Catalytic C−O Bond Cleavage of Allylic Alcohols Using Diphosphinidenecyclobutene-Coordinated Palladium Complexes. A Mechanistic Study

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The mechanism of C−O bond cleavage of allylic alcohols promoted by the hydridopalladium complexes PdH(OTf)(DPCB-Y) (**2**), bearing 1,2-diaryl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)-phosphinidene]cyclobutene ligands (DPCB-Y), has been investigated (aryl = 4-(trifluoromethyl)phenyl (DPCB-CF_3), phenyl (DPCB), 4-methoxyphenyl (DPCB-OMe), 4-octyloxyphenyl (DPCB-OOct)). This reaction forms the (π-allyl)palladium complexes [Pd(π-allyl)(DPCB-Y)]-OTf (**1**), which are key intermediates for the catalytic allylation of aniline with allylic alcohols. The platinum analogue of **2** is obtained as the hydrido-bridged dimer [$Pt_2(\mu$-H$)_2$(DPCB$)_2$]-$(OTf)_2$ (**4**) by the treatment of PtMe(OTf)(DPCB) (**5**) with $HSiMe_2Ph$ in the presence of a small amount of water. Complex **4** cleaves the C−O bond of allylic alcohols at 50 °C, yielding the π-allyl complexes [Pt(π-allyl)(DPCB)]OTf (**7**). Although complex **2**, similarly prepared by the reaction of PdMe(OTf)(DPCB) (**5**) with $HSiMe_2Ph$ and water, is too unstable to be identified, its formation is confirmed by trapping experiments using dienes to give the corresponding π-allyl complexes. Complex **2**, thus generated, instantly reacts with allylic alcohols at room temperature to afford the π-allyl complex **1** in high yield. The intermediacy of **2** in the catalytic allylation is further examined by kinetic experiments on actual catalytic systems, leading to mechanistic details of C−O bond cleavage promoted by **2**.

Introduction

The palladium-catalyzed allylation is a widely used method for constructing C−C, C−N, and C−O bonds in organic synthesis.[1] Although this reaction is generally conducted with allylic esters synthesized from allylic alcohols as allylation agents, there have been continuous research interests in direct conversion of allylic alcohols into allylation products.[2,3] This is mainly because such a reaction forms water as the only coproduct and possibly serves as an environmentally benign process with high atom efficiency.[4] However, owing to the poor leaving ability of the OH group, most of the catalytic systems so far examined required rather severe reaction conditions;[2] otherwise, the reactions were conducted with in situ activation of allylic alcohols using considerable amounts of Lewis acids.[3] On the other hand, we recently found that (π-allyl)palladium complexes bearing 1,2-diaryl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutene ligands (DPCB-Y) with sp^2-hybridized phosphorus as coordination atoms efficiently catalyze the direct conversion of allylic alcohols in the absence of Lewis acids under mild conditions (Scheme 1).[5] For example, aniline is smoothly monoallylated with a variety of allylic alcohols at room temperature in over 90% yields. This reaction retains stereochemistry of the allylic carbon, showing a catalytic process involving a

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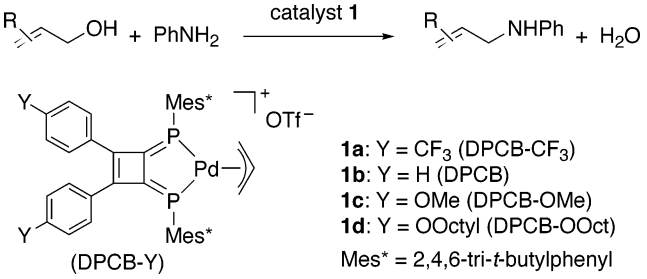
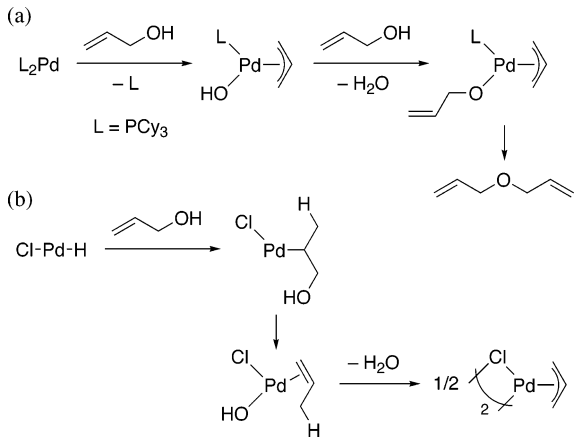
Scheme 1



Scheme 2

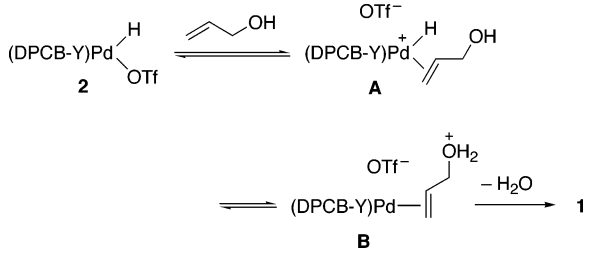


(π-allyl)palladium intermediate. In this paper we report full details of our study on the mechanism of this novel catalysis.

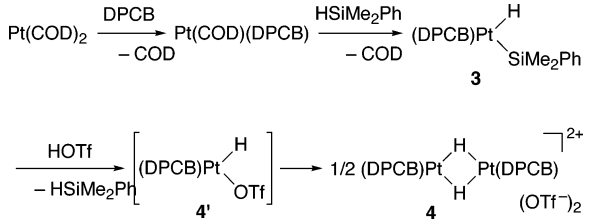
A key to catalytic conversion of allylic alcohols is C−O bond cleavage affording (π-allyl)palladium intermediates, which subsequently react with carbon, nitrogen, and oxygen nucleophiles to give allylation products. Previously, Yamamoto et al. examined this process in a stoichiometric system using $Pd(PCy_3)_2$ and proposed an oxidative-addition mechanism, as commonly assumed for the reactions of allylic esters (Scheme 2a).[6,7] A characteristic feature of this system using a Pd(0) complex is concomitant formation of diallyl ethers via allyl−allyloxy intermediates. More recently, Hosokawa et al. proposed a sequence of insertion and elimination for the π-allyl complex formation from [PdCl]OTf and allylic alcohols (Scheme 2b).[8,9]

On the other hand, we proposed a novel mechanism involving the hydridopalladium intermediate **2** (Scheme 3). Thus, coordination of allyl alcohol to **2** followed by proton transfer from the palladium to the OH group in **A** forms **B**, which undergoes dehydration to give the π-allyl complex **1**. We considered that a strong π-backbonding between palladium and DPCB-Y effectively stabilizes the Pd(0) intermediate **B** to facilitate the proton transfer in **A**. It is known that sp^2-hybridized

Scheme 3



Scheme 4



phosphorus compounds such as DPCB-Y possess significantly low-lying π^* orbitals mainly located around the phosphorus atoms, serving as strong π-acceptors toward transition metals.[10]

In this paper, we examine this mechanism in stoichiometric systems. Although the hydridopalladium complex **2** was too unstable to be isolated, we could successfully prepare its platinum analogue and examined its capability for the C−O bond cleavage of allylic alcohols.

Results and Discussion

Preparation of Hydridoplatinum(II) Triflate Complexes. First of all, we tried to prepare a platinum analogue of **2** by oxidative addition of HOTf to Pt(cod)(DPCB) generated in situ from $Pt(cod)_2$ and DPCB in toluene. However, the resulting complex was not the hydride complex but a cyclooctenyl complex with the formula [Pt(κ^2-η^2:η^1-cycloocten-4-yl)(DPCB)]OTf. On the other hand, treatment of $PtH(SiMe_2Ph)$(DPCB) (**3**) with HOTf in Et_2O led to the desirable complex **4**, which was isolated as a brownish red solid in 89% yield (Scheme 4). It is likely that this reaction initially affords the monomeric complex **4′**, which is successively dimerized to **4**. The parent **3** was synthesized from Pt(cod)(DPCB) and $HSiMe_2Ph$ in 72% yield.

Figure 1 shows the $^{31}P\{^1H\}$ NMR spectrum of **4**, which exhibits a singlet at δ 152.4 with ^{195}Pt satellites. Although there are small peaks due to second-order couplings, the two sets of satellites with medium intensities are attributed to $^1J_{PtP}$ and $^3J_{PtP}$ couplings of 3455 and 342 Hz, respectively. The ^1H NMR spectrum measured in CD_2Cl_2 at room temperature exhibited a quintet at δ −8.10 ($^2J_{PH}$ = 60 Hz, $^1J_{PtH}$ = 521 Hz, 2H), which is assignable to the bridging hydrides symmetrically bonded to two Pt(DPCB) moieties. These signal patterns are similar to those reported for $[Pt_2(\mu\text{-}H)_2(dppe)_2]^{2+}$.[11]

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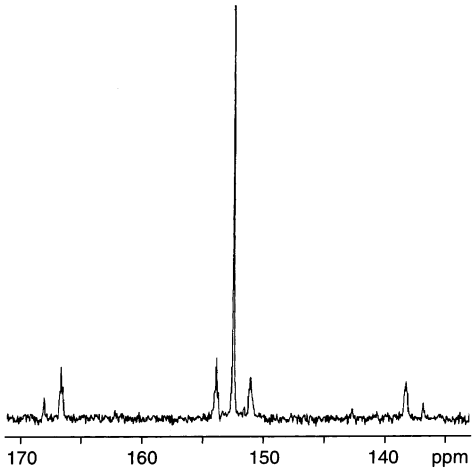
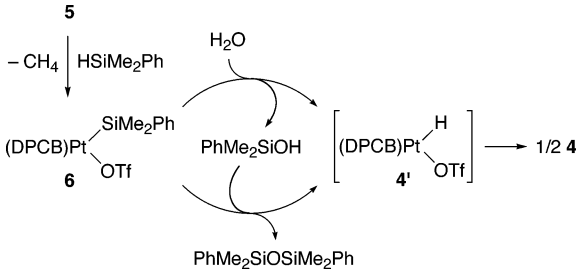
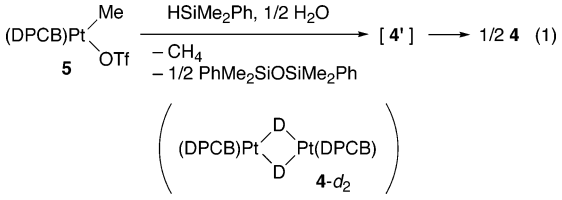


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2 at room temperature (121.49 MHz).

Scheme 5



The hydridoplatinum complex **4** could be synthesized quantitatively also by the treatment of PtMe(OTf)(DPCB) (**5**) with $HSiMe_2Ph$ (1 equiv) in CD_2Cl_2, as confirmed by NMR spectroscopy. This reaction provided methane (1 equiv/**5**) and $PhMe_2SiOSiMe_2Ph$ (0.5 equiv/**5**) as byproducts. Accordingly, the reaction stoichiometry suggested the participation of 0.5 equiv of water, as summarized in eq 1. Actually, the reaction performed

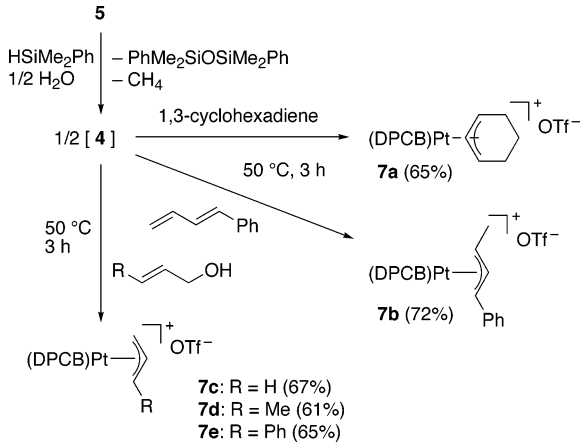


with D_2O formed the deuterido complex **4**-d_2 instead of **4**. Furthermore, the reaction using $DSiMe_2Ph$ formed CH_3D, selectively.

