) The stoichiometric reaction of bis- π -allylpalladium complex with CO₂ and SO₂ was reported; Hung, T.; Jolly, P. W.; Wilke, G. J. *J. Organomet. Chem.* **1980**, *190*, C5.

(9) Amphiphilic substrates are well-known, for example, see: Lee, V. J. In *Comprehensive Organic Synthesis*; Semmelhack, M. F., Ed.; Pergamon: Oxford, 1991, Vol. 4, pp 69–137, and references cited therein.

(10) One referee posed a question whether bis- π -allylpalladium is really catalytically active or not. The meaning of “catalytic” in the title is that bis- π -allylpalladium is produced *catalytically*, although its reaction with **3** proceeds *stoichiometrically*.