Origin of Protonation Side Products in Pd-Catalyzed Decarboxylative Allylation Reactions: Evidence for In Situ Modification of Triphenylphosphine Ligand

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Abstract: Palladium-catalyzed decarboxylative allylation (DcA) is a well-established method of carbon-carbon bond formation. This type of coupling is quite attractive, as the only byproduct is CO_2. While a wide variety of ligands have been employed with Pd(0) or Pd(II) precatalysts in DcA reactions, the ligand structure is most often based on a triarylphosphine core. Despite their demonstrated utility, DcA processes have been hindered by the formation of protonation side products. While this phenomenon has been widely acknowledged, little has been reported on the origin of the proton. Herein, we address this and provide multiple lines of experimental evidence for the proton originating from the triarylphosphine ligand.

Introduction: The palladium-catalyzed decarboxylative reaction of allylic β-keto esters was reported simultaneously by Tsuji[1] and Saegusa[2] in 1980, while the substrate scope was expanded to allyl enol carbonates by Tsuji in 1983.[3] Enantioselective versions of these reactions were reported by Tunge (for allylic β-keto esters),[4] and by Stoltz[5] and Trost[6] (for allylic enol carbonates) in the mid-2000s (Scheme 1a). The scope of substrates suitable for DcA has greatly expanded beyond simple β-keto esters to include ketimines,[7] nitronates,[8] alkyl nitrobenzenes,[9] alkyl heteroaromatics,[10] and nitriles,[11] among others (Scheme 1b). Details of the substrate

scope, as well as applications in total synthesis, have been described in detail in reviews by Tunge[12] and Guiry.[13] A variety of palladium precatalysts have been employed, including $Pd(PPh_3)_4$, $Pd_2(dba)_3$, $Pd_2(dba)_3{\cdot}CHCl_3$, $Pd(OAc)_2$, and $PdCp(\eta^3\text{-}C_3H_5)$. A core triarylphosphine structure is common amongst the range of ligands that have been employed, including mono- and bidentate triarylphosphines, PHOX-type P,N-ligands, as well as DACH bisphosphines, pioneered by Trost. While many Pd-catalyzed processes have moved away from triarylphosphines toward NHCs[14] or biarylphosphines,[15] DcA processes remain a significant outlier and triarylphosphines continue to be the dominant class of ligand. Despite the utility and aforementioned applications of DcA, these processes have been plagued by the formation of protonation side products (Figure 1). The distribution between allylation and protonation products typically varies with solvent and ligand choice; minimization of the undesired side product is usually accomplished by optimization of these variables. While this phenomenon has been widely acknowledged, there has been little reported on the origin of the proton.[16] Herein, we address this issue and provide experimental evidence that suggest the proton originates from the triarylphosphine ligand.