These observations are consistent with the reaction process given in Scheme 5. The first step is metathesis of the Pt−Me bond with the Si−H bond, giving the silylplatinum compound **6** and methane. A similar process has been documented for $[PdMe(OEt_2)(phen)]^+$.[12] The Pt−Si bond in **6** is then hydrolyzed to the monomeric hydride **4′** and silol ($PhMe_2SiOH$), and the latter product further reacts with **6** to afford **4′** and siloxane ($PhMe_2SiOSiMe_2Ph$). Finally, **4′** is dimerized to **4**.

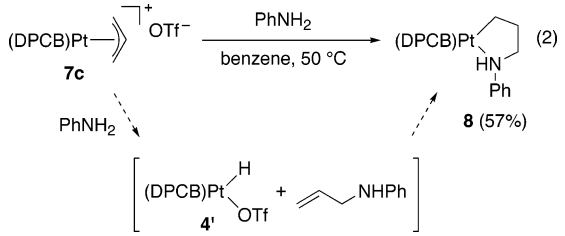
Reactions of Hydridoplatinum(II) Triflate Complexes. The hydrido complex having a DPCB ligand reacted with dienes and allylic alcohols (10 equiv each)

Scheme 6



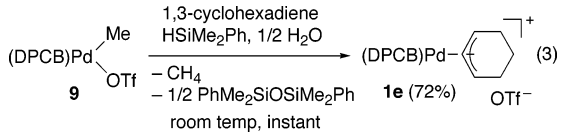
to afford the corresponding π-allyl complexes in good to high yields (Scheme 6). Thus, complex **4** generated in situ from **5**, $HSiMe_2Ph$, and water in $ClCH_2CH_2Cl$ underwent the insertion of 1,3-cyclohexadiene and 1-phenylbutadiene at 50 °C, giving **7a**,**b** in 65 and 72% yields, respectively, after isolation. Complex **7a** could be also prepared from isolated **4**. Similarly, complexes **7c**−**e** were obtained in 61−67% yields by the reactions of the in situ generated **4** with three kinds of allylic alcohols, respectively.

The resulting **7c** reacted with aniline (5 equiv) in benzene at 50 °C to give an aminopropyl complex **8** with a five-membered chelate ring (eq 2). This reaction very



probably proceeds via nucleophilic attack of aniline on the allyl ligand in **7c**, followed by insertion of the resulting *N*-allylaniline into PtH(OTf)(DPCB) (**4′**).

Generation and Reactions of Hydridopalladium(II) Triflate Complexes. Having the above findings about platinum complexes, we next examined the synthesis of palladium hydrides. Thus, PdMe(OTf)(DPCB) (**9**) was treated with $HSiMe_2Ph$ (1 equiv) and residual water in CH_2Cl_2. However, the system quickly turned darker even at −50 °C, and no identifiable palladium species was detected by NMR spectroscopy. On the other hand, in the presence of 1,3-cyclohexadiene (1.2 equiv), the same reaction system selectively formed the π-allyl complex **1e**, which was isolated in 72% yield (eq 3). This result may be taken as an indirect evidence

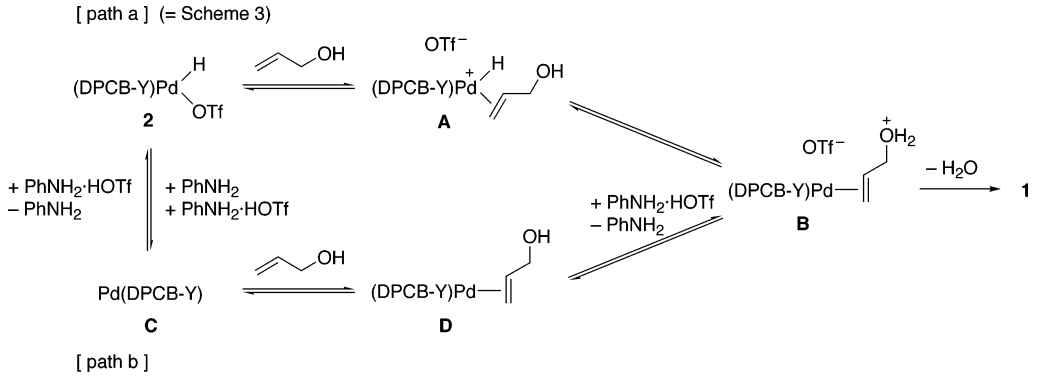


for the formation of hydridopalladium **2** in the reaction system.

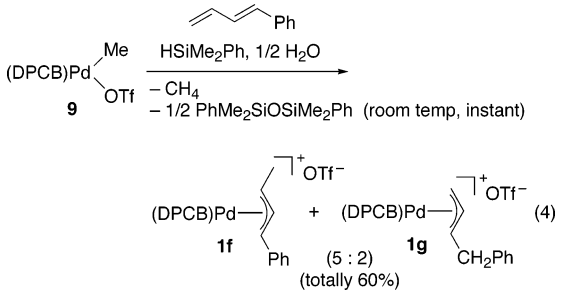
Similarly, the reaction of **9** with $HSiMe_2Ph$ (1 equiv) and residual water in CH_2Cl_2 in the presence of phen-

(12) LaPointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906.

Scheme 7

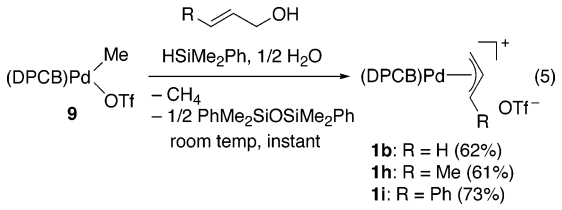


ylbutadiene (1.2 equiv) formed a 5:2 mixture of π-allyl complexes **1f**,**g** in 60% isolated yield (eq 4). When this



reaction was carried out in the presence of D_2O, the methyl group of the η^3-1-methyl-3-phenylallyl ligand in **1f** and the benzylic methylene group of the η^3-benzylallyl ligand in **1g** were deuterated as CH_2D and CHD, respectively. These observations strongly suggest the formation of PdH(OTf)(DPCB) (**2**) according to a process similar to that in Scheme 5.

π-Allyl complexes were also successfully prepared from allylic alcohols (eq 5). All reactions rapidly pro-



ceeded with stoichiometric amounts of allylic alcohols at room temperature, giving nearly quantitative yields of π-allyl complexes as confirmed by NMR spectroscopy. Unlike the reaction in Scheme 2a, no trace of diallyl ether was formed. Furthermore, no incorporation of deuterium into the allyl ligand of **1b** took place when the reaction was carried out in the presence of D_2O. It should be noted that the C−O bond cleavage process given in Scheme 2b very probably causes deuteration of allyl ligands by the sequence of insertion and elimination.

We could obtain a line of evidence for the C−O bond cleavage of allylic alcohols promoted by the hydridopalladium complex **2** (Scheme 3). However, we must still consider another possibility, as described in Scheme 7. Thus, complex **2** is possibly in a rapid equilibrium with the Pd(0) species **C** in solution. Coordination of allyl alcohol to **C** followed by protonation of the OH group in **D** forms **B**, which affords the π-allyl complex **1** simply by the elimination of water (path b). In this case, the relative ease of these two processes should be significantly affected by reaction conditions, especially by polarity and basicity of reaction media. Therefore, we next tried to examine these two possibilities using actual catalytic systems.

Table 1. Kinetic Data for Catalytic Allylation of Aniline with Allyl Alcohol

run[a]	$[PhNH_2]_0$ (M)	$[H_2O]_0$ (mM)[b]	$10^3 k_{obsd}$ (s^{-1})
1	0.48	1.2	0.39(1)
2	0.48	3.0	0.84(5)
3	0.48	4.0	0.91(4)
4	0.48	5.9	0.94(5)
5	0.48	7.8	0.91(3)
6	0.76	2.1	0.72(1)
7	1.10	2.9	0.76(2)
8[c]	0.48	6.0	2.0(1)

[a] All runs were examined at 10.0 ± 0.1 °C in toluene using **1c** as a catalyst. Initial concentration: $[C_3H_5OH]_0 = 0.048$ M, $[\mathbf{1c}]_0 = 0.26$ mM, except for run 8. [b] Initial concentration of water determined by the Karl Fischer method. [c] $[\mathbf{1c}]_0 = 0.51$ mM.

Kinetic Examinations for Catalytic Systems. Catalytic allylation of aniline with allyl alcohol at 10.0 °C in toluene in the presence of a catalytic amount of **1c** was followed by measuring the amounts of *N*-allylaniline formed at intervals by GLC. Table 1 lists the first-order rate-constants (k_{obsd}) thus observed. All runs were performed with 10 times or more excess amounts of aniline to hold the pseudo-first-order conditions. The first-order plots showed linearity over 90% conversion of allyl alcohol.

The reaction rate is notably enhanced as the initial concentration of water increases (runs 1−5) but much less sensitive to the concentration of aniline (runs 2, 6, and 7). Furthermore, the reaction became twice as fast when the amount of catalyst was increased 2-fold (runs 4 and 8). These tendencies are more clearly seen from the plot of k_{obsd} values against initial concentrations of water (Figure 2). Thus, the rate constant significantly increases with an increasing amount of water, while it becomes constant in the presence of over 4.0 mM of water. Although the exact reason for this unexpected effect of water is presently unclear, it seems reasonably that the present catalysis involving ionic intermediates (Scheme 7) is highly sensitive to the polarity of reaction media.[13]

(13) As suggested by a reviewer, the saturation behavior observed for water at higher concentrations is probably due to the limited solubility of water in toluene. We thank the reviewer for alerting us to this possibility.

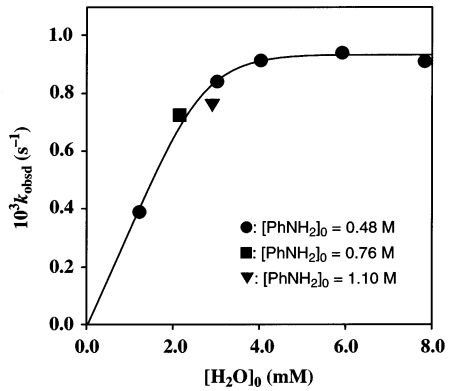


Figure 2. Plot of k_{obsd} values against the initial concentrations of H_2O. The experimental conditions are given in Table 1.

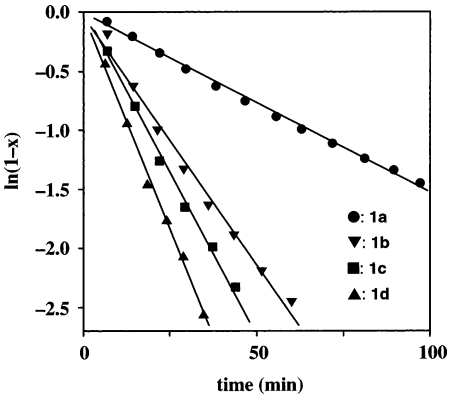


Figure 3. First-order plots for the reactions of allyl alcohol with aniline in toluene in the presence of **1a**−**d** as catalysts at 10.0 °C. The experimental conditions are given in Table 2.

