Palladium-Catalyzed Deallylation of Allyl Ethers with a Xanthene Phosphole Ligand. Experimental and DFT Mechanistic Studies

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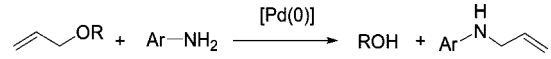
A cationic xanthene phosphole palladium allyl complex efficiently catalyzes the deallylation of allyl ethers into alcohols and the concomitant formation of allyl amines. Parallel experiments and DFT calculations show that acidic catalysis plays a significant role in promoting the cleavage of the C−O bond in a 16 VE complex featuring an allyl ether as η^2-ligand.

Introduction

Allyl groups have found a widespread use in organic synthesis as versatile protecting groups of alcohols, amines, and acids, due to their availability and to the stability of the corresponding allyl derivatives formed toward various reactions conditions.[1,2] For instance, allylic protecting groups proved to be very useful in both carbohydrate chemistry and peptide synthesis, where protecting and deprotecting steps are often crucial.[1b,2b] Deprotection of allyl ethers through direct C−O bond cleavage has therefore been widely studied and various more or less convenient catalytic procedures have been devised,[3] often with palladium,[4–11] but also with other metals.[12–15] However, catalytic processes allowing the formation of the desired alcohols concomitantly with that of a new allyl derivative of synthetic relevance are very attractive and have not been exploited much with allyl ethers.[1,2] These methods have been used extensively with allyl esters, carbonates, and carbamates[16–23] and were hardly used with allyl ethers because of the difficulty of usual palladium(0) complexes to promote the cleavage of the $C_{allyl}-O_{ether}$ bond. Toward this aim, new ligands have been designed in order to combine both the $C_{allyl}-O$ bond cleavage of allyl ethers and the interesting $C_{allyl}-$nucleophile bond formation. Over the past few years, nucleophiles such as amines,[4] sulfinic acids,[5,6] or *N*,*N*′-dimethylbarbituric acid[7] proved to be efficient as allyl scavengers. This process, which is related to the Tsuji−Trost nucleophilic allylation,[24] was thought to involve palladium−allyl complexes as intermediates, and when aryl amines are employed as co-reagent, its mechanism is probably very close to that accounting for the direct allylation with allyl alcohols[25] (Scheme 1).

Scheme 1. Palladium-Catalyzed Allylation of Arylamines through C−O Bond Cleavage of Allyl Ethers



Very recently, we reported on the synthesis of monomeric and dimeric palladium(0) complexes of the xanthene phosphole ligand and showed that these complexes act as very efficient catalysts in the allylation of arylamines from allyl alcohols.[26] Herein, we present results of a study aimed at exploring the catalytic activity of these new complexes in the allylation of amines through the C−O bond cleavage of allyl ethers. Furthermore, evidence on the mechanism of this transformation, obtained through experimental and theoretical studies, is also presented.

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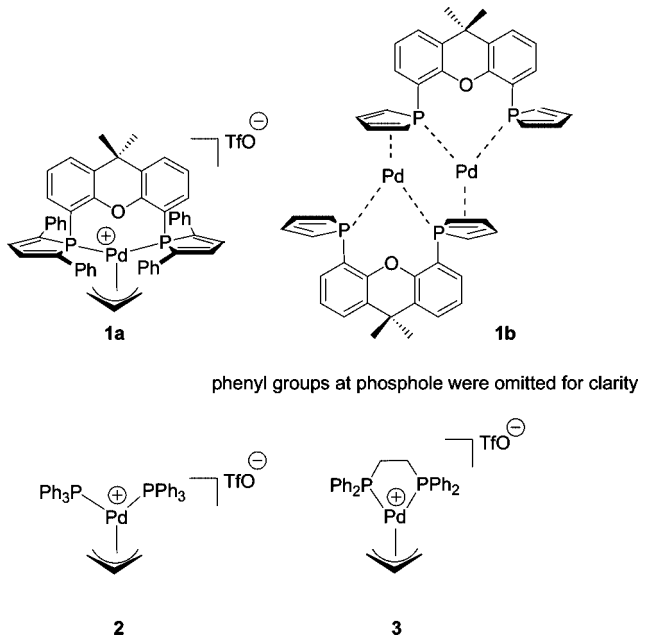
Scheme 2. Catalysts Investigated in the Deallylation of Allyl Ethers