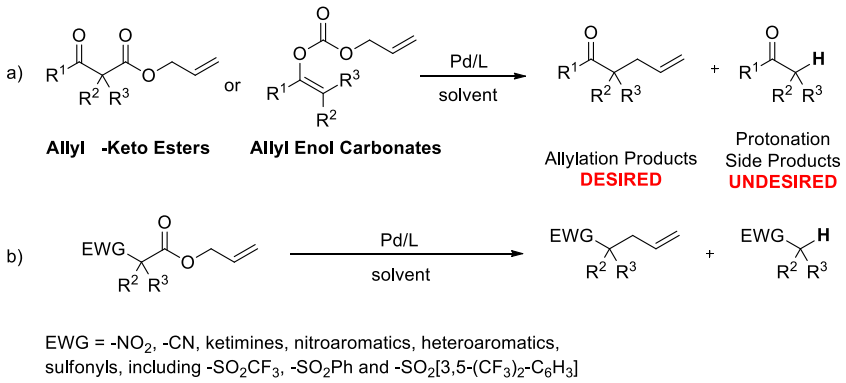
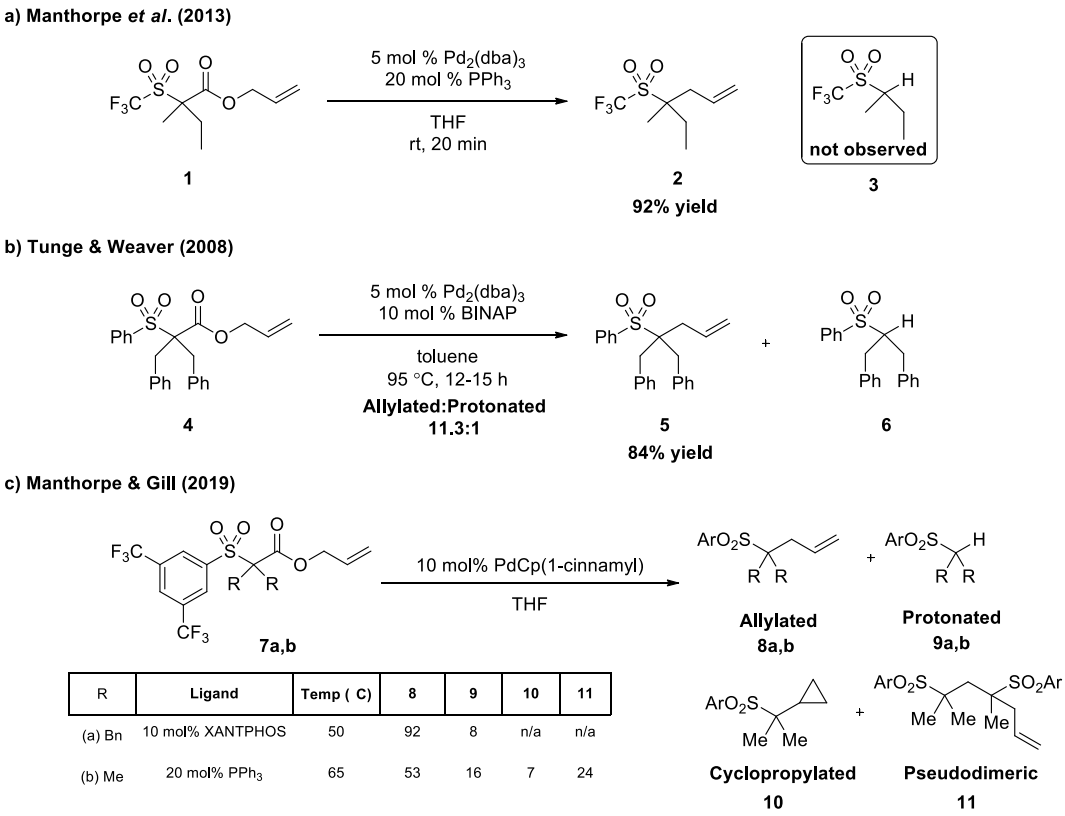


Figure 1 Pd-Catalyzed Decarboxylative Allylation Reactions Yielding Allylation & Protonation Products with (a)β-keto Esters or Allyl Enol Carbonates and (b) Non-Enolate Based Substrates

Our work on DcA began with trifluoromethyl sulfone (triflone) **1**, which gave exclusively allylation product **2** in high yield; protonation product **3** was not observed (Scheme 1a).[17,18] While this result was exciting, the substrate scope could not be expanded due to limitations of the synthetic methodology. In related work, Tunge and Weaver reported the DcA of phenyl sulfones such as **4**; the protonation side product **6** was observed alongside allylation product **5** (Scheme 1b).[19] Reaction conditions that minimized the formation of **6** were determined via standard optimization. To expand our work on DcA of electron-deficient sulfones, we turned attention to more easily synthesized 3,5-bis-trifluoromethylphenyl (BTMP) sulfones, such as **7a,b**, to give homoallylic sulfone products **8a,b**. This work, however, was hindered by the persistent formation of protonation side products **9a,b** (Scheme 1c).[18] When the alkyl group R is

anything other than a methyl group, only allylation and protonation adducts are observed. Interestingly, when R = Me, two additional products are observed; cyclopropane **10** and pseudodimeric product **11**. We proposed a mechanism for the formation of **10** and **11** in the original report, however the origin of the protonation product **9** remained unclear; there are no obvious exchangeable protons in the system. The only species present in the reaction mixture are the substrate, the solvent (usually THF, but protonation occurs in a wide range of solvents), the palladium precatalysts and the ligand. The current mechanistic understanding of non-enolate DcA cannot account for the proton (Figure 2a).