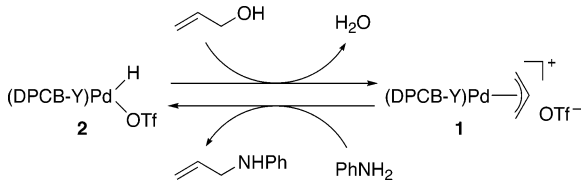
Table 2. Comparison of Catalytic Activity for Allylation of Aniline with Allyl Alcohol

run[a]	catalyst (Y) [σ_p]	$10^3 k_{obsd}$ (s^{-1})
1	**1a** (CF_3) [0.54]	0.253(5)
2	**1b** (H) [0.0]	0.70(3)
3	**1c** (OMe) [−0.27]	0.91(4)
4	**1d** (Ooctyl)[b]	1.22(7)

[a] All runs were examined in toluene at 10.0 ± 0.1 °C. Initial concentration: $[C_3H_5OH]_0$ = 0.048 M, $[PhNH_2]_0$ = 0.48 M, $[catalyst]_0$ = 0.26 mM, $[H_2O]_0$ = 3.9 ± 0.1 mM. [b] The σ_p value is unknown.

Figure 3 shows first-order plots for the reactions using catalysts **1a**−**d**, which were examined under the same reaction conditions. The catalytic activity increases in the order **1a** < **1b** < **1c** < **1d**, depending on substituents Y of the DPCB-Y ligands. Table 2 lists the rate constants estimated from the plots, together with the Hammett parameters of Y (σ_p). It is obvious that the catalytic activity is enhanced as the electron-donating ability of Y increases. We previously pointed out, on the basis of the X-ray structure of **1b**, that DPCB-Y complexes have a wide π-conjugation system, spread over the two phenyl groups, the diphosphinidenecyclobutene skeleton, and palladium.[14] This is due to the strong $d_\pi-p_\pi$ interaction between palladium and sp^2-hybridized phosphorus atoms. As a result, the catalytic activity is highly sensitive to the electronic nature of Y, despite its rather remote position from the metal center. The rate variation observed in Table 2 constitutes a representative example.

Scheme 8



Scheme 8 represents the catalytic cycle of the present allylation reaction, where hydrido and π-allyl complexes (**2** and **1**, respectively) are assumed as the key intermediates. Since the reaction rate is almost independent of the concentration of aniline, the C−O bond cleavage of allyl alcohol on the interaction with **2** should be rate determining and responsible for the dependence of the reaction rates on Y. In this situation, in contrast to the experimental results, one might consider that the more electron-withdrawing Y causes the higher acidity and reactivity toward the C−O bond cleavage. However, this apparent discrepancy may be reasonably resolved by assuming the equilibrium between **2** and **C** in Scheme 7 to be crucial for the rate of C−O bond cleavage.

The hydridopalladium species **2** is a Pd(II) complex, whereas **C** is a Pd(0) complex. Accordingly, the DPCB-Y ligands with low-lying π^* orbitals must stabilize more effectively the electron-rich, low-valent metal species **C**, rather than **2**, by π-back-donation. This tendency should be more remarkable for the ligand with an electron-withdrawing substituent Y. Thus, the equilibrium between **2** and **C** is expected to be shifted toward the side of **C** in the order **1d** < **1c** < **1b** <**1a**, as the electron-withdrawing ability of Y increases. This order is the reverse of that observed for the actual catalytic systems.

It should be noted that the present catalytic reactions are operative in the presence of a large excess amount of aniline, compared with the amount of palladium catalyst (i.e., $[aniline]_0/[catalyst]_0$ > 1800 for kinetic runs). Accordingly, the HOTf released with **C**, if any, must be neutralized by aniline in the catalytic solution (see Scheme 7). It is also noted that allyl alcohol is much less basic than aniline, making the protonation of the OH group in the catalytic solution very difficult. Hence, it is concluded that the C−O bond cleavage of allyl alcohol is promoted by hydrido complex **2** via the process given in path a in Scheme 7 (i.e., Scheme 3).

Conclusion

We could examine the mechanism of C−O bond cleavage of allylic alcohols in both stoichiometric and catalytic systems. All experimental observations were fully consistent with the process given in Scheme 3, where the hydridopalladium complex **2** bearing the DPCB-Y ligand serves as a key intermediate. The catalytic activity of this species is rather sensitive to the electronic property of Y on the ligand. Thus, the electron-donating nature of Y enhanced the catalytic activity, and this tendency could be rationalized by considering the thermodynamic stability of **2** in the equilibrium with the Pd(0) species **C**. It is interesting

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that the electron-donating nature is of importance in the stability of **2**, whereas the electron-accepting ability of DPCB-Y becomes crucial for generating a highly acidic hydride in **A** to cause the C−O bond cleavage of allylic alcohols under very mild conditions. The DPCB-Y ligands bearing sp^2-hybridized phosphorus atoms may interact very flexibly with palladium by σ-donation and π-back-donation interactions in an electronic sense, and this flexibility is the origin of the high catalytic activity of DPCB-Y complexes.

Experimental Section

General Considerations. All manipulations were performed under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was purified by passing through a column of P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 spectrometer (^{1}H NMR, 300.10 MHz; ^{13}C NMR, 75.46 MHz; ^{31}P NMR, 121.49 MHz). Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (of residual protons) and ^{13}C signals of the deuterated solvents or to the ^{31}P signal of external 85% H_3PO_4 standard. GLC analysis was performed on Shimadzu GC-14B (FID; CBP-1, 25 m × 0.25 mm) and GC-8A (TCD; PEG-20M, 1 m × 5 mm) instruments. IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Elemental analysis was performed on a Perkin-Elmer 2400II CHN analyzer. Residual water in reaction solutions was analyzed by the Karl Fisher method using a Hiranuma AQ-2000 instrument. Hexane, benzene, and Et_2O were dried over sodium benzophenone ketyl and distilled prior to use. Toluene was distilled from sodium benzophenone ketyl and stored over activated molecular sieves (MS4A). CH_2Cl_2 and $ClCH_2CH_2Cl$ were dried over CaH_2 and distilled prior to use. DPCB-CF_3 (**1a**),[14] DPCB (**1b**),[14,15] DPCB-OMe (**1c**),[14] Pt(cod)$_2$,[16] [Pd(η^3-C_3H_5)(μ-Cl)]$_2$,[17] PtMe(OTf)(DPCB) (**5**),[18] and PdMe(OTf)(DPCB) (**9**)[18] were prepared according to the literature. Allyl alcohol was distilled and stored over activated molecular sieves (MS4A). Aniline was distilled and stored under a nitrogen atmosphere. All other chemicals were obtained from commercial suppliers and used without purification.

Preparation of PtH(SiMe$_2$Ph)(DPCB) (3). DPCB (227 mg, 0.30 mmol) was added to a solution of Pt(cod)$_2$ (120 mg, 0.29 mmol) in toluene (6 mL) at −50 °C. The reaction mixture was stirred for 30 min at room temperature, and then $HSiMe_2Ph$ (445 μL, 2.90 mmol) was added. The solution changed from black to dark red. After the solution was stirred for 12 h, the solvent was removed by pumping. The residue was washed with Et_2O (2 mL × 4) at −50 °C and dried under vacuum to give a brownish red powder of **3** (227 mg, 72%), which was analytically pure. A crystalline compound was obtained by slow diffusion of a CH_2Cl_2 solution into Et_2O at −50 °C using a double-layer system (38%). ^{1}H NMR (CD_2Cl_2, 20 °C): δ −4.49 (dd, $^2J_{PH}$ = 229.6 and 15.0 Hz, $^1J_{PtH}$ = 1393.1 Hz, 1H, PtH), 0.38 (d, $^4J_{PH}$ = 3.9 Hz, $^3J_{PtH}$ = 33.6 Hz, 6H, SiMe), 1.43 (s, 9H, *p*-*t*-Bu), 1.44 (s, 9H, *p*-*t*-Bu), 1.58 (d, $^5J_{PH}$ = 1.2 Hz, 18H, *o*-*t*-Bu), 1.63 (d, $^5J_{PH}$ = 0.6 Hz, 18H, *o*-*t*-Bu), 6.80−6.87 (m, 4H, *o*-Ph), 6.92 (t, $^3J_{HH}$ = 7.8 Hz, 4H, *m*-Ph), 7.10−7.23 (m, 5H, *p*-Ph and SiPh), 7.56 (d, $^4J_{PH}$ = 2.7 Hz, 2H, *m*-PAr), 7.59 (d, $^4J_{PH}$ = 2.7 Hz, 2H, *m*-PAr), 7.67 (m, 2H, SiPh). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 7.1 (dd, $^3J_{PC}$ = 10 and 7 Hz, $^2J_{PtC}$ = 88 Hz, SiMe), 31.6 (s, *p*-C*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$), 34.2 (d, $^3J_{PC}$ = 3 Hz, $^2J_{PtC}$ = 9 Hz, *o*-C*Me*$_3$), 34.4 (s, $^3J_{PC}$ = 2 Hz, $^2J_{PtC}$ = 10 Hz, *o*-C*Me*$_3$), 35.7 (s, *p*-C*Me*$_3$), 38.9 (s, *o*-*C*Me$_3$), 39.6 (s, *o*-*C*Me$_3$), 122.8 (d, $^3J_{PC}$ = 6 Hz, *m*-PAr), 124.0 (d, $^3J_{PC}$ = 7 Hz, *m*-PAr), 126.9 (s, *o*- and *m*-SiPh), 127.8 (d, $^4J_{PC}$ = 6 Hz, *o*-Ph), 128.2 (d, $^4J_{PC}$ = 5 Hz, *o*-Ph), 128.4 (d, $^5J_{PC}$ = 2 Hz, *m*-Ph), 128.5 (d, $^5J_{PC}$ = 2 Hz, *m*-Ph), 129.3 (d, $^6J_{PC}$ = 4 Hz, *p*-Ph), 129.4 (d, $^6J_{PC}$ = 4 Hz, *p*-Ph), 131.4 (s, *ipso*-Ph), 131.6 (s, *ipso*-Ph), 132.0 (d, $^1J_{PC}$ = 3 Hz, *ipso*-PAr), 132.3 (d, $^1J_{PC}$ = 3 Hz, *ipso*-PAr), 135.2 (d, $^4J_{PC}$ = 1 Hz, $^3J_{PtC}$ = 34 Hz, *o*-SiPh), 147.9 (dd, J_{PC} = 53 and 34 Hz, P═C−*C*), 150.4 (dd, J_{PC} = 55 and 32 Hz, P═C−*C*), 150.9 (d, $^3J_{PC}$ = 7 Hz, *ipso*-SiPh), 153.0 (d, $^4J_{PC}$ = 1 Hz, *p*-PAr), 153.2 (d, $^4J_{PC}$ = 2 Hz, *p*-PAr), 155.8 (s, $^3J_{PtC}$ = 10 Hz, *o*-PAr), 156.6 (s, *o*-PAr), 174.3 (dd, J_{PC} = 44 and 33 Hz, P═C), 176.0 (dd, J_{PC} = 25 and 18 Hz, P═C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 178.9 (d, $^2J_{PP}$ = 13 Hz, $^1J_{PtP}$ = 2247 Hz), 186.2 (d, $^2J_{PP}$ = 13 Hz, $^1J_{PtP}$ = 915 Hz). IR (KBr): 2090 cm^{-1} (ν_{PtH}). Anal. Calcd for $C_{60}H_{80}P_2PtSi$: C, 66.33; H, 7.42. Found: C, 66.07; H, 7.50.