Results and Discussion

Catalytic Experiments. A first series of experiments were carried out with complex [Pd(allyl)(DPP-Xantphos)][OTf], **1a** (Scheme 2), whose synthesis was reported in a recent article.[26] Reactions were conducted on alkyl- and phenyl-substituted allyl ethers using 10 equiv of aniline, which was used as both reagent and solvent. As can be viewed in Table 1 (see entries 1 to 4), deallylation of phenyl allyl ether proceeded much more faster than that of alkyl derivatives and can be completed using only 0.1 mol % of catalyst at 30 °C within 40 min (Table 1, entry 1). Longer reaction times, heating, and higher loading of catalyst (1 mol %) were needed to reach completion with alkyl derivatives (Table 1, entries 2 to 4). Large excess of aniline and the absence of solvent (aniline is the solvent) were shown to significantly accelerate the reaction rate. Under the same experimental conditions (1 mol % of catalyst **1a**, 50 °C) but with only 2 equiv of aniline and THF as solvent, the deallylation of allyl hexyl ether and allyl 2,5-dimethylcyclohexyl ether was completed in 12 h (instead of 1 h). However allyl phenyl ether remains easier to convert, the complete conversion being obtained in 4 h, at 30 °C. Addition of the ammonium NH_4PF_6 (20 mol %) considerably improves the catalytic performance of **1a**. Complete conversion for the deallylation of allyl alkyl ethers can thus be obtained with 1 mol % of **1a** at room temperature (Table 2, entries 1 to 3, compare with Table 1) in less than 8 h.

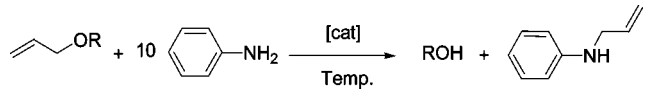
Strong π-acceptor ligands such as the DPP−Xantphos (DPP = diphenylphosphole) were shown to efficiently catalyze the allylation of arylamines with allylic alcohols, promoting the decomplexation of the allylammonium from the transient 16 VE complexes [Pd(L_2)(η^2-olefin)] formed (L_2 being two monodentate or a bidentate four-electron donor ligand).[25,26] In order to assess the specificity of DPP−Xantphos palladium allyl complex **1a**, [Pd(PPh_3)$_2$(η^3-allyl)][OTf] (**2**) and [Pd(DPPE)(η^3-allyl)][OTf] (**3**) (DPPE = 1,2-bis(diphenylphosphino)ethane) were synthesized and tested in the deallylation of allyl ether (Scheme 2). These two complexes were shown to act as very modest catalysts, suggesting that this deallylation process probably follows the same reaction path as that of the allylation of arylamines. Thus, under neat conditions (10 equiv of amines without solvent) with 2 mol % of catalyst at 50 °C only a partial conversion of 45% was recorded (Table 1, entry 6) with complex **2**, whereas no conversion was observed with complex **3** (Table 1, entry 7) when *n*-octyl allyl ether was used as substrate (compare with entry 4 using **1a** as catalyst). Addition of NH_4PF_6 (20 mol %) slightly improves the catalytic activity of complex **2**, while complex **3** remains inefficient (Table 2, entries 4 and 5).

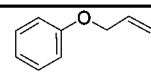
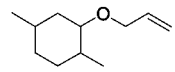
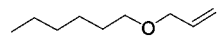
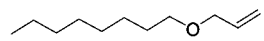
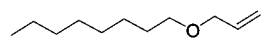
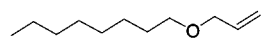
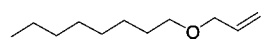
To complete this study, additional experiments were carried out using the insoluble dimeric complex **1b** (Scheme 2) as catalyst and again NH_4PF_6 as acidic promoter (20 mol %). **1b** is a catalytic intermediate of the allylation of aniline with allyl alcohol, resulting from the addition of excess aniline on the palladium(allyl) complex **1a**. As previously noted during our study on the allylation of amines, catalytic performances of this dimer assisted with the proton source were found to be quite similar to that of catalyst **1a** (Table 1, entry 5).[26]

