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O₂-Promoted Allylic Acetoxylation of Alkenes: Assessment of “Push” vs. “Pull” Mechanisms and Comparison between O₂ and Benzoquinone

Tianning Diao and Shannon S. Stahl

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706

Shannon S. Stahl: stahl@chem.wisc.edu

Abstract

Palladium-catalyzed acetoxylation of allylic C–H bonds has been the subject of extensive study. These reactions proceed via allyl-palladium(II) intermediates that react with acetate to afford the allyl acetate product. Benzoquinone and molecular oxygen are two common oxidants for these reactions. Benzoquinone has been shown to promote allyl acetate formation from well-defined π -allyl palladium(II) complexes. Here, we assess the ability of O₂ to promote similar reactions with a series of “unligated” π -allyl palladium(II) complexes (i.e., in the absence of ancillary phosphorus, nitrogen or related donor ligands). Stoichiometric and catalytic allyl acetate formation is observed under aerobic conditions with several different alkenes. Mechanistic studies are most consistent with a “pull” mechanism in which O₂ traps the Pd⁰ intermediate following reversible C–O bond-formation from an allyl-palladium(II) species. A “push” mechanism, involving oxidatively induced C–O bond formation, does not appear to participate. These results and conclusions are compared with benzoquinone-promoted allylic acetoxylation, in which a “push” mechanism seems to be operative.

Introduction

Palladium-catalyzed acetoxylation of allylic C–H bonds provides an appealing method for anti-Markovnikov functionalization of alkenes (Scheme 1).^{1–3} The vast majority of these reactions employ benzoquinone (BQ) as the stoichiometric oxidant; however, reactions with molecular oxygen, hypervalent iodine and other oxidants have also been reported.^{2,3}

Fundamental studies have shown that BQ promotes C–O reductive elimination⁴ from well-defined π -allyl-palladium(II) species to form allyl acetates.^{1f,g,i,5,6} These observations potentially explain the beneficial effect of BQ in allylic acetoxylation reactions.^{1–2} BQ

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Correspondence to: Shannon S. Stahl, stahl@chem.wisc.edu.

Supporting Information Available: Experimental procedures, and characterization data.

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could promote the acetoxylation of π -allyl-Pd^{II} intermediates via two possible pathways: (1) BQ coordination to the π -allyl-Pd^{II} intermediate could withdraw electron density from the Pd^{II} center in an oxidatively-induced reductive elimination pathway (“push” mechanism, Scheme 2),⁷ or (2) BQ could trap the Pd⁰ intermediate that forms in a reversible C–O reductive elimination step (“pull” mechanism, Scheme 2). In both cases, BQ also serves as the oxidant for conversion of Pd⁰ to Pd^{II}.⁸ The former mechanism is commonly invoked in the literature, and tentative NMR spectroscopic evidence has been offered in support of this pathway.^{5c} On the other hand, Bercaw and coworkers observed reversible C–O reductive elimination from a bipyrimidine-ligated allyl-Pd^{II} species in the absence of BQ and proposed a “pull” mechanism.¹ⁱ

Allylic acetoxylation reactions would be more appealing if BQ could be replaced with O₂ as the stoichiometric oxidant,⁹ and several groups have recently reported progress toward this goal. Kaneda and coworkers reported aerobic allylic acetoxylation in *N,N*-dimethylacetamide as the solvent under elevated pressures (6 atm) of O₂ (eq 1).¹⁰ Liu and coworkers achieved aerobic allylic imidation under similar conditions by employing 40 mol % of maleic anhydride as an additive in the reaction (eq 2).¹¹ Finally, we reported that use of 4,5-diazafluorenone as an ancillary ligand enables aerobic allylic acetoxylation of alkenes under 1 atm O₂ (eq 3).¹²

(1)

(2)

(3)

In connection with our previous study,¹² we sought to probe the potential role of O₂ in promoting CO reductive elimination from π -allyl-Pd^{II} complexes. Such reactivity could be combined with the ability of O₂ to oxidize palladium(0) to palladium(II)¹³ to achieve catalytic aerobic allylic C–H acetoxylation. Here, we describe the reactivity of “unligated” π -allyl-Pd^{II} complexes (i.e., lacking a well-defined ancillary neutral donor ligand) in the presence of O₂. Selected π -allyl-Pd^{II} complexes undergo stoichiometric acetoxylation in the presence of O₂, and these observations have been extended to catalytic reactivity. Kinetic and mechanistic studies of the stoichiometric reactions suggest that O₂ promotes C–O reductive elimination by a “pull”-type mechanism.¹² These observations are compared to reactions involving BQ.