Preparation of [Pt$_2$(μ-H)$_2$(DPCB)$_2$](OTf)$_2$ (4) from 3. An Et_2O solution of HOTf (0.48 M, 0.96 mL, 0.46 mmol) was added to a suspension of PtH(SiMe$_2$Ph)(DPCB) (**3**; 501 mg, 0.46 mmol) in Et_2O (8 mL) at −50 °C. The dark red suspension changed to a reddish black solution. The reaction mixture was stirred for 30 min at room temperature, and then the solvent was removed by pumping. The residue was washed with a 3:1 mixture of hexane and Et_2O (3 mL × 5) and dried under vacuum to give a brownish red powder of **4** (451 mg, 89%), which was sufficiently pure for elemental analysis. Several attempts to obtain a crystalline product were unsuccessful. ^{1}H NMR (CD_2Cl_2, 20 °C): δ −8.10 (quin, $^2J_{PH}$ = 60.0 Hz, $^1J_{PtH}$ = 521.0 Hz, 2H, PtH), 1.45 (s, 36H, *p*-*t*-Bu), 1.53 (s, 72H, *o*-*t*-Bu), 6.88 (d, $^3J_{HH}$ = 8.2 Hz, 8H, *o*-Ph), 6.94 (t, $^3J_{HH}$ = 8.0 Hz, 8H, *m*-Ph), 7.22 (t, $^3J_{HH}$ = 6.6 Hz, 4H, *p*-Ph), 7.62 (br, 8H, PAr). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 31.5 (s, *p*-C*Me*$_3$), 34.5 (s, *o*-C*Me*$_3$), 35.9 (s, *p*-*C*Me$_3$), 39.2 (s, *o*-*C*Me$_3$), 120.6 (q, $^1J_{FC}$ = 321 Hz, CF_3), 123.8 (s, *m*-PAr), 127.4 (t, *J* = 8 Hz, *ipso*-PAr), 128.1 (s, *o*-Ph), 129.0 (s, *m*-Ph), 130.4 (s, *ipso*-Ph), 130.9 (s, *p*-Ph) 150.2 (m, P═C*C*), 155.3 (s, *p*-PAr), 157.3 (s, *o*-PAr), 171.2 (m, J_{PC} = 56 and 21 Hz, P═C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 152.4 (s, $^1J_{PtP}$ = 3455 Hz, $^3J_{PtP}$ = 342 Hz). IR (KBr): 2067 cm^{-1} (ν_{PtH}). Anal. Calcd for $C_{106}H_{138}F_6O_6P_4Pt_2S_2$: C, 57.86; H, 6.32. Found: C, 57.47; H, 6.51.

Preparation of 4 from PtMe(OTf)(DPCB) (5). $HSiMe_2Ph$ (44 μL, 0.29 mmol) was added to a solution of PtMe(OTf)(DPCB) (**5**; 312 mg, 0.28 mmol) in CH_2Cl_2 (10 mL; pretreated with water) at room temperature. The solution instantly changed from orange to dark red. GLC analysis revealed the formation of $PhMe_2SiOSiMe_2Ph$ (0.15 mmol) and methane (qualitative). The ^{31}P{^{1}H} NMR spectrum exhibited a set of signals assignable to the title compound. The solvent was removed by pumping, and the dark red solid was washed repeatedly with pentane and dried under vacuum to give a brownish red powder of **4** (160 mg, 52%).

The reaction of **5** (30 mg, 0.027 mmol) and $HSiMe_2Ph$ (4.1 μL, 0.027 mmol) was carried out in CD_2Cl_2 (0.7 mL, pretreated with D_2O) at room temperature in an NMR sample tube. The ^{31}P{^{1}H} NMR analysis revealed the formation of **4**, whereas no trace of the PtH signal was observed in the ^{1}H NMR spectrum. Similarly, **5** (30 mg) was treated with $DSiMe_2Ph$ (4.1 mL) in CD_2Cl_2 pretreated with H_2O. The ^{1}H NMR spectrum exhibited a triplet at δ 0.07 ($^2J_{HD}$ = 2.0 Hz, 3H) assignable to CH_3D, together with the signals of **4** and $PhMe_2SiOSiMe_2Ph$.

Reaction of 4 with 1,3-Cyclohexadiene. PtMe(OTf)(DPCB) (**5**; 250 mg, 0.22 mmol) and 1,3-cyclohexadiene (210 μL, 2.2 mmol) were dissolved in $ClCH_2CH_2Cl$ (5 mL, pretreated with H_2O) at room temperature. $HSiMe_2Ph$ (35 μL, 0.23 mmol) was added to generate the hydridoplatinum complex. The resulting solution was stirred at 50 °C for 3 h, and then volatile materials were removed by pumping. The residue was washed with Et_2O and dried under vacuum to give an orange powder of [Pt(η^3-cyclo-C_6H_9)(DPCB)]OTf (**7a**; 169 mg, 65%). ^{1}H NMR

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(CD_2Cl_2, 20 °C): δ 1.22−1.38 (m, 2H, $CH_2CH_2CH_2$), 1.47 (s, 18H, *p*-*t*-Bu), 1.53 (s, 18H, *o*-*t*-Bu), 1.65 (s, 18H, *o*-*t*-Bu), 2.07 (m, 2H, $CHCH_2$), 2.36 (m, 2H, $CHCH_2$), 5.46 (m, 3H, allyl H), 6.83 (d, $^3J_{HH}$ = 8.1 Hz, 4H, *o*-Ph), 7.01 (t, $^3J_{HH}$ = 7.8 Hz, 4H, *m*-Ph), 7.30 (t, $^3J_{HH}$ = 7.2 Hz, 2H, *p*-Ph), 7.71 (br, 4H, *m*-PAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 21.6 (s, $^3J_{PtC}$ = 12 Hz, $CH_2CH_2CH_2$), 27.8 (t, $^3J_{PC}$ = 4 Hz, $^2J_{PtC}$ = 24 Hz, $CHCH_2$), 31.4 (s, *p*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 34.1 (s, *o*-C*Me*$_3$), 35.9 (s, *p*-*C*Me$_3$), 39.0 (s, *o*-*C*Me$_3$), 39.1 (s, *o*-*C*Me$_3$), 79.7 (m, $^1J_{PtC}$ = 153 Hz, allyl $C^{1,3}$), 106.3 (t, $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 40 Hz, allyl C^2), 121.4 (q, $^1J_{FC}$ = 321 Hz, CF_3), 124.3 (t, *J* = 5 Hz, *m*-PAr), 125.0 (t, *J* = 7 Hz, *ipso*-PAr), 128.5 (s, *o*-Ph), 129.1 (s, *m*-Ph), 129.3 (s, *ipso*-Ph), 131.8 (s, *p*-Ph), 152.7 (m, J_{PtC} = 59 and 35 Hz, P═*C*C), 156.0 (s, *p*-PAr), 157.4 (s, $^3J_{PtC}$ = 13 Hz, *o*-PAr), 157.8 (s, $^3J_{PtC}$ = 14 Hz, *o*-PAr), 175.2 (m, J_{PC} = 66 and 7 Hz, P═C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 137.8 (s, $^1J_{PtP}$ = 4422 Hz). Anal. Calcd for $C_{59}H_{77}F_3O_3P_2PtS$: C, 60.04; H, 6.58. Found: C, 60.03; H, 6.81.

Reaction of 4 with 1-Phenylbutadiene. Complex **5** (250 mg, 0.22 mmol) was treated with 1-phenylbutadiene (286 mg, 2.2 mmol) and $HSiMe_2Ph$ (35 μL, 0.23 mmol) in $ClCH_2CH_2Cl$ (5 mL; pretreated with water) in a similar procedure. The product complex [Pt(η^3-1-methyl-3-phenylallyl)(DPCB)]OTf (**7b**) was isolated as an orange powder (195 mg, 72%). ^1H NMR (CD_2Cl_2, 20 °C): δ 0.99 (d, $^5J_{PH}$ = 1.5 Hz, 9H, *o*-*t*-Bu), 1.47 (s, 9H, *p*-*t*-Bu), 1.48 (s, 9H, *p*-*t*-Bu), 1.55 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 1.63 (d, $^5J_{PH}$ = 1.2 Hz, 9H, *o*-*t*-Bu), 1.73 (d, $^5J_{PH}$ = 1.2 Hz, 9H, *o*-*t*-Bu), 1.97 (m, 3H, CH*Me*), 4.16 (ddq, $^3J_{HH}$ = 12.2 and 6.0 Hz, $^3J_{PH}$ = 12.2 Hz, $^2J_{PtH}$ = 47.6 Hz, 1H, allyl H_{anti}), 4.99 (dd, $^3J_{HH}$ = 12.2 Hz, $^3J_{PH}$ = 13.0 Hz, $^2J_{PtH}$ = 52.0 Hz, 1H, allyl H_{anti}), 5.77 (t, $^3J_{HH}$ = 12.2 Hz, $^2J_{PtH}$ = 64.7 Hz, 1H, allyl $H_{central}$), 6.94−7.08 (m, 10H, Ph), 7.11−7.18 (m, 2H, Ph), 7.26−7.33 (m, 3H, Ph), 7.45 (dd, $^4J_{PH}$ = 3.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*-PAr), 7.70−7.80 (m, 3H, *m*-PAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 18.3 (d, $^3J_{PC}$ = 3 Hz, CH*Me*), 31.3 (s, *p*-C*Me*$_3$), 33.3 (s, *o*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 33.9 (s, *o*-C*Me*$_3$), 34.5 (s, *o*-C*Me*$_3$), 35.8 (s, *p*-*C*Me$_3$), 35.9 (s, *p*-*C*Me$_3$), 38.9 (d, $^3J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 39.4 (d, $^3J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 39.4 (d, $^3J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 39.7 (d, $^3J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 79.7 (m, $^1J_{PtC}$ = 119 Hz, allyl *C*HMe), 80.2 (s, $^1J_{PtC}$ = 117 Hz, allyl *C*HPh), 110.1 (t, $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 45 Hz, allyl $C_{central}$), 119.4 (m, *J* = 11 and 2 Hz, *ipso*-PAr), 119.8 (m, *J* = 12 and 2 Hz, *ipso*-PAr), 121.4 (q, $^1J_{FC}$ = 320 Hz, CF_3), 124.2 (d, J_{PC} = 6 Hz, Ph), 124.6 (m, $^3J_{PC}$ = 7 and 6 Hz, *m*-PAr), 125.9 (d, $^3J_{PC}$ = 9 Hz, *m*-PAr), 127.0 (d, J_{PC} = 2 Hz, Ph), 128.6−129.2 (m, Ph), 131.7 (d, $^6J_{PC}$ = 5 Hz, *p*-Ph), 131.9 (d, $^6J_{PC}$ = 5 Hz, *p*-Ph), 135.6 (d, J_{PC} = 6 Hz, Ph), 152.2 (m, J_{PC} = 55 and 32 Hz, P═C*C*), 156.1 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 156.3 (d, $^4J_{PC}$ = 2 Hz, *p*-PAr), 156.6 (d, $^4J_{PC}$ = 2 Hz, *o*-PAr), 157.3 (d, $^4J_{PC}$ = 2 Hz, *o*-PAr), 157.6 (d, $^4J_{PC}$ = 2 Hz, *o*-PAr), 171.2 (dd, J_{PC} = 66 and 13 Hz, P═C), 172.6 (dd, J_{PC} = 65 and 11 Hz, P═C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 137.2 (d, $^2J_{PP}$ = 20 Hz, $^1J_{PtP}$ = 4664 Hz), 140.5 (d, $^2J_{PP}$ = 20 Hz, $^1J_{PtP}$ = 4879 Hz). Anal. Calcd for $C_{63}H_{79}F_3O_3P_2PtS$: C, 61.50; H, 6.47. Found: C, 61.15; H, 6.27.