During the initial development of DcA chemistry by Tsuji *et al*., persistent formation of the protonation side product was observed.[1] The same group followed up their initial allylation



R	Ligand	Temp (C)	8	9	10	11
(a) Bn	10 mol% XANTPHOS	50	92	8	n/a	n/a
(b) Me	20 mol% PPh_3	65	53	16	7	24

Scheme 1 Decarboxylative Allylation of Sulfones

paper with a report in 1985 describing optimized conditions for exclusive formation of protonation product as a means to access ketones with tertiary α-carbons. Deallyloxycarbonylation of β-keto esters was achieved using $Pd(OAc)_2$ (2.5 mol %), PPh_3 (5 mol %) and triethylammonium formate in THF at room temperature (Figure 2c).[20] Muzart and co-workers later reported modest enantioselectivities from the first asymmetric decarboxylative protonation using a chiral amino alcohol as the proton source.[21] Stoltz and co-workers followed up their report of asymmetric DcA with an analogous asymmetric decarboxylative protonation with high enantioselectivities (up to 95% ee). The use of a PHOX ligand and excess formic acid was required to minimize allylation.[22] Further work to expand the types of substrates for decarboxylative protonation has been since carried out and this has been reviewed extensively recently by Guiry[23] and Muzart.[24] Notably, independent mechanistic experiments have demonstrated that formic acid is not the sole proton source (Figure 2d).[22,25]