Results and Discussion

Stoichiometric Acetoxylation of π -Allyl-PdCl Complexes in the Presence and Absence of Oxidants

Well-defined π -allyl-PdCl complexes derived from propene (**1a**), methyl-3-butenolate (**1b**) and allyl benzene (**1c**) (Table 1), were prepared according to literature procedures¹⁴ and dissolved in a mixture of AcOH-*d*₄ and CD₃CN in a ratio of 4:2.5. The use of CD₃CN ensured solubility of the Pd complexes and LiOAc, which served as the acetate source. These solutions were then heated for 12 h in the presence of BQ (12 equiv), O₂ (2.3 atm) or under an inert (N₂) atmosphere. All reactions carried out in the presence of BQ afforded the terminal allylic acetate in good yields (Table 1, entries 1, 4 and 7). For the reactions carried out in the presence of O₂, **1a** yielded trace acetate product (entry 2), while **1b** and **1c** reacted to afford allylic acetates **2b** and **2c** in 94% and 31% yields, respectively. In the reaction with **1c** under O₂, multiple unidentified by-products started to emerge after 5 hours and formation of the allylic acetate product stopped at 31% yield. Complexes **1a** and **1c** exhibit negligible reactivity in the absence of BQ or O₂ (entries 3 and 9), while the electron-deficient π -allyl-PdCl complex **1b** underwent slow acetoxylation under N₂, resulting in a 19% yield of **2b** after 12 h together with the formation of Pd black (entry 6). No Pd black was observed in the other reactions.

Characterization of the π -Allyl-PdCl Complexes in the AcOH/CH₃CN Solvent Mixture

The allylbenzene-derived π -allyl-PdCl complex **1c** was selected for further study because it exhibits virtually no reactivity in the absence of an oxidant, but reacts to form cinnamyl acetate **2c** in the presence of O₂ or benzoquinone. The speciation of **1c** in solution was evaluated by UV-visible and ¹H NMR spectroscopy. The UV-visible spectrum of the **1c** in AcOH exhibits a strong absorption peak at 290 nm (Fig. 2A). Upon addition of CH₃CN into the solution, the 290 nm band maximum shifts to 270 nm with a clean isosbestic point (Fig. 1A). A plot of the absorption at 270 nm versus [CH₃CN] fits a hyperbolic function (i.e., saturation behavior) (Fig. 1B). A similar titration experiment was evaluated by ¹H NMR spectroscopy in deuterated solvent, starting with a somewhat higher concentration of **1c** (Fig. 2), and similar behavior was observed. The benzylic proton resonance of the π -allyl ligand shifts downfield upon addition of CD₃CN to a solution of **1c** in AcOH-*d*₄ (Fig. 3). The data fit a hyperbolic dependence on [CD₃CN] up to approximately [CD₃CN] = 2 M, and follow a linear trend at high concentrations.

π -Allyl-PdCl complexes exist as dimers in AcOH; however, neutral donor ligands, such as pyridine, can coordinate to Pd^{II} and convert the dimeric species into monomers.¹⁵ The data in Figs. 2 and 3 are consistent with this behavior, and the hyperbolic dependence of the UV-visible absorption and ¹H NMR chemical shift is attributed to the conversion of **1c** into a monomer **1c'** upon coordination of CH₃CN (eq 4). The linear dependence of the ¹H NMR resonance observed at high [CD₃CN] is attributed to a solvent effect, associated with the bulk change from 100% AcOH to a large fraction of CD₃CN as the solvent. Based on the UV-visible spectra, the equilibrium constant of this dimer-monomer equilibrium (K_{eq}) is calculated to be $4.3 \times 10^{-6} \text{ M}^{-1}$ ($\pm 0.2 \times 10^{-6} \text{ M}^{-1}$). An equilibrium constant of $3.7 \times 10^{-6} \text{ M}^{-1}$ ($\pm 0.2 \times 10^{-6} \text{ M}^{-1}$) is calculated on the basis of the ¹H NMR spectra (see Supporting Information for details).