Reaction of 4 with Allyl Alcohol. PtMe(OTf)(DPCB) (**5**; 250 mg, 0.22 mmol) and allyl alcohol (150 μL, 2.2 mmol) were dissolved in $ClCH_2CH_2Cl$ (5 mL, pretreated with water) at room temperature. $HSiMe_2Ph$ (35 μL, 0.23 mmol) was added to the solution to generate the hydridoplatinum complex. The resulting solution was stirred at 50 °C for 5 h and then concentrated to dryness by pumping. The residue was washed with Et_2O and dried under vacuum to give an orange powder of [Pt(η^3-C_3H_5)(DPCB)]OTf (**7c**; 168 mg, 67%). ^1H NMR (CD_2Cl_2, 20 °C): δ 1.47 (s, 18H, *p*-*t*-Bu), 1.55 (s, 18H, *o*-*t*-Bu), 1.64 (s, 18H, *o*-*t*-Bu), 3.24 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 12.6 Hz, $^2J_{PtH}$ = 47.4 Hz, 2H, allyl H_{anti}), 4.71 (br, 2H, allyl H_{syn}), 5.33 (tt, $^3J_{HH}$ = 12.6 and 6.8 Hz, $^2J_{PtH}$ = 66.6 Hz, 1H, allyl $H_{central}$), 6.88 (d, $^3J_{HH}$ = 8.2 Hz, 4H, *o*-Ph), 7.03 (t, $^3J_{HH}$ = 7.7 Hz, 4H, *m*-Ph), 7.32 (t, $^3J_{HH}$ = 7.3 Hz, 2H, *p*-Ph), 7.71 (m, 4H, *m*-PAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 31.4 (s, *p*-C*Me*$_3$), 33.8 (s, *o*-C*Me*$_3$), 34.0 (s, *o*-C*Me*$_3$), 36.0 (s, *p*-*C*Me$_3$), 39.0 (s, *o*-*C*Me$_3$), 39.2 (s, *o*-*C*Me$_3$), 64.8 (m, $^2J_{PC}$ = 37 Hz, $^1J_{PtC}$ = 125 Hz, allyl $C^{1,3}$), 115.5 (t, $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 39 Hz, allyl C^2), 121.3 (q, $^1J_{FC}$ = 321 Hz, CF_3), 124.2 (t, *J* = 5 Hz, *m*-PAr), 124.4 (m, *ipso*-PAr), 128.5 (m, *o*-Ph), 129.2 (s, *m*-Ph), 129.2 (s, *ipso*-Ph), 132.0 (s, *p*-Ph), 152.9 (m, J_{PC} = 57 and 32 Hz, P═C*C*), 156.3 (s, *p*-PAr), 157.6 (s, $^3J_{PtC}$ = 16 Hz, *o*-PAr), 158.0 (s, $^3J_{PtC}$ = 14 Hz, *o*-PAr), 174.2 (dd, J_{PC} = 67 and 12 Hz, P═C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 133.6 (s, $^1J_{PtP}$ = 4549 Hz). Anal. Calcd for $C_{56}H_{73}F_3O_3P_2PtS$: C, 58.99; H, 6.45. Found: C, 58.89; H, 6.41.

Reaction of 4 with Crotyl Alcohol. In a similar procedure, an orange powder of [Pt(η^3-1-methylallyl)(DPCB)]OTf (**7d**) was obtained in 61% yield (155 mg) from **5** (250 mg, 0.22 mmol), crotyl alcohol (281 μL, 2.2 mmol), and $HSiMe_2Ph$ (35 μL, 0.23 mmol). ^1H NMR (CD_2Cl_2, 20 °C): δ 1.47 (s, 18H, *p*-*t*-Bu), 1.48 (d, $^5J_{PH}$ = 1.2 Hz, 9H, *o*-*t*-Bu), 1.57 (d, $^5J_{PH}$ = 1.0 Hz, 9H, *o*-*t*-Bu), 1.59 (d, $^5J_{PH}$ = 1.1 Hz, 9H, *o*-*t*-Bu), 1.68 (d, $^5J_{PH}$ = 1.1 Hz, 9H, *o*-*t*-Bu), 1.98 (m, 3H, CH*Me*), 3.01 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 12.9 Hz, $^2J_{PtH}$ = 46.0 Hz, 1H, allyl H_{anti}), 4.08 (ddq, $^2J_{HH}$ = 12.8 and 6.2 Hz, $^3J_{PH}$ = 12.8 Hz, $^2J_{PtH}$ = 51.0 Hz, 1H, allyl H_{anti}), 4.36 (br, 1H, allyl H_{syn}), 5.21 (m, $^3J_{HH}$ = 13.2 and 7.3 Hz, $^2J_{PtH}$ = 68.7 Hz, 1H, allyl $H_{central}$), 6.87 (m, 2H, *o*-Ph), 6.93 (m, 2H, *o*-Ph), 7.03 (t, $^3J_{HH}$ = 7.0 Hz, 4H, *m*-Ph), 7.31 (t, $^3J_{HH}$ = 7.1 Hz, 2H, *p*-Ph), 7.68 (dd, $^4J_{PH}$ = 4.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, *m*-PAr), 7.69 (dd, $^4J_{PH}$ = 3.8 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, *m*-PAr), 7.70 (dd, $^4J_{PH}$ = 4.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*-PAr), 7.76 (dd, $^4J_{PH}$ = 4.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, *m*-PAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 18.6 (d, $^3J_{PC}$ = 3 Hz, CH*Me*), 31.4 (s, *p*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 33.9 (d, $^4J_{PC}$ = 2 Hz, *o*-C*Me*$_3$), 34.0 (d, $^4J_{PC}$ = 2 Hz, *o*-C*Me*$_3$), 36.0 (s, *p*-*C*Me$_3$), 39.1 (d, $^3J_{PC}$ = 2 Hz, *o*-*C*Me$_3$), 39.2 (d, $^3J_{PC}$ = 2 Hz, *o*-*C*Me$_3$), 39.3 (d, $^3J_{PC}$ = 2 Hz, *o*-*C*Me$_3$), 39.3 (d, $^3J_{PC}$ = 2 Hz, *o*-*C*Me$_3$), 59.7 (d, $^2J_{PC}$ = 36 Hz, $^1J_{PtC}$ = 150 Hz, allyl CH_2), 84.2 (d, $^2J_{PC}$ = 34 Hz, $^1J_{PtC}$ = 94 Hz, allyl *C*HMe), 115.6 (t, $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 44 Hz, allyl $C_{central}$), 120.3 (d, $^1J_{PC}$ = 14 Hz, *ipso*-PAr), 121.2 (q, $^1J_{FC}$ = 321 Hz, CF_3), 123.6 (d, $^1J_{PC}$ = 7 Hz, *ipso*-PAr), 124.1 (d, $^3J_{PC}$ = 10 Hz, *m*-PAr), 124.3 (d, $^3J_{PC}$ = 10 Hz, *m*-PAr), 124.8 (d, $^3J_{PC}$ = 10 Hz, *m*-PAr), 128.3 (d, $^4J_{PC}$ = 6 Hz, *o*-Ph), 128.5 (d, $^4J_{PC}$ = 6 Hz, *o*-Ph), 129.0 (s, *m*-Ph), 129.3 (d, $^3J_{PC}$ = 3 Hz, *ipso*-Ph), 131.7 (d, $^6J_{PC}$ = 4 Hz, *p*-Ph), 131.8 (d, $^6J_{PC}$ = 4.0 Hz, *p*-Ph), 152.5 (dd, J_{PC} = 56 and 31 Hz, P═C*C*), 152.6 (dd, J_{PC} = 56 and 31 Hz, P═C*C*), 156.0 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 156.1 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 157.2 (m, $^2J_{PC}$ = 4 Hz, *o*-PAr), 157.3 (m, $^2J_{PC}$ = 2 Hz, *o*-PAr), 157.7 (m, $^2J_{PC}$ = 2 Hz, *o*-PAr), 157.8 (m, $^2J_{PC}$ = 1 Hz, *o*-PAr), 173.1 (dd, J_{PC} = 51 and 14 Hz, P═C), 174.1 (dd, J_{PC} = 51 and 13 Hz, P═C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 132.3 (d, $^2J_{PP}$ = 16 Hz, $^1J_{PtP}$ = 4641 Hz), 141.8 (d, $^2J_{PP}$ = 16 Hz, $^1J_{PtP}$ = 4584). Anal. Calcd for $C_{57}H_{75}F_3O_3P_2PtS$: C, 59.31; H, 6.55. Found: C, 59.23; H, 6.62.

Reaction of 4 with Cinnamyl Alcohol. The complex [Pt(η^3-1-phenylallyl)(DPCB)]OTf (**7e**) was similarly prepared in 65% yield (174 mg) as an orange powder, starting from **5** (250 mg, 0.22 mmol), cinnamyl alcohol (283 μL, 2.2 mmol), and $HSiMe_2Ph$ (35 μL, 0.23 mmol). ^1H NMR (CD_2Cl_2, 20 °C): δ 0.97 (d, $^5J_{PH}$ = 1.5 Hz, 9H, *o*-*t*-Bu), 1.45 (s, 9H, *p*-*t*-Bu), 1.46 (s, 9H, *p*-*t*-Bu), 1.58 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 1.60 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 1.73 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 3.24 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 12.3 Hz, $^2J_{PtH}$ = 48.2 Hz, 1H, allyl H_{anti}), 4.53 (m, 1H, H_{syn}), 5.22 (dd, $^3J_{HH}$ = 13.2 Hz, $^3J_{PH}$ = 13.5 Hz, $^2J_{PtH}$ = 53.1 Hz, 1H, allyl H_{anti}), 5.88 (m, $^3J_{HH}$ = 12.3 and 7.2 Hz, $^2J_{PtH}$ = 64.8 Hz, 1H, allyl $H_{central}$), 6.87 (m, $^3J_{HH}$ = 7.3 Hz, 2H, *o*-Ph), 6.97−7.04 (m, 8H, Ph), 7.11 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Ph), 7.20 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ph), 7.29 (m, 2H, Ph), 7.43 (dd, $^4J_{PH}$ = 3.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*-PAr), 7.66 (dd, $^4J_{PH}$ = 4.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*-PAr), 7.72 (dd, $^4J_{PH}$ = 4.2 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*-PAr), 7.76 (dd, $^4J_{PH}$ = 3.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*-PAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 31.4 (s, *p*-C*Me*$_3$), 33.3 (s, *o*-C*Me*$_3$), 34.0 (s, *o*-C*Me*$_3$), 34.6 (s, o−C*Me*$_3$), 35.9 (s, *p*-*C*Me$_3$), 36.0 (s, *p*-*C*Me$_3$), 39.0 (d, $^3J_{PC}$ = 2 Hz, *o*-*C*Me$_3$), 39.2 (d, $^3J_{PC}$ = 2 Hz, *o*-*C*Me$_3$), 39.3 (d, $^3J_{PC}$ = 2 Hz, *o*-*C*Me$_3$), 39.7 (d, $^3J_{PC}$ = 2 Hz, *o*-*C*Me$_3$), 60.9 (d, $^2J_{PC}$ = 33 Hz, $^1J_{PtC}$ = 148 Hz, allyl CH_2), 86.1 (d, $^2J_{PC}$ = 33 Hz, $^1J_{PtC}$ = 76 Hz, allyl