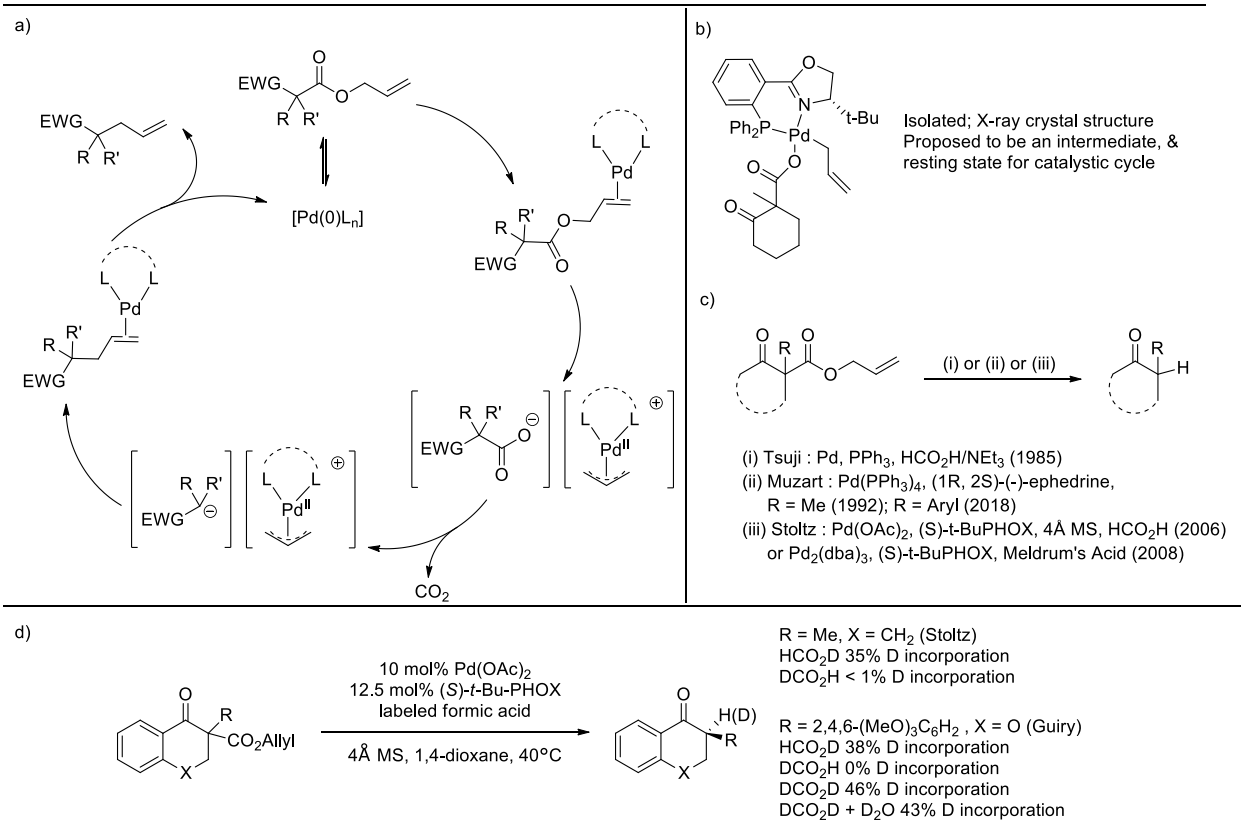


Figure 2 (a) Current Mechanistic Understanding for Non-Enolate DcA (b) Proposed Resting State for DcA (c) Overview of Decarboxylative Protonation (d) Mechanistic studies evaluating source of the proton

Troubled by the lack of mechanistic understanding of the origin of the proton, as well as believing that there may be wider implications for the DcA field, we undertook a mechanistic study to attempt to determine the source of this atom. To begin, we explored the possibility of a β-hydride elimination from the η^1-bound allyl **12** to form a palladium hydride species and an allene (which may or may not be bound to the Pd center) (Figure 3a). Subsequent reductive elimination of the alkyl sulfone and hydride would yield the protonation product **9** and regenerate the Pd(0) catalyst. While the chemistry of palladium hydrides[26] and palladium allene[27] species is quite rich, examples of a β-hydride elimination from an allyl group onto palladium are scarce in the literature. The lone example was from Wendt and co-workers from their report on the preparation of a thermally unstable η^1-allyl palladium pincer complex (Figure

3b).[28] The decomposition product was the corresponding palladium hydride species, observed spectroscopically by ^{31}P and ^{1}H NMR. The authors hypothesized that the product was the result of a β-hydride elimination to form allene, although they are careful to note that no allene was ever detected and they could not rule out other possible mechanisms.

A series of labeled substrates (**13a-13d**) were prepared via the previously reported procedure of esterification of the S-aryl thioglycolic acid, followed by sulfide oxidation and alkylation of the α-position.[18] Each substrate was treated with 10 mol% Pd(η^3-1-PhC_3H_4)Cp[29] and 20 mol% PPh_3 in THF at 65 °C for 5 hours (the conditions previously determined to promote full conversion of **7b**). Judicious chromatography of the crude mixtures permitted isolation of the protonation product **9b** from the allylation product **8b**, along with cyclopropyl **10** and pseudodimeric product **11** (Figure 3c).[18]

