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(π-Allyl)palladium Complexes Bearing Diphosphinidenecyclobutene Ligands (DPCB): Highly Active Catalysts for Direct Conversion of Allylic Alcohols

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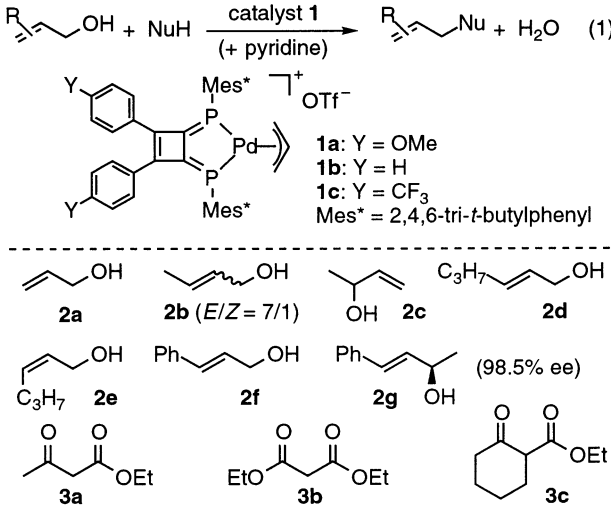
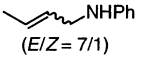
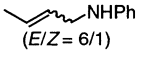
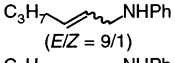
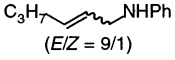
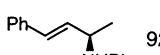
Palladium-catalyzed allylation is a reliable and widely used method for constructing C−C, C−N, and C−O bonds in organic synthesis.[1] This catalysis is generally performed with allylic carboxylates, carbonates, phosphates, and related compounds as substrates. Because these substrates are synthesized from the corresponding allylic alcohols, palladium catalysts that enable the conversion of allylic alcohols directly into allylation products are highly desirable, especially from the viewpoint of the atom economy.[2] Although several attempts have been reported in this connection,[3] most of them require rather severe reaction conditions, and the design of really effective catalysts for direct conversion of allylic alcohols still remains a major objective in catalytic allylation. This is apparently due to the poor leaving ability of the OH group. Accordingly, catalytic conversion of allylic alcohols has been examined in most cases through in situ activation of the OH group with the aid of Lewis acids (e.g., $Ti(OPr^i)_4$, BEt_3, BPh_3, $SnCl_2$)[4] or by converting it into the esters of inorganic acids (e.g., As_2O_3, B_2O_3, CO_2).[5] We herein report that (π-allyl)palladium complexes (**1**) bearing sp^2-hybridized phosphorus ligands (diphosphinidenecyclobutene: DPCB-Y)[6,7] effectively catalyze the direct conversion of allylic alcohols in the absence of activating agents (eq 1).



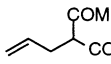
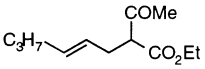
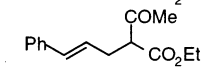
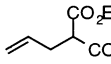
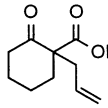
Tables 1 and 2 list the representative results. It has been reported that, in the presence of $Pd(OAc)_2$/4PPh_3 (1 mol %) as a catalyst and $Ti(OPr^i)_4$ (25 mol %) as an activating agent, catalytic allylation of aniline derivatives with allylic alcohols takes place under heated conditions (50−80 °C).[4b] On the other hand, similar reactions between aniline and six kinds of allylic alcohols (**2a**−**f**) proceeded only with 0.1 mol % **1a** at room temperature (Table 1, runs 1 and 4−8). Complexes **1b** and **1c** exhibited comparable catalytic activity, although the amount of diallylation product was higher than that for **1a** (runs 2 and 3). Catalysts **1a**−**c** are fairly stable toward oxidation, and the catalytic reactions could be carried out in the air.[8] The two regioisomers of butenyl alcohol (**2b** and **2c**) were converted into *N*-(2-butenyl)aniline and *N*-(1-methyl-2-propenyl)-

Table 1. Catalytic Allylation of Aniline with Allylic Alcohols[a]

run	(allyl)OH	time (h)	(allyl)NHPh (%)[b]		(allyl)$_2$NPh (%)
1	**2a**	2		96	3
2[c]	**2a**	2		91	8
3[d]	**2a**	2		82	16
4	**2b**	6	 (E/Z = 7/1)	85	 10	4
5	**2c**	6	 (E/Z = 6/1)	84	 11	4
6	**2d**	7	 (E/Z = 9/1)	97		3
7	**2e**	7	 (E/Z = 9/1)	96		3
8	**2f**	10		90		8
9[e]	**2g**	3		92 (98.5% ee)		<1

[a] Reaction conditions: 1.0 mmol (allyl)OH, 2.0 mmol $PhNH_2$, 0.1 mol % **1a**, 1 mL of toluene, 0.25 g of $MgSO_4$, room temperature. [b] Monoallylation products in runs 4−7 were obtained as a mixture of stereo- and/or regioisomers, whose ratio was determined by GLC. [c] **1b** was used in place of **1a**. [d] **1c** was used in place of **1a**. [e] **1a** was used in 2 mol %.

Table 2. Catalytic Allylation of Active Methylene Compounds[a]

run	(allyl)OH	CH_2Z_2	time (h)	(allyl)CHZ_2 (%)		(allyl)$_2CZ_2$ (%)
1	**2a**	**3a**	3		92	7
2	**2d**	**3a**	10		93	<1
3	**2f**	**3a**	7		85	12
4	**2a**	**3b**	12		92	<1
5	**2a**	**3c**	12		95	

[a] Reaction conditions: 2.0 mmol (allyl)OH, 4.0 mmol CH_2Z_2, 2 mol % **1a**, 10 mol % pyridine, 0.25 g of $MgSO_4$, 50 °C.