*C*HPh), 109.0 (t, $^2J_{PC}$ = 5 Hz, $^1J_{PtC}$ = 42 Hz, allyl $C_{central}$), 121.4 (q, $^1J_{FC}$ = 321 Hz, CF_3), 119.4 (d, $^1J_{PC}$ = 16 Hz, *ipso*-PAr), 124.2−124.8 (m, Ph, PAr), 127.2 (d, $^4J_{PC}$ = 2 Hz, *o*-Ph), 128.4 (d, J_{PC} = 2 Hz, Ph), 128.5 (d, J_{PC} = 2 Hz, Ph), 129.0−129.2 (m, Ph), 129.5 (s, *ipso*-Ph), 131.8 (d, $^6J_{PC}$ = 4 Hz, *p*-Ph), 132.1 (d, $^6J_{PC}$ = 5 Hz, *p*-Ph), 135.4 (d, J_{PC} = 6 Hz, Ph), 152.2 (m, J_{PC} = 55 and 31 Hz, P═C*C*), 152.7 (m, J_{PC} = 56 and 31 Hz, P═C*C*), 156.3 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 156.4 (d, $^4J_{PC}$ = 3.0 Hz, *p*-PAr), 156.7 (d, $^2J_{PC}$ = 1 Hz, $^3J_{PtC}$ = 11 Hz, *o*-PAr), 157.3 (d, $^2J_{PC}$ = 2 Hz, $^3J_{PtC}$ = 12 Hz, *o*-PAr), 157.6 (d, $^2J_{PC}$ = 3 Hz, $^3J_{PtC}$ = 14 Hz, *o*-PAr), 158.0 (d, $^2J_{PC}$ = 2 Hz, $^3J_{PtC}$ = 15 Hz, *o*-PAr), 171.5 (dd, J_{PC} = 67 and 14 Hz, P═C), 173.7 (dd, J_{PC} = 66 and 12 Hz, P═C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 128.5 (d, $^2J_{PP}$ = 12 Hz, $^1J_{PtP}$ = 4657 Hz), 142.5 (d, $^2J_{PP}$ = 12 Hz, $^1J_{PtP}$ = 4763 Hz). Anal. Calcd for $C_{62}H_{77}F_3O_3P_2PtS$: C, 61.22; H, 6.38. Found: C, 60.98; H, 6.29.

Reaction of 7c with $PhNH_2$. To a solution of **7c** (106 mg, 93.0 μmol) in benzene (4 mL) was added aniline (150 mg, 1.61 mmol). The mixture was stirred at 50 °C for 24 h. The solvent was removed by pumping, and the residue was repeatedly extracted with Et_2O and hexane (1:4). The combined extract was evaporated by pumping to give a brown oil, which was washed with hexane and dried under vacuum to afford a brownish yellow powder of [Pt($CH_2CH_2CH_2$NHPh-κ-*C*,*N*)(DPCB)]OTf (**8**; 81 mg, 71%). ^1H NMR (CD_2Cl_2, 20 °C): δ 0.99 (s, 9H, *p*-*t*-Bu), 1.43 (s, 9H, *o*-*t*-Bu), 1.47 (s, 9H, *o*-*t*-Bu), 1.63 (s, 9H, *p*-*t*-Bu), 1.75 (s, 9H, *o*-*t*-Bu), 1.78 (s, 9H, *o*-*t*-Bu), 2.49 (m, 2H, $PtCH_2$), 2.49 (m, 1H, NCH_2), 3.04 (m, 2H, CH_2CH_2-CH_2), 3.61 (brd, $^2J_{PH}$ = 74.4 Hz, 1H, NH), 3.63 (m, 1H, NCH_2), 6.85−7.25 (m, 15H, Ph), 7.68 (s, 3H, *m*-PAr), 7.77 (m, 1H, *m*-PAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 31.3 (s, *p*-C*Me*$_3$), 31.5 (s, *p*-C*Me*$_3$), 32.4 (m, $CH_2CH_2CH_2$), 32.5 (dd, $^2J_{PC}$ = 93 and 3 Hz, $PtCH_2$), 33.9 (s, *o*-C*Me*$_3$), 34.1 (dd, $^3J_{PC}$ = 9 and 4 Hz, NCH_2), 34.3 (s, *o*-C*Me*$_3$), 34.4 (m, *o*-C*Me*$_3$), 35.7 (s, *p*-*C*Me$_3$), 35.9 (s, *p*-*C*Me$_3$), 39.0 (s, *o*-*C*Me$_3$), 39.4 (s, *o*-*C*Me$_3$), 39.8 (m, *o*-*C*Me$_3$), 40.1 (m, *o*-*C*Me$_3$), 120.0 (d, $^1J_{PC}$ = 35 Hz, *ipso*-PAr), 121.3 (q, $^1J_{FC}$ = 321 Hz, CF_3), 122.6 (s, *o*-NAr), 124.2 (d, $^3J_{PC}$ = 8 Hz, *m*-PAr), 124.7 (d, $^3J_{PC}$ = 11 Hz, *m*-PAr), 124.9 (d, $^3J_{PC}$ = 7 Hz, *m*-PAr), 125.0 (d, $^1J_{PC}$ = 10 Hz, *ipso*-PAr), 125.3 (d, $^3J_{PC}$ = 11 Hz, *m*-PAr), 127.2 (s, *p*-NAr), 128.3 (d, $^2J_{PC}$ = 6 Hz, *o*-PAr), 128.5 (d, $^2J_{PC}$ = 6 Hz, *o*-PAr), 128.8 (s, *m*-Ph), 129.7 (s, *m*-NPh), 130.2 (s, *ipso*-Ph), 130.4 (s, *ipso*-Ph), 130.8 (d, $^6J_{PC}$ = 5 Hz, *p*-Ph), 130.9 (d, $^6J_{PC}$ = 5 Hz, *p*-Ph), 148.4 (d, $^3J_{PC}$ = 3 Hz, *ipso*-NPh), 151.7 (dd, J_{PC} = 58 and 33 Hz, P═C*C*), 152.5 (dd, J_{PC} = 54 and 29 Hz, P═C*C*), 154.5 (d, $^4J_{PC}$ = 2 Hz, *p*-PAr), 155.8 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 156.1 (d, $^2J_{PC}$ = 2 Hz, *o*-PAr), 156.9 (d, $^2J_{PC}$ = 3 Hz, *o*-PAr), 157.0 (s, *o*-PAr), 157.5 (d, $^2J_{PC}$ = 2 Hz, *o*-PAr), 166.8 (dd, J_{PC} = 79 and 21 Hz, P═C), 168.1 (dd, J_{PC} = 48 and 9 Hz, P═C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 117.3 (d, $^2J_{PP}$ = 16 Hz, $^1J_{PtP}$ = 5157 Hz, trans to NHPh), 174.9 (d, $^2J_{PP}$ = 16 Hz, $^1J_{PtP}$ = 1569 Hz, trans to CH_2). IR (KBr): 3200 cm^{-1} (ν_{NH}). Anal. Calcd for $C_{62}H_{80}F_3NO_3P_2PtS$: C, 60.38; H, 6.54; N, 1.14. Found: C, 60.31; H, 6.71; N, 1.28.

Reaction of PdMe(OTf)(DPCB) (9) with $HSiMe_2Ph$ in the Presence of 1,3-Cyclohexadiene. To a solution of **9** (51 mg, 50 μmol) in CH_2Cl_2 (3 mL; pretreated with water) were successively added 1,3-cyclohexadiene (5.7 μL, 60 μmol) and $HSiMe_2Ph$ (7.7 μL, 50 μmol) at room temperature. The solution instantly changed from orange to red. The resulting solution was stirred for 30 min and then filtered. The solvent was evaporated under reduced pressure, and the residue was washed with Et_2O and dried under vacuum to give [Pd(η^3-cyclo-C_6H_9)(DPCB)]OTf (**1e**) as a yellow powder (40 mg, 72%). ^1H NMR (CD_2Cl_2, 20 °C): δ 1.45 (s, 18H, *p*-*t*-Bu), 1.51 (s, 18H, *o*-*t*-Bu), 1.63 (s, 18H, *o*-*t*-Bu), 1.70 (br, 2H, $CH_2CH_2CH_2$), 2.20 (br, 4H, $CHCH_2$), 5.71 (t, $^3J_{HH}$ = 7.2 Hz, 1H, allyl $H_{central}$), 5.97 (m, 2H, allyl H_{syn}), 6.74 (t, $^3J_{HH}$ = 8.1 Hz, 4H, *o*-Ph), 6.97 (t, $^3J_{HH}$ = 7.9 Hz, 4H, *m*-Ph), 7.25 (t, $^3J_{HH}$ = 7.2 Hz, 2H, *p*-Ph), 7.66 (d, $^4J_{HH}$ = 9.7 Hz, 4H, *m*-PAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 0 °C): δ 21.5 (s, $CH_2CH_2CH_2$), 28.3 (s, $CHCH_2$), 31.3 (s, *p*-C*Me*$_3$), 33.4 (s, *o*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 35.7 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 94.3 (t, $^2J_{PC}$ = 18 Hz, allyl $C^{1,3}$), 111.6 (t, $^2J_{PC}$ = 8 Hz, allyl C^2), 120.9 (q, $^1J_{FC}$ = 320 Hz, CF_3), 123.6 (t, J = 4 Hz, *m*-PAr), 123.8 (t, J = 4 Hz, *m*-PAr), 126.3 (t, J = 5 Hz, *ipso*-PAr), 128.3 (s, *o*-Ph), 128.7 (s, *m*-Ph), 129.2 (s, *ipso*-Ph), 131.2 (s, *p*-Ph), 154.3 (m, J_{PC} = 62 and 42 Hz, P═C*C*), 154.9 (s, *p*-PAr), 156.7 (s, *o*-PAr), 156.9 (s, *o*-PAr), 174.6 (dd, J_{PC} = 29 and 26 Hz, P═C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 144.9 (s). Anal. Calcd for $C_{59}H_{77}F_3O_3P_2PdS$: C, 64.91; H, 7.11. Found: C, 64.53; H, 6.98.