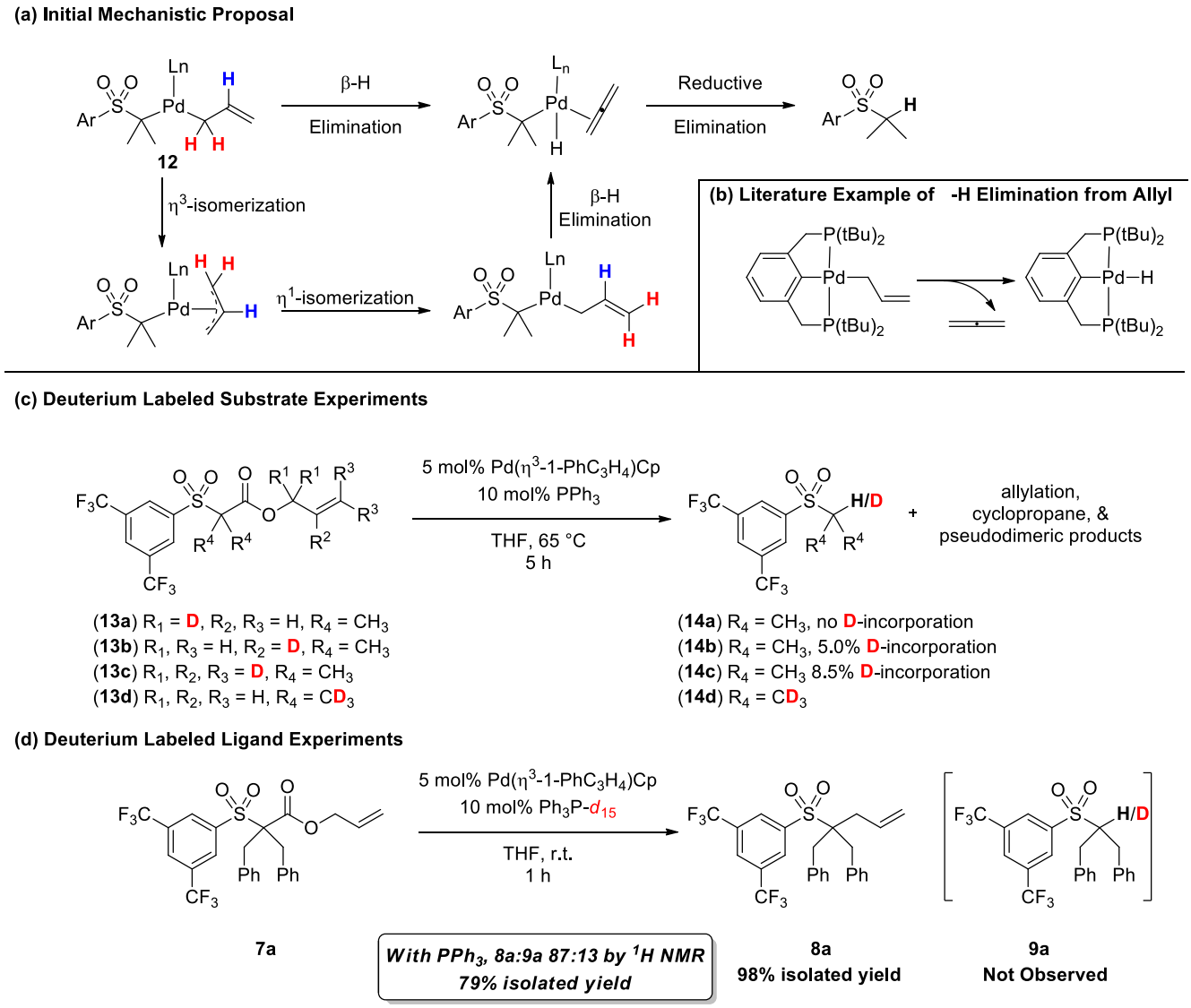


Figure 3 Initial Mechanistic Proposal & Deuterium Labeling Experiments

Substrate **13a**, with deuterium labels in the allylic R^1 position, gave exclusively unlabeled **14a**. There was no evidence of deuterium incorporation, as determined by NMR and MS. However, substrate **13b**, with a deuterium label on the central R^2 position, gave **14b** with 5.0% deuterium incorporation (determined by NMR and MS – see SI). To ensure that the low deuterium incorporation was not the result of a reversible process that was influenced by a

kinetic isotope effect including an $\eta^1/\eta^3/\eta^1$ isomerization, the reaction of allylic perdeuterated substrate **13c** was evaluated. The isolated protonation product **14c** was found to have 8.5% D-incorporation. The results of these experiments yielded strong evidence that the proton is not originating from the allyl moiety of the substate, or at least not in a substantial fashion. To evaluate the possibility of a β-hydride elimination from the α-alkyl substituents, the reaction of a fourth isotopically labelled substrate, bis(trideuteriomethyl)substrate **13d**, was evaluated. Exposure to identical reaction conditions and chromatographic separation of the products yielded **14d** exclusively; there was no evidence of deuterium incorporation.