In order to gain further insights on the mechanism of this transformation, each allyl ether was reacted with complex **1b** at 50 °C in acetonitrile in order to establish the transient formation of an η^2-allyl ether palladium complex. In each case a new complex was systematically formed highlighted by the fact that the mixture turned from unclear orange to pale yellow. Formation of this new complex was also evidenced by ^{31}P NMR spectroscopy, which revealed the appearance of a singlet around 0 ppm (complex **1b** being NMR silent because of its insolubility). This chemical shift was attributed to the formation of complex **1c** (Scheme 3). Unfortunately despite many attempts, complex **1c** could not be spectroscopically nor structurally characterized probably because of the lability of the coordinated alkene. Indeed, any purification attempts and crystallizations resulted in the re-formation of the insoluble dimer **1b**. Therefore without any further spectroscopic data we could not determine whether **1c** is a 16 VE or a 18 VE complex featuring one or two η^2-coordinated molecules of allyl ether. Importantly, analysis of a crude catalytic mixture by ^{31}P NMR spectroscopy also revealed the unique presence of this signal around 0 ppm, suggesting the involvement of **1c** as an intermediate in the reaction process. An important indirect evidence of the formation of this mono or bis η^2-allyl complex was given by the reaction of **1c** with a proton source (NH_4PF_6). Indeed, this reaction results in the formation of the cationic palladium allyl complex **1d** (**1a** with PF_6^- as counteranion), which was fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of hexanes in a saturated dichloromethane solution of the complex. This structure, which is analogous to that of the triflate salt reported in a previous study,[26] is described in the Supporting Information available. Interestingly, when the complex **1d** was crystallized from the crude reaction mixture, the unit cell also contains half a phenol molecule formed during the deallylation of the allyl phenyl ether.

Formation of the allyl complex **1d** from the hypothetical complex **1c** constitutes an interesting insight on the reaction mechanism since it shows that the C−O bond cleavage can be assisted by a proton source. Indeed it is important to keep in mind that in the mechanism proposed for the allylation of primary amines from allylic alcohols, initiation of the process is also promoted by the protonation of the alcohol group.[25a] When cationic allyl complexes are employed as catalysts without any proton source as additive, the allylammonium released after the attack of the amine on the allyl ligand serves as an acidic promoter. When palladium(0) complexes are used as catalysts, such as in the case of dimer **1b**, a proton source can be added

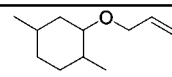
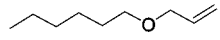
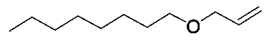
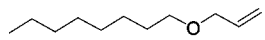
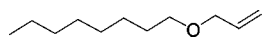
Table 1. Deallylation of Allyl Alkyl Ethers in Aniline Using Catalysts 1a, 1b, 2, and 3[a]



Entry	Catalyst (mol %)	Substrate	Temp.(°C)	Time	Yield
1	**1a** (0.1mol %)		30	40 min	98%
2	**1a** (1mol %)		50	1h	95%
3	**1a** (1mol %)		50	1h	98%
4	**1a** (1mol %)		50	4h	95%
5[b]	**1b** (0.5 mol %)		50	4h	96%
6	**2** (2mol %)		50	24h	45%
7	**3** (2 mol %)		50	24h	0%

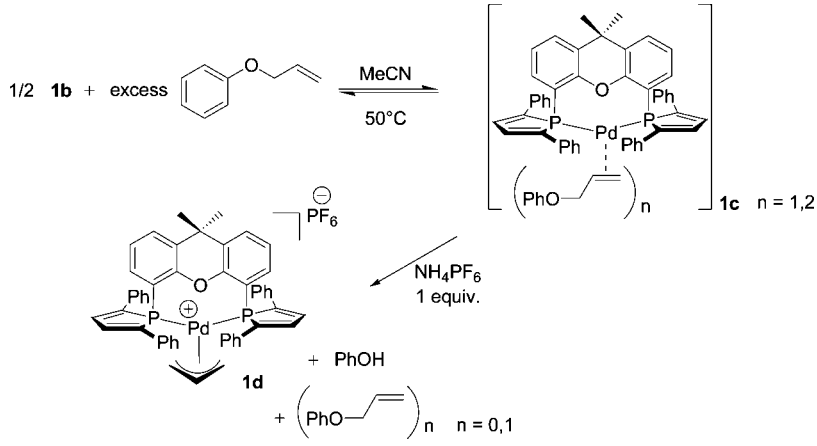
[a] Reactions conditions: 0.5 mmol of ROC_3H_5, 5 mmol of $PhNH_2$, and catalyst. After the reaction time indicated corresponding to a complete conversion by GC, the reaction mixture was evaporated, diluted into water, and extracted with ether. After usual workup, the organic layer was purified by flash column chromatography. [b] Additive NH_4PF_6 20 mol %.