Reaction of 9 with $HSiMe_2Ph$ in the Presence of 1-Phenylbutadiene. The reaction was similarly conducted with **9** (103 mg, 0.10 mmol), 1-phenylbutadiene (15.6 mg, 0.12 mmol), and $HSiMe_2Ph$ (15.1 μL, 0.10 mmol) in CH_2Cl_2 (3 mL, pretreated with water), and a 5:2 mixture of [Pd(η^3-1-methyl-3-phenylallyl)(DPCB)]OTf (**1f**) and [Pd(η^3-1-benzylallyl)(DPCB)]OTf (**1g**) was obtained (69 mg, 60%). **1f**: ^1H NMR ($CDCl_3$, 20 °C) δ 0.93 (d, $^5J_{PH}$ = 1.5 Hz, 9H, *o*-*t*-Bu), 1.44 (s, 9H, *p*-*t*-Bu), 1.46 (s, 9H, *p*-*t*-Bu), 1.50 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 1.53 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 1.60 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 1.89 (m, $^3J_{HH}$ = 6.3 Hz, $^4J_{PH}$ = 12.6 Hz, 3H, CH*Me*), 4.83 (ddq, $^3J_{HH}$ = 12.0 and 6.0 Hz, $^3J_{PH}$ = 12.0 Hz, 1H, allyl H_{anti}), 5.49 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 13.3 Hz, 1H, allyl H_{anti}), 6.39 (t, $^3J_{HH}$ = 12.5 Hz, 1H, allyl $H_{central}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 148.4 (d, $^2J_{PP}$ = 39 Hz), 150.8 (d, $^2J_{PP}$ = 39 Hz). **1g**: ^1H NMR ($CDCl_3$, 20 °C) δ 1.44 (s, 9H, *p*-*t*-Bu), 1.46 (s, 9H, *p*-*t*-Bu), 1.57 (s, 18H, *o*-*t*-Bu), 1.70 (d, $^5J_{PH}$ = 0.9 Hz, 18H, *o*-*t*-Bu), 3.41 (m, 2H, $PhCH_2$), 3.53 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 13.0 Hz, 1H, allyl H_{anti}), 4.66 (m, 1H, allyl H_{anti}), 4.80 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 6.8 Hz, 1H, allyl H_{syn}), 6.04 (td, $^3J_{HH}$ = 11.9 and 7.3 Hz, 1H, allyl $H_{central}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 143.7 (d, $^2J_{PP}$ = 33 Hz), 146.9 (d, $^2J_{PP}$ = 33 Hz). Anal. Calcd for $C_{63}H_{79}F_3O_3P_2PdS$: C, 66.27; H, 6.97. Found: C, 65.97; H, 6.96.

Reaction of 9 with $HSiMe_2Ph$ in the Presence of Allyl Alcohol. To a solution of **9** (51 mg, 50 μmol) in CH_2Cl_2 (2 mL, pretreated with water) were successively added allyl alcohol (4.1 μL, 60 μmol) and $HSiMe_2Ph$ (7.7 μL, 50 μmol) at room temperature. The solution instantly changed from orange to red. After 30 min, the solution was filtered and concentrated to dryness by pumping. The residue was washed with Et_2O and dried under vacuum to give a yellow powder of [Pd(η^3-C_3H_5)(DPCB)]OTf (**1b**; 33 mg, 62%). This product was identified by NMR spectroscopy using an authentic sample (vide infra).

Reaction of 9 with $HSiMe_2Ph$ in the Presence of Crotyl Alcohol. The complex [Pd(η^3-1-methylallyl)(DPCB)]OTf (**1h**) was similarly prepared in 61% yield using crotyl alcohol in place of allyl alcohol. ^1H NMR ($CDCl_3$, 20 °C): δ 1.45 (s, 27H, *o*- and *p*-*t*-Bu), 1.55 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 1.58 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 1.66 (d, $^5J_{PH}$ = 0.9 Hz, 9H, *o*-*t*-Bu), 1.92 (m, $^3J_{HH}$ = 6.0 Hz, $^4J_{PH}$ = 10.8 Hz, 3H, CH*Me*), 3.53 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 12.9 Hz, 1H, allyl H_{anti}), 4.71 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 7.1 Hz, 1H, allyl H_{syn}), 4.72 (ddq, $^3J_{HH}$ = 12.5 and 6.0 Hz, $^3J_{PH}$ = 12.5 Hz, 1H, allyl H_{anti}), 5.82 (ddd, $^3J_{HH}$ = 12.9, 12.5 and 7.1 Hz, 1H, allyl $H_{central}$), 6.77 (m, $^3J_{HH}$ = 7.7 Hz, 4H, *o*-Ph), 6.96 (t, $^3J_{HH}$ = 7.7 Hz, 4H, *m*-Ph), 7.24 (m, $^3J_{HH}$ = 7.7 Hz, 2H, *p*-Ph), 7.57 (dd, $^4J_{PH}$ = 3.0 Hz, $^4J_{HH}$ = 2.1 Hz, 1H, *m*-PAr), 7.61 (dd, $^4J_{PH}$ = 3.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, *m*-PAr), 7.62 (dd, $^4J_{PH}$ = 3.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*-PAr), 7.67 (dd, $^4J_{PH}$ = 3.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*-PAr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 19.7 (d, $^3J_{PC}$ = 4 Hz, CH*Me*), 31.4 (s, *p*-C*Me*$_3$), 33.3 (d, $^4J_{PC}$ = 2 Hz, *o*-C*Me*$_3$), 33.5 (d, $^4J_{PC}$ = 3 Hz, *o*-C*Me*$_3$), 33.7 (d, $^4J_{PC}$ = 3 Hz, *o*-C*Me*$_3$), 33.8 (d, J_{PC} = 2 Hz, *o*-C*Me*$_3$), 35.6 (s, *p*-C*Me*$_3$), 38.8 (s, *o*-C*Me*$_3$), 38.9 (s, *o*-C*Me*$_3$), 71.6 (dd, $^2J_{PC}$ = 30 and 5 Hz, allyl CH_2), 98.4 (dd, $^2J_{PC}$ = 30 and 6 Hz, allyl *C*HMe), 120.8 (q, $^1J_{FC}$ = 321 Hz, CF_3), 121.1 (t, $^2J_{PC}$ = 8 Hz, allyl $C_{central}$), 122.1 (d, $^1J_{PC}$ = 7 Hz, *ipso*-PAr), 123.3 (d, $^2J_{PC}$ = 8 Hz, *m*-PAr), 123.4 (d, $^2J_{PC}$ = 8 Hz, *m*-PAr), 123.8 (d, $^2J_{PC}$ = 8 Hz, *m*-PAr), 125.9 (d, $^1J_{PC}$ = 6 Hz, *ipso*-PAr), 128.0 (m, *o*-Ph), 128.5 (s, *m*-Ph), 128.6 (s, *m*-Ph), 129.0 (s, *ipso*-Ph), 131.1 (s, *p*-Ph), 131.2 (s, *p*-Ph), 153.9 (dd, J_{PC} = 53 and 33 Hz, P═C*C*), 154.9 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 155.0 (d,

$^4J_{PC}$ = 2 Hz, *p*-PAr), 156.6 (s, *o*-PAr), 156.8 (s, *o*-PAr), 156.9 (s, *o*-PAr), 157.2 (s, *o*-PAr), 173.6 (dd, J_{PC} = 40 and 20 Hz, P=C), 173.8 (dd, J_{PC} = 37 and 21 Hz, P=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 144.3 (d, $^2J_{PP}$ = 31 Hz), 148.7 (d, $^2J_{PP}$ = 31 Hz). Anal. Calcd for $C_{57}H_{75}F_3O_3P_2PdS$: C, 64.24; H, 7.09. Found: C, 64.17; H, 7.00.

Reaction of 9 with $HSiMe_2Ph$ in the Presence of Cinnamyl Alcohol. A similar reaction was performed with cinnamyl alcohol, and [Pd(η^3-1-phenylallyl)(DPCB)]OTf (**1i**) was isolated as a yellow powder in 73% yield. ^1H NMR ($CDCl_3$, 20 °C): δ 0.95 (s, 9H, *o*-*t*-Bu), 1.43 (s, 9H, *p*-*t*-Bu), 1.45 (s, 9H, *p*-*t*-Bu), 1.59 (s, 9H, *o*-*t*-Bu), 1.62 (s, 9H, *o*-*t*-Bu), 1.72 (s, 9H, *o*-*t*-Bu), 3.83 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 12.9 Hz, 1H, allyl H_{anti}), 4.94 (dd, $^3J_{HH}$ = 7.5 Hz, 1H, allyl H_{syn}), 5.73 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 13.5 Hz, 1H, allyl CH_{anti}Ph), 6.52 (ddd, $^3J_{HH}$ = 13.5, 12.9 and 7.5 Hz, 1H, allyl $H_{central}$), 6.76 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph), 6.82 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph), 6.93 (t, $^3J_{HH}$ = 8.1 Hz, 4H, Ph), 6.95 (t, $^3J_{HH}$ = 8.1 Hz, 1H, Ph), 7.06 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 7.36 (m, 1H, *m*-PAr), 7.40 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ph), 7.59 (m, 1H, *m*-PAr), 7.65 (s, 2H, *m*-PAr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 31.3 (s, *p*-C*Me*$_3$), 32.8 (d, $^4J_{PC}$ = 2 Hz, *o*-C*Me*$_3$), 33.6 (d, $^4J_{PC}$ = 2 Hz, *o*-C*Me*$_3$), 33.7 (d, $^4J_{PC}$ = 3 Hz, *o*-C*Me*$_3$), 34.1 (d, $^4J_{PC}$ = 3 Hz, o−C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.3 (s, *o*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 39.1 (s, *o*-*C*Me$_3$), 72.6 (dd, $^2J_{PC}$ = 28 and 5 Hz, allyl CH_2), 98.5 (dd, $^2J_{PC}$ = 30 and 6 Hz, allyl *C*HPh), 114.3 (t, $^2J_{PC}$ = 8 Hz, allyl $C_{central}$), 121.4 (q, $^1J_{FC}$ = 321 Hz, CF_3), 121.6 (m, J_{PC} = 9 and 1 Hz, *ipso*-PAr), 123.4 (s, *m*-PAr), 123.5 (s, *m*-PAr), 123.6 (d, $^3J_{PC}$ = 9 Hz, *ipso*-Ph), 126.1 (d, $^1J_{PC}$ = 7 Hz, *ipso*-PAr), 127.6 (t, J_{PC} = 4 Hz, *o*-Ph), 127.9 (d, $^4J_{PC}$ = 2 Hz, *o*-Ph), 128.0 (d, $^4J_{PC}$ = 1 Hz, *o*-Ph), 128.3 (d, $^4J_{PC}$ = 2 Hz, *o*-Ph), 128.4 (d, $^4J_{PC}$ = 1 Hz, *o*-Ph), 128.5 (d, $^5J_{PC}$ = 2 Hz, *m*-Ph), 128.6 (d, $^5J_{PC}$ = 2 Hz, *m*-Ph), 129.1 (t, *J* = 7 Hz, *m*-Ph), 129.5 (t, J_{PC} = 3 Hz, *ipso*-Ph), 131.1 (d, $^6J_{PC}$ = 4 Hz, *p*-Ph), 131.3 (d, $^6J_{PC}$ = 4 Hz, *p*-Ph), 134.9 (dd, J_{PC} = 8 and 4 Hz, *p*-Ph), 153.4 (dd, J_{PC} = 53 and 43 Hz, P=C*C*), 153.8 (dd, J_{PC} = 54 and 44 Hz, P=C*C*), 154.9 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 155.1 (d, $^4J_{PC}$ = 3.0 Hz, *p*-PAr), 156.2 (s, *o*-PAr), 156.6 (s, *o*-PAr), 156.9 (d, $^2J_{PC}$ = 2 Hz, *o*-PAr), 157.1 (s, *o*-PAr), 172.0 (dd, J_{PC} = 40 and 22 Hz, P=C), 173.8 (dd, J_{PC} = 38 and 20 Hz, P=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 143.5 (d, $^2J_{PP}$ = 48 Hz), 151.4 (d, $^2J_{PP}$ = 48 Hz). Anal. Calcd for $C_{62}H_{77}F_3O_3P_2PdS$: C, 66.03; H, 7.30. Found: C, 65.64; H, 6.96.