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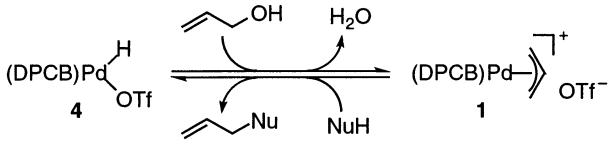
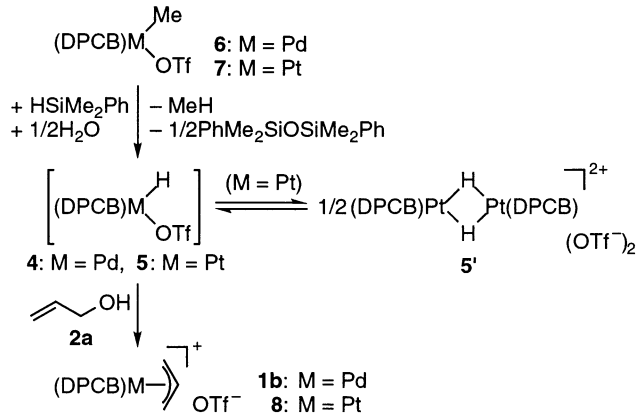
Scheme 1



Scheme 2



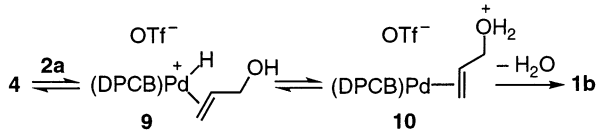
aniline in almost the same regio- and stereoselectivity (runs 4 and 5). Similarly, the reactions of the (*E*)- and (*Z*)-isomers of 2-hexenyl alcohol (**2d** and **2e**) gave a nearly identical distribution of products (runs 6 and 7). These results are consistent with a catalytic mechanism involving rapid interconversion between the syn- and anti-isomers of the π-allyl intermediate. Optically active alcohol **2g** (98.5% ee) was converted into the corresponding monoallylated aniline without a notable loss of optical purity (run 9). Catalytic allylation of active methylene compounds (CH_2Z_2; **3a**−**c**) was also successful (Table 2); the reactions proceeded at 50 °C in the presence of 2 mol % **1a** and 10 mol % pyridine[9] to give monoallylation products in 85−95% yields.

Scheme 1 shows our proposed catalytic mechanism. The key to direct conversion of allylic alcohol is the C−O bond cleavage giving (π-allyl)palladium intermediate **1**. On the basis of the stoichiometric observations summarized in Scheme 2, we assumed hydride complex **4** to be responsible for this process. First of all, platinum hydride **5** was prepared as a model of **4**. After several attempts, this complex was synthesized by the reaction of methyl complex **7** with $HSiMe_2Ph$ in wet CH_2Cl_2 and was isolated as a hydrido-bridged dimer (**5′**) in 52% yield. Complex **5′** reacted with 2-propenyl alcohol (**2a**) at 50 °C to give (π-allyl)platinum **8**, which was isolated in 67% yield. A similar set of experiments was carried out with methylpalladium **6** instead of **7**. Unlike the platinum system, the hydride complex **4** could not be detected, while π-allyl complex **1b** was successfully prepared from 2-propenyl alcohol (**2a**). Thus, the treatment of **6** with $HSiMe_2Ph$ in wet CD_2Cl_2 in the presence of **2a** at room temperature led to instant formation of **1b** in quantitative yield as confirmed by NMR spectroscopy; the complex was isolated in 62% yield.[10]

We have demonstrated that DPCB-coordinated palladium complexes exhibit hitherto unknown catalytic activity toward direct conversion of allylic alcohols. We have also described the evidence for C−O bond cleavage of 2-propenyl alcohol (**2a**) promoted by **4**. The mechanistic details of the π-allyl complex formation may be depicted by Scheme 3. Coordination of **2a** followed by proton transfer from Pd to OH forms intermediate **10**, which undergoes elimination of water to give **1b**.

In this scheme, the hydridopalladium moiety in **9** should be significantly acidic. On the other hand, it is known that hydrido ligands in transition metal complexes are commonly charged

Scheme 3



negatively in the ground state and the acidity develops when a special driving force that causes deprotonation exists.[11] In the present case, we may consider the unique coordination property of DPCB to serve as a powerful driving force. Thus, DPCB as a low-coordinate phosphorus compound bears an extremely low-lying π^* orbital, mainly located around the sp^2 phosphorus atoms, and has a marked tendency to engage in metal-to-phosphorus π back-bonding.[12] Consequently, DPCB may effectively stabilize **10** as a Pd(0) species, rather than **9** having a cationic Pd(II) center. This situation should facilitate the conversion of **9** to **10** via proton transfer and results in the C−O bond cleavage of allylic alcohols.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Although $MgSO_4$ was added in an attempt to remove water concomitantly generated with the allylation reactions, the addition appeared not to be essential. For example, the reaction of aniline with **2a** in toluene in the presence of **1a** (0.5 mol %) without $MgSO_4$ at room temperature for 30 min gave a 96% yield of *N*-(2-propenyl)aniline.

(9) Pyridine was added to enhance the nucleophilicity of active methylene compounds.

(10) Complex **1b** reacts rapidly with aniline at room temperature to give *N*-(2-propenyl)aniline.[6]

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