Having explored the allyl and alkyl portions of the substrate as the origin of the proton, the possibility of ligand involvement was considered. There is literature precedent for the *in situ* cyclometallation of a ligand, yielding the active catalyst. Hartwig and Helmchen independently found the chiral phosphoramidite ligand was forming a cyclometalated iridium complex for enantioselective allylic substitution.[30,31] Grubbs and co-workers found that their ruthenium-based metathesis catalysts was, in fact, undergoing a C–H activation of an mesityl substituent on the ligand to form the active catalyst.[32] Most notably, while exploring the chemistry of $Pd(P\textit{t}Bu_3)_2$, Hartwig and co-workers isolated a Pd species in which the phosphine ligand had undergone a cyclometallation.[33]

Using a substrate that gave a simpler product distribution (i.e. only allylation and protonation), the impact of an isotopically labelled ligand was evaluated. The dibenzyl substrate **7a** was treated with 10 mol% $Pd(\eta^3\text{-}1\text{-}PhC_3H_4)Cp$ and 20 mol% $Ph_3P\text{-}d_{15}$ in THF at room temperature for 30 minutes. ^1H NMR analysis of the crude reaction mixture showed no evidence of protonation product **8b**, and upon chromatographic purification, the isolated yield

of **8a** was 98%. It is important to note that this yield is even greater than obtained with triflone **1**. The change from PPh_3 to Ph_3P-d_{15} appears to inhibit the formation of the protonation side product; it is conceivable that there are kinetically competitive pathways to each of the allylation and protonation products. It would follow that the mechanism for side product formation contains a kinetically relevant step involving a C–H bond cleavage on the ligand and that a kinetic isotope effect is responsible for inhibition of the side product formation pathway.

Previously, Stoltz and co-workers proposed that a carboxylate-bound palladium intermediate was the catalytic resting state in the decarboxylative allylation of β-keto allylic esters.[34] If one considers a similar carboxylate-bound intermediate in the DcA of BTMP sulfones, one can envision that the protonation side product arises from here. Carboxylate-assisted C–H activation has been extensively reported over the last 20 years;[35] we hypothesized that the carboxylate resulting from the oxidative addition of the allylic ester to a Pd(0) catalyst could also act as a base in the same way that acetate and pivalate have been shown to act in a variety of C–H activation processes. It was proposed that the proton from the undesired side product is the result of a cyclopalladation of an ortho-H on the triarylphosphine ligand. One could envision a γ-agostic interaction,[36] as illustrated in Figure 4. A plausible transition state can be drawn that is similar to other carboxylate-assisted C–H activations reported in the literature via a concerted metalation deprotonation (CMD) process.[37] This would result in the corresponding carboxylic acid, as well as cyclopalladated Pd(II) intermediate. Reductive elimination of this species would transfer the allyl group to the ortho-position of the triarylphosphine, thus regenerating a Pd(0) species, albeit with a modified ligand. A Pd(IV)-hydride intermediate as the result of the C–H activation can't be discounted. This intermediate

could undergo successive reductive eliminations to yield the same carboxylic acid and a Pd(0) species. Guo and co-workers studied the gas-phase fragmentation of cationic bis(triphenylphosphine)palladium(II) acetate and obtained mass spectral evidence for a cyclopalladated intermediate. PM3 calculations suggested that there was only a small activation barrier to form a cyclopalladated Pd(IV) hydride intermediate.[38] If either of these mechanisms are operational, the modified triarylphosphine ligand should be detectable.