Preparation of [Pd(η^3-C_3H_5)(DPCB-CF_3)]OTf (1a). To a solution of DPCB-CF_3 (500 mg, 0.56 mmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (92 mg, 0.25 mmol) in CH_2Cl_2 (15 mL) was added AgOTf (130 mg, 0.51 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h and then filtered through a Celite pad to remove AgCl precipitated in the system. The solvent was removed by pumping. The residue was washed with Et_2O (20 mL) at −78 °C and dried under vacuum to give a yellow powder of **1a** (555 mg, 93%). This product was dissolved in a minimum amount of CH_2Cl_2 (ca. 0.5 mL), the solution was layered with Et_2O (5 mL), and this mixture was allowed to stand at room temperature to give yellow crystals (85%). ^1H NMR ($CDCl_3$, 20 °C): δ 1.44 (s, 18H, *p*-*t*-Bu), 1.52 (s, 18H, *o*-*t*-Bu), 1.62 (s, 18H, *o*-*t*-Bu), 3.91 (dt, $^3J_{HH}$ = 13.2 Hz, J_{PH} = 7.0 Hz, 2H, allyl H_{anti}), 5.11 (dt, $^3J_{HH}$ = 7.1 Hz, J_{PH} = 3.3 Hz, 2H, allyl H_{syn}), 6.06 (tt, $^3J_{HH}$ = 13.2 and 7.1 Hz, 1H, allyl $H_{central}$), 6.83 (d, $^3J_{HH}$ = 8.2 Hz, 4H, *o*-Ar), 7.23 (d, $^3J_{HH}$ = 8.2 Hz, 4H, *m*-Ar), 7.61 (d, $^4J_{PH}$ = 1.0 Hz, 2H, *m*-PAr), 7.64 (d, $^4J_{PH}$ = 1.0 Hz, 2H, *m*-PAr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 31.2 (s, *p*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 33.9 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 78.3 (t, $^2J_{PC}$ = 18 Hz, allyl $C^{1,3}$), 120.8 (q, $^1J_{FC}$ = 321 Hz, CF_3S), 123.2 (q, $^1J_{FC}$ = 273 Hz, Ar*C*F_3), 123.2 (t, $^2J_{PC}$ = 8 Hz, allyl C^2), 123.6 (t, $^3J_{PC}$ = 3 Hz, *m*-PAr), 123.7 (t, $^3J_{PC}$ = 3 Hz, *m*-PAr), 125.1 (t, *J* = 3 Hz, *ipso*-PAr), 125.7 (q, $^3J_{FC}$ = 4 Hz, *m*-Ar), 128.2 (s, *o*-Ar), 132.2 (s, *ipso*-Ar), 132.5 (q, $^2J_{FC}$ = 33 Hz, *p*-Ar), 152.2 (m, J_{PC} = 66 and 45 Hz, P=C*C*), 155.7 (s, *p*-PAr), 157.1 (s, *o*-PAr), 157.4 (s, *o*-PAr), 172.2 (dd, J_{PC} = 32 and 29 Hz, P=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 155.1 (s). Anal. Calcd for $C_{58}H_{71}F_9O_3P_2PdS$: C, 58.66; H, 6.03. Found: C, 58.27; H, 5.91.

The (π-allyl)palladium complexes **1b**−**d** were similarly prepared in 96, 89, and 56% yields, respectively.

[Pd(η^3-C_3H_5)(DPCB)]OTf (1b). ^1H NMR ($CDCl_3$, 20 °C): δ 1.44 (s, 18H, *p*-*t*-Bu), 1.51 (s, 18H, *o*-*t*-Bu), 1.61 (s, 18H, *o*-*t*-Bu), 3.73 (dt, $^3J_{HH}$ = 13.5 Hz, J_{PH} = 6.9 Hz, 2H, allyl H_{anti}), 4.99 (dt, $^3J_{HH}$ = 6.9 Hz, J_{PH} = 3.3 Hz, 2H, allyl H_{syn}), 5.94 (tt, $^3J_{HH}$ = 13.5 and 6.9 Hz, 1H, allyl $H_{central}$), 6.76 (d, $^3J_{HH}$ = 7.8 Hz, 4H, *o*-Ph), 6.96 (t, $^3J_{HH}$ = 7.8 Hz, 4H, *m*-Ph), 7.25 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *p*-Ph), 7.60 (d, $^4J_{PH}$ = 1.5 Hz, 2H, *m*-PAr), 7.63 (d, $^4J_{HH}$ = 1.5 Hz, 2H, *m*-PAr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 31.3 (s, *p*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 33.8 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 76.8 (t, $^2J_{PC}$ = 19 Hz, allyl $C^{1,3}$), 120.9 (q, $^1J_{FC}$ = 321 Hz, CF_3), 122.2 (t, $^2J_{PC}$ = 8 Hz, allyl C^2), 123.4 (t, *J* = 5 Hz, *m*-PAr), 123.5 (t, *J* = 4 Hz, *m*-PAr), 125.7 (t, *J* = 2 Hz, *ipso*-PAr), 128.1 (s, *o*-Ph), 128.7 (s, *m*-Ph), 128.9 (s, *ipso*-Ph), 131.4 (s, *p*-Ph), 154.0 (m, J_{PC} = 68 and 47 Hz, P=C*C*), 155.2 (s, *p*-PAr), 156.9 (s, *o*-PAr), 157.1 (s, *o*-PAr), 173.8 (dd, J_{PC} = 32 and 29 Hz, P=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 144.3 (s). Anal. Calcd for $C_{56}H_{73}F_3O_3P_2PdS$: C, 63.96; H, 7.00. Found: C, 63.81; H, 7.04.

[Pd(η^3-C_3H_5)(DPCB-OMe)]OTf (1c). ^1H NMR ($CDCl_3$, 20 °C): δ 1.45 (s, 18H, *p*-*t*-Bu), 1.52 (s, 18H, *o*-*t*-Bu), 1.61 (s, 18H, *o*-*t*-Bu), 3.64 (dt, $^3J_{HH}$ = 13.2 Hz, J_{PH} = 7.0 Hz, 2H, allyl H_{anti}), 3.74 (s, 6H, OMe), 4.92 (dt, $^3J_{HH}$ = 7.3 Hz, J_{PH} = 3.3 Hz, 2H, allyl H_{syn}), 5.86 (tt, $^3J_{HH}$ = 13.2 and 7.3 Hz, 1H, allyl $H_{central}$), 6.46 (d, $^3J_{HH}$ = 8.9 Hz, 4H, *m*-Ph), 6.71 (d, $^3J_{HH}$ = 8.9 Hz, 4H, *o*-Ph), 7.62 (d, $^4J_{PH}$ = 1.2 Hz, 2H, *m*-PAr), 7.64 (d, $^4J_{PH}$ = 1.2 Hz, 2H, *m*-PAr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 31.3 (s, *p*-C*Me*$_3$), 33.5 (s, *o*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 55.4 (s, OMe), 76.0 (t, $^2J_{PC}$ = 19 Hz, allyl $C^{1,3}$), 114.2 (s, *m*-Ar), 120.9 (q, $^1J_{FC}$ = 321 Hz, CF_3), 121.4 (s, *ipso*-Ar), 121.6 (t, $^2J_{PC}$ = 7 Hz, allyl C^2), 123.3 (t, *J* = 3 Hz, *m*-PAr), 123.4 (t, *J* = 4 Hz, *m*-PAr), 126.2 (t, *J* = 1 Hz, *ipso*-PAr), 130.1 (s, *o*-Ar), 152.9 (m, J_{PC} = 70 and 49 Hz, P=C*C*), 155.0 (s, *p*-PAr), 157.0 (s, *o*-PAr), 157.2 (s, *o*-PAr), 161.9 (s, *p*-Ar), 174.3 (dd, J_{PC} = 32 and 29 Hz, P=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 135.2 (s). Anal. Calcd for $C_{58}H_{77}F_3O_5P_2PdS$: C, 62.67; H, 6.98. Found: C, 62.55; H, 7.02.

[Pd(η^3-C_3H_5)(DPCB-OOct)]OTf (1d). ^1H NMR ($CDCl_3$, 20 °C): δ 0.89 (t, $^3J_{HH}$ = 6.7 Hz, 6H, $O(CH_2)_7CH_3$), 1.20−1.36 (m, 20H, $OCH_2CH_2(CH_2)_5$), 1.66−1.80 (m, 4H, OCH_2CH_2), 1.46 (s, 18H, *p*-*t*-Bu), 1.52 (s, 18H, *o*-*t*-Bu), 1.62 (s, 18H, *o*-*t*-Bu), 3.66 (dt, $^3J_{HH}$ = 13.4, J_{PH} = 7.0 Hz, 2H, allyl H_{anti}), 3.86 (t, $^3J_{HH}$ = 6.6 Hz, 4H, OCH_2), 4.94 (dt, *J* = 7.1, J_{PH} = 3.6 Hz, 2H, allyl H_{syn}), 5.89 (tt, *J* = 13.4 and 7.1 Hz, 1H, allyl $H_{central}$), 6.43 (d, $^3J_{HH}$ = 9.0 Hz, 4H, *m*-Ph), 6.70 (d, $^3J_{HH}$ = 9.0 Hz, 4H, *o*-Ph), 7.62 (d, $^4J_{PH}$ = 1.2 Hz, 2H, *m*-PAr), 7.64 (d, $^4J_{PH}$ = 1.2 Hz, 2H, *m*-PAr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 14.1 (s, $O(CH_2)_7CH_3$), 22.6 (s, $O(CH_2)_6CH_2$), 25.9 (s, $O(CH_2)_5CH_2$), 28.9 (s, $O(CH_2)_4CH_2$), 29.2 (s, $O(CH_2)_3CH_2$), 29.2 (s, $O(CH_2)_2CH_2$), 31.4 (s, *p*-C*Me*$_3$), 31.8 (s, OCH_2CH_2), 33.6 (s, *o*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 68.3 (s, OCH_2), 76.2 (t, $^2J_{PC}$ = 20 Hz, allyl $C^{1,3}$), 114.6 (s, *m*-Ph), 120.9 (q, $^1J_{FC}$ = 321 Hz, CF_3), 121.3 (s, *ipso*-Ph), 121.7 (t, $^2J_{PC}$ = 8 Hz, allyl C^2), 123.3 (t, *J* = 4 Hz, *m*-PAr), 123.4 (t, *J* = 4 Hz, *m*-PAr), 126.3 (t, *J* = 2 Hz, *ipso*-PAr), 130.2 (s, *o*-Ar), 152.9 (m, J_{PC} = 70 and 47 Hz, P=C*C*), 155.0 (s, *p*-PAr), 157.0 (s, *o*-PAr), 157.2 (s, *o*-PAr), 161.5 (s, *p*-Ar), 174.3 (dd, J_{PC} = 32 and 29 Hz, P=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 135.2 (s). Anal. Calcd for $C_{72}H_{105}F_3O_5P_2PdS$: C, 66.11; H, 8.09. Found: C, 66.24; H, 8.39.

Kinetic Examinations. Two Schlenk tubes (A and B) equipped with a water jacket were connected to a thermostated bath controlled to 10.0 ± 0.1 °C. Complex **1c** (2.3 mg, 2.1 μmol) was introduced into A and dissolved in 5.5 mL of toluene containing a known amount of water. On the other hand, allyl alcohol (35.7 mg, 0.61 mmol), aniline (572.2 mg, 6.1 mmol), and diphenyl (94.7 mg, 0.61 mmol) as an internal standard for GLC analysis were placed in B and dissolved in the desired

amounts of wet and dry toluenes to adjust the total volume of the solution to 4.0 mL. A part of this solution (1.5 mL) was subjected to the Karl Fischer analysis to determine the concentration of water. The remaining part of the solution in B was transferred into A by cannulation to start the catalytic reaction. The amounts of *N*-allylaniline produced at intervals were followed by GLC.

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