Table 2. Deallylation of Allyl Alkyl Ethers in Acetonitrile Using Catalyst 1a, 2, and 3 and Additive NH_4PF_6[a]

Entry	Catalyst (mol %)	Substrate	Temp.(°C)	Time	Yield
1	**1a** (1mol %)		RT	4h	99%
2	**1a** (1mol %)		RT	6h	94%
3	**1a** (1mol %)		RT	8h	97% (23%)[b]
4	**2** (2 mol %)		50	24h	73%
5	**3** (2 mol %)		50	24h	0%

[a] Reaction conditions: 0.5 mmol of ROC_3H_5, 5 mmol of $PhNH_2$, catalyst, 0.1 mmol of NH_4PF_6 (20 mol %), and 1 mL of acetonitrile have been added. [b] Without the use of NH_4PF_6.

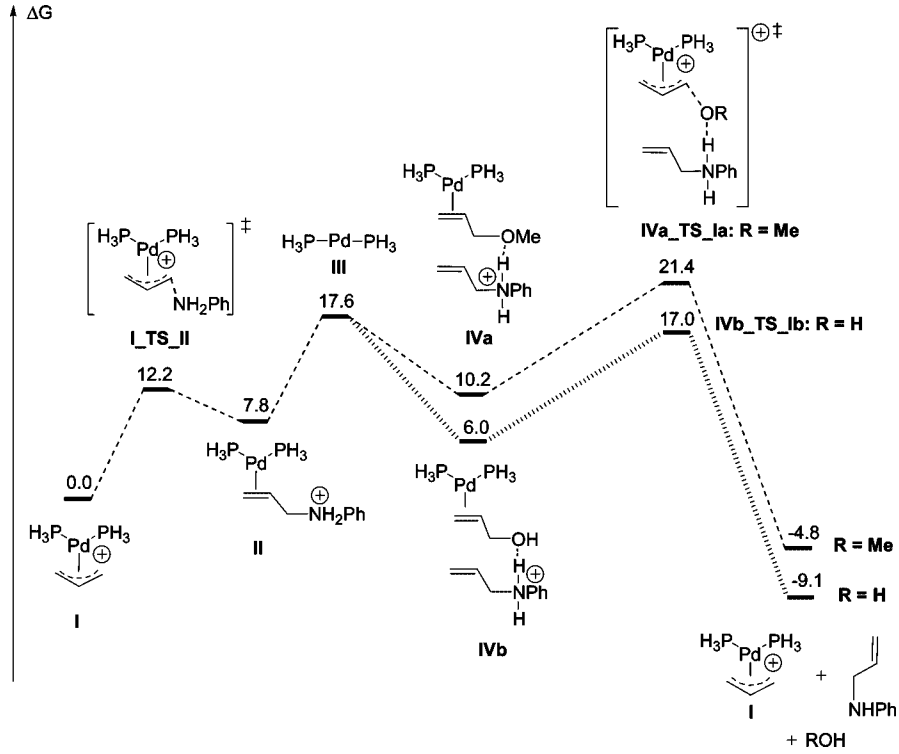
Scheme 3. Formation of an η^2-Allyl Ether Palladium Complex and Protonation with NH_4PF_6 to Form the Corresponding η^3-Allyl Complex



or nonpurified amines, featuring traces of the corresponding ammonium salts, can also be employed. The better results obtained in the presence of 20 mol % of NH_4PF_6 (Table 2, compare with Table 1) are thus due to the rise of probability for **1c** to be protonated by an ammonium salt. Thus the addition of a proton source to the catalytic systems should constitute an interesting improvement of the nucleophile-assisted deallylation processes.

DFT Study. A DFT study was carried out in order to check whether, as proposed, the two mechanisms are identical, the

Scheme 4. Comparison of the Energetic Profiles of the Allylation Reaction and the Deallylation Reaction (energies are given in kcal/mol)



main difference residing in the elimination of an alcohol versus the elimination of water in the allylation of amines from primary alcohols. All calculations were carried out using the Gaussian 03 set of programs[27] with the B3PW91[28,29] functional, the 6-31+G* basis set for all nonmetallic atoms (H, C, O, P, N), and the Hay and Wadt[30] small core quasirelativistic effective core potential with the double-ζ valence basis set (441s/2111p/311d) augmented with an f-polarization function (exponent = 1.472)[31] for palladium. Structures of the intermediates and transition states were optimized without symmetry constraints, and transition states were identified by having one imaginary frequency in the Hessian matrix. Given the size of the ligand, calculations were carried out using PH_3 as model ligand. This approach already proved to be successful in a previous study on the allylation of primary amines,[25a] the main purpose of the present study being to establish whether the replacement of the alcohol group by an ether group significantly affects the energetic profile of the process. Therefore the two mechanisms were compared and the two computed energetic pathways are presented in Scheme 4. As can be seen, these two pathways differ only by the coordination of the second alkene (allyl alcohol versus allyl ether) and the elimination step.