(4)

Mechanistic Studies of Stoichiometric Acetoxylation of the π -Allyl-PdCl Complex **1c**

The reaction of **1c** proceeds to incomplete conversion to cinnamyl acetate **2c** in the presence of O₂ (cf. Table 1, entry 8); however, the reaction is well behaved at early times and was investigated by the method of initial rates (eq 5). Formation of **2c** was monitored by ¹H NMR spectroscopy and quantified by integrating the acetate methylene doublet at 4.76 ppm (C₆H₅CHCHCH₂OAc). The acetoxylation of **1c** in the presence of O₂ exhibits first order dependence on [**1c**] and [O₂] (Fig. 3). The effect of BQ on the acetoxylation of **1c** was determined under similar reaction conditions. The initial rate displays a first order dependence on [**1c**] and [BQ] (Fig. 4). The slope of the reaction rate as a function of [BQ] is almost 10 times greater relative to the rate as a function of [O₂].

(5)

A Hammett study was performed to assess electronic effects on the acetoxylation of *p*-substituted allylbenzene-derived π -allyl-Pd^{II} complexes in the presence of BQ and O₂ (eq 6). The rho (ρ) values obtained from these reactions, 0.90 and 1.0 for the reactions with BQ and O₂, respectively, show that electron-deficient allyl-Pd^{II} complexes react more rapidly (Fig. 5). We attribute this effect to ground-state destabilization of the π -allyl-Pd^{II} species by

electron-withdrawing substituents, resulting in more facile reduction of Pd^{II} to Pd⁰ and nucleophilic attack by acetate on the π -allyl ligand.¹⁶

(6)

In order to probe whether the reductive C–O bond formation is reversible, we conducted an acetate scrambling experiment with **2c**. Cinnamyl acetate, **2c**, and a catalytic quantity of **1c** (3 mol %) were mixed with LiOAc-*d*₃ under an inert atmosphere (eq 7). After 12 hours, the overall concentration of cinnamyl acetate **2c** and **1c** remained constant, but 17% of the total cinnamyl acetate **2c** was converted to deuterium labeled cinnamyl acetate **2c-d**₃. Accordingly, the same quantity of free AcOH was formed.

(7)

Pd(OAc)₂-Catalyzed Aerobic Allylic Acetoxylation of Alkenes

Following these stoichiometric reactions, we investigated catalytic allylic C–H acetoxylation reactions of alkenes with Pd(OAc)₂ under the conditions similar to those used in the stoichiometric experiments (cf. Tables 1 and 2). 1-Octene was used as a representative alkyl olefin, and no acetoxylation product was observed with this substrate under 60 psi of O₂ after 24 hours (Table 2, entry 1). Instead, isomerization of the C=C bond occurred, resulting in a mixture of octene isomers. In contrast, methyl 3-butenate and allyl benzene yielded the corresponding *trans*-allylic acetate products in 75% and 67% yields, respectively (Table 2, entries 2 and 3), together with unreacted alkene. The reaction of β -methylstyrene was also tested and led to a 30% yield of cinnamyl acetate (Table 2, entry 4). The favorable reactivity of allylbenzene relative to β -methylstyrene may be attributed to the increased acidity of the allylic C–H bond and/or the more-favorable binding of the terminal alkene in allylbenzene. Overall, the relative reactivity of these alkenes under catalytic conditions, methyl-3-butenate > allyl benzene > 1-octene, correlates with the acidity of the allylic C–H bond.¹⁷ The catalytic reactivity also tracks with the relative rates of the stoichiometric reactions of π -allyl-Pd^{II} complexes (cf. Table 1).

Consideration of the Mechanism of O₂-Promoted Acetoxylation and Comparison of O₂ and BQ as Stoichiometric Oxidants

The stoichiometric and catalytic results presented above demonstrate that O₂ can promote stoichiometric and catalytic allylic C–H acetoxylation reactions with “unligated” Pd^{II} complexes; however, this effect appears to be limited to activated (i.e., electron deficient) alkenes. The origin of O₂ promotion in stoichiometric reactions of π -allyl-Pd^{II} complexes could potentially arise from a “push” or a “pull” effect (Scheme 3; see also, Scheme 2).^{1c} Specifically, O₂ could coordinate to Pd^{II} to generate a more electrophilic or oxidized π -allyl-Pd species that is more susceptible to nucleophilic attack by acetate (“push” mechanism), or O₂ could trap the Pd⁰ species generated in C–O bond-forming step (“pull” mechanism).

The kinetic data cannot definitively distinguish between these two mechanisms

The rate laws in