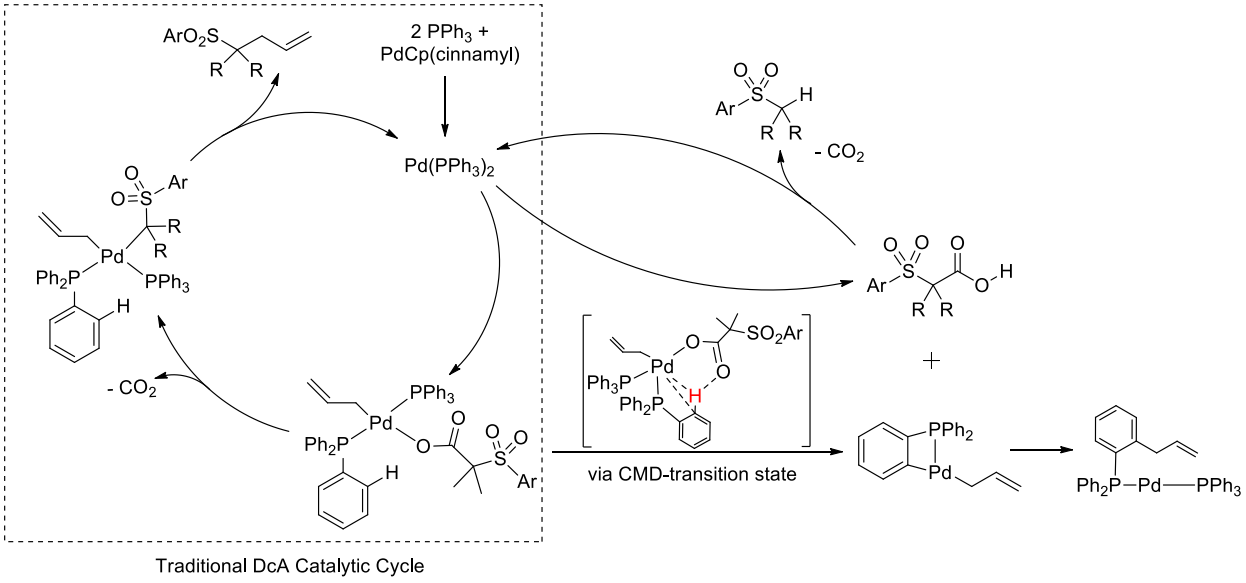
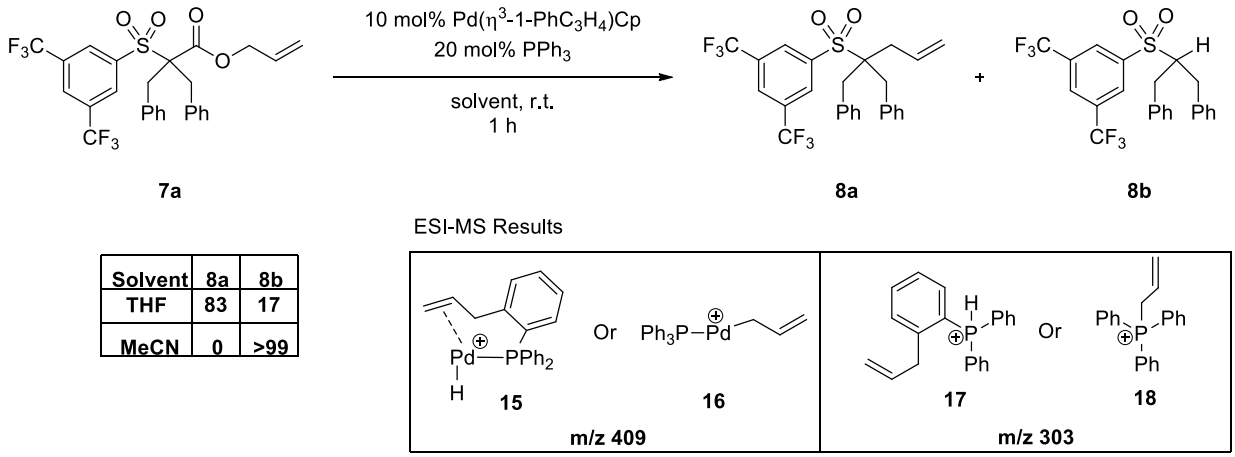


Figure 4 Proposed Mechanism for Generation of Protonation Product

ESI-MS was performed on the crude reaction mixture from the reaction of **7a** in THF (Figure 5). A set of peaks were observed at m/z 409 and 303 that could correspond to a cationic Pd species **15** with an *ortho*-allyl triphenylphosphine ligand and the corresponding ortho-allyl triphenylphosphine **17**. However, it wasn't possible to distinguish these species from isobaric species with the allyl group on palladium **16** or on phosphine **18**. The experiment was repeated using acetonitrile as solvent, conditions under which the protonation product was preferentially