Indeed, the kinetics ($\Delta G_{\mathbf{IVa\_TS\_Ia}}^{\ddagger} = 11.2$ kcal mol^{-1} vs $\Delta G_{\mathrm{IVb\_TS\_Ib}}^{\ddagger} = 11.0$ kcal mol^{-1}) as well as the thermodynamics ($\Delta G_{\mathbf{IVa_TS_Ia}} = 15.0$ kcal mol^{-1} vs $\Delta G_{\mathbf{IVb\_TS\_Ib}} = 15.1$ kcal mol^{-1}) of these two processes were found to be broadly similar. The main difference results in the coordination step of the allyl ether, which is less exothermic than that of the allyl alcohol ($\Delta G_{\mathbf{III_IVa}} = -7.5$ kcal mol^{-1} vs $\Delta G_{\mathbf{III\_IVb}} = -11.5$ kcal mol^{-1}), thus rendering the elimination step more difficult by about 4 kcal mol^{-1}. A view of transition state **IVa_TS_Ia** is presented in Figure 1, and the most significant theoretical bond lengths and bond angles are listed in the corresponding legend.

In conclusion, we devised a very efficient catalytic system for the deallylation of allyl ethers as well as for the allylation of primary amines using allyl ether alcohols as substrates. As initially proposed, the mechanism of this transformation is similar to that of the allylation of amines from allylic alcohols and relies on the transient formation of 16 VE [Pd(L_2)(η^2-allyl ether)] complexes, which under acidic catalysis eliminate one molecule of the corresponding alcohol and generate palladium(allyl) complexes, which are the real active species. Further

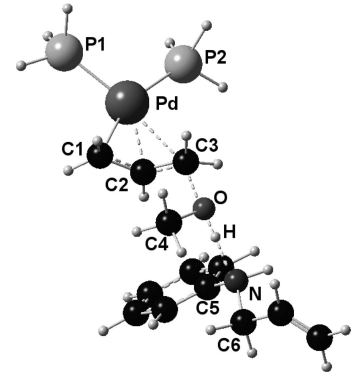


Figure 1. View of the transition state **IVa_TS_Ia** explaining the formation of alcohols through a combined Pd/H^+ catalysis. Most significant bond distances (Å) and angles (deg): Pd−P1, 2.334; Pd−P2, 2.363; Pd−C1, 2.111; Pd−C2, 2.184;Pd−C3, 2.783; C3−O, 1.844; O−C4, 1.431; O−H, 1.037; H−N, 1.640; N−C5, 1.433; N−C6, 1.488; P1−Pd−P2, 103.0, C3−O−H, 109.7; O−H−N, 177.2.

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experiments aimed at expanding this metal/H^+ combination in other related catalytic processes are currently underway in our laboratories.

Experimental Section

Synthesis. All reactions were routinely performed under an inert atmosphere of argon or nitrogen using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry hexanes were obtained by distillation from Na/benzophenone. Dry dichloromethane was distilled on P_2O_5 and dry toluene on metallic Na. Nuclear magnetic resonance spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for 31P. Solvent peaks are used as internal reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. DPP−Xantphos and [Pd(allyl)(DPP−Xantphos)] (**1a**) were prepared as previously reported.[26] Allyl hexyl ether was synthesized as described in the literature.[7] Allyl 2,5-dimethylcyclohexyl ether was synthesized using the same protocol (NMR descriptions in the Supporting Information). All other reagents and chemicals were obtained commercially and used as received. Elemental analyses were performed by the "Service d'Analyse du CNRS", at Gif sur Yvette, France. The GC conversions were determined on a Perichrom 2100 gas chromatograph equipped with a Perichrom column (Silicone OV1, CP-SIL 5 CB), 30 m × 0.22 mm.