Figure 5 DcA Experiments Analyzed by ESI-MS



Solvent	8a	8b
THF	83	17
MeCN	0	>99

formed. Thus, DcA was performed with **7a** in acetonitrile, and the crude material was analyzed by ESI-MS in the same fashion (Figure 6).[39] While there were similarities to the results of the previous experiment in THF, a new series of peaks were also observed; peaks at m/z 303, 343, 383, 423 and 463 corresponding to masses of mono-, di-, tri-, tetra-, and pentaallylated triphenylphosphine. Collision-induced dissociation (CID) and tandem MS (MS/MS) of these ions follows the well-known fragmentations of triarylphosphines.[40] This result supports the mechanistic proposal of cyclopalladation and that the proton in the side product originates from the ligand. Quite remarkably, these results suggest that multiple cyclopalladations are

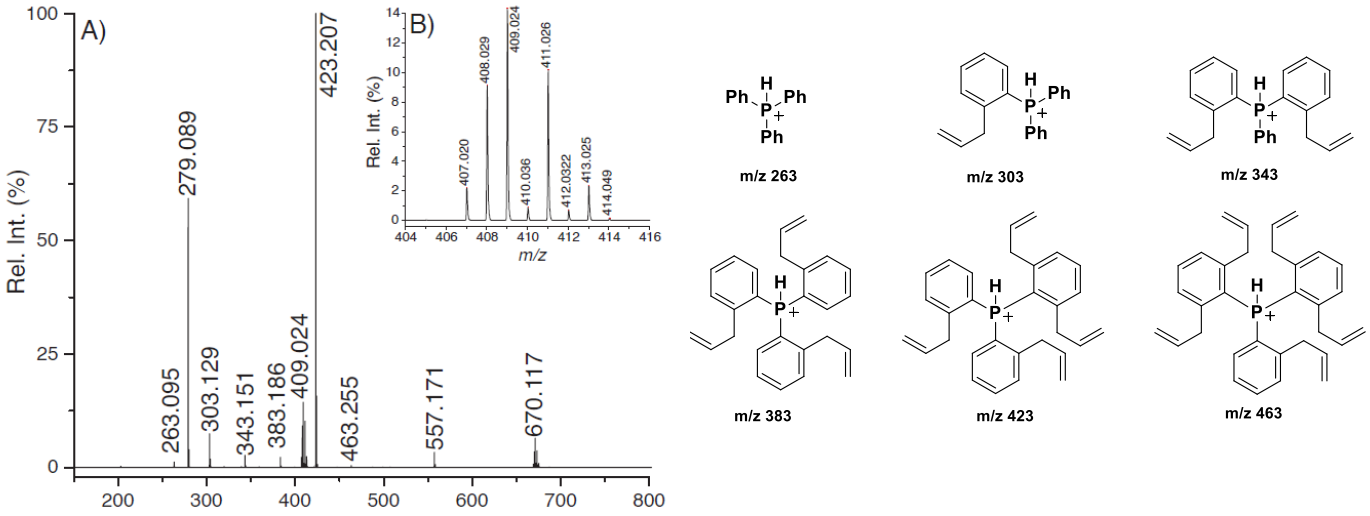


Figure 6 ESI-MS of Crude Reaction Mixture in MeCN

possible on each molecule of triphenylphosphine, thus explaining how loadings of 20 mol % triarylphosphine can afford high yields of protonation side products. The tetraallyl triphenylphosphine is the most abundant peak.

To further distinguish between the two potential structures for m/z 303, the allyl phosphonium bromide salt was prepared synthetically and analyzed by ESI-MS. While the MS/MS of m/z 303 for the crude mixture gave fragments with m/z 261, 225, 183, and 108, the allyl phosphonium salt m/z 303 fragments with m/z 261, 183, and 108. The absence of a m/z 225 fragment peak for the allyl triphenylphosphonium bromide suggests that the peak at m/z 303 cannot be solely originating from a P-centered allyl group (see Supporting Information for further details).

In summary, we have presented evidence via deuterium-labeling experiments combined with ESI-MS/MS analysis that suggests that the source of the proton in the side product observed in DcA reactions is the triarylphosphine ligand. It is proposed that a concerted metalation-deprotonation (CMD) step may occur at the ortho-position of triphenylphosphine. This type of mechanism has not been previously suggested, and has potential to be relevant to the reactivity of ligands containing a triarylphosphine core.

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Data Availability

Experimental details, characterization, and additional spectral data are available in the Supporting Information.

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