Synthesis of Complex [Pd(C_3H_5)(DPP−Xantphos)][PF_6], 1d. To a solution of complex **1b** [Pd_2(DPP−Xantphos)$_2$] (100 mg, 0.064 mmol) in acetonitrile (3 mL) was added allyl phenyl ether (45 μL, 5 equiv) at room temperature. The solution was heated and stirred for 2 h. The mixture turned pale yellow, and no more insoluble red complex **1b** was detectable. The formation of a new intermediate was confirmed by ^{31}P NMR with the appearance of a new signal at 0.5 ppm. Ammonium hexafluorophosphate salt (42 mg, 2 equiv/Pd) was then added to the solution at room temperature. The mixture was stirred 15 min, and the ^{31}P NMR signal was shifted to −1 ppm. The mixture was evaporated and diluted in dichloromethane, and excess salts were filtered off. The filtrate was evaporated, then washed in dichloromethane/ether (1:5) to remove excess allyl phenyl ether. After centrifugation, the solid was again washed two times with diethyl ether. The solid obtained was dried under reduced pressure (88 mg, 71%).

Anal. Calcd for $C_{50}H_{41}F_6OP_3Pd$: C, 61.83; H, 4.26. Found: C, 61.98; H, 4.28. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −1 ppm (s), −146.2 (sept, $^1J_{PF}$ = 705 Hz). ^{1}H NMR (CD_2Cl_2): δ 1.58 (s, 3H, C(CH_3)$_2$), 1.63 (s, 3H, C(CH_3)$_2$), 3.30 (dd, 2H, $^3J_{HH}$ = 13.4 Hz, $^4J_{HP}$ = 7.8 Hz, H_{allyl}), 3.95 (d, $^3J_{HH}$ = 7.1 Hz, 2H, H_{allyl}), 5.50 (vsept, $\sum J$ = 41.3 Hz, 1H, H_{allyl}), 7.13−7.32 (m, 16H, $H_{aromatic}$), 7.48−7.63 (m, 14H, $H_{aromatic}$). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 27.0 (C(*C*H_3)$_2$), 27.5 (C(*C*H_3)$_2$), 37.5 (*C*(CH$_3$)$_2$), 82.5 (vt, $\sum J$ = 23.7 Hz, *C*H_{allyl}), 111.0 (*C*H_{allyl}), 122.5 ($C_{aromatic}$), 126.5 ($C_{aromatic}$), 127.1 ($C_{aromatic}$), 127.3 ($C_{aromatic}$), 129.3 ($C_{aromatic}$), 129.5 ($C_{aromatic}$), 129.7 ($C_{aromatic}$), 129.8 ($C_{aromatic}$), 129.9 ($C_{aromatic}$), 130.0 ($C_{aromatic}$), 133.4 (vt, $\sum J$ = 14.6 Hz, *C*P), 135.0 (vt, $\sum J$ = 12.2 Hz, $C_{\beta\text{-phosphole}}$), 135.4 (vt, $\sum J$ = 12.2 Hz, $C_{\beta\text{-phosphole}}$), 136.6 (vt, $\sum J$ = 4.6 Hz, $C_{aromatic}$), 148.2 (AXX′, $\sum J$ = 57.9 Hz, $C_{\alpha\text{-phosphole}}$), 149.5 (AXX′, $\sum J$ = 57.9 Hz, $C_{\alpha\text{-phosphole}}$), 157.1 (vt, J = 9.5 Hz, *C*O).

General Procedure for the Catalyzed Deallylation. All catalytic reactions were carried out in a 10 mL Schlenk tube. Catalyst (4.9 mg, 0.005 mmol for **1a** 1%; 0.5 mg, 0.0005 mmol for **1a** 0.1%; 3.9 mg, 0.0025 mmol for **1b**; 8.2 mg, 0.01 mmol for **2**; 6.9 mg, 0.01 mmol for **3**) was first introduced and dissolved in allyl alkyl ether (0.5 mmol). Both NH_4PF_6 (16 mg, 0.1 mmol) and acetonitrile (1 mL) were introduced in the mixture when mentioned above. Aniline (455 μL, 5 mmol) was then added, and the Schlenk tube was placed at the desired temperature and stirred for the indicated time. The reaction mixture was then evaporated, diluted into water, and extracted with ether. After the usual workup, the corresponding layer was purified by flash column chromatography to yield the alcohols as listed in Tables 1 and 2.

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Supporting Information Available: Complete ref 27, computed Cartesian coordinates, thermochemistry, energies, three lower frequencies of all theoretical structures, CIF file, X-ray structure of **1d**, and its crystallographic data (including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters). This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data can also be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk] with the deposition number CCDC 675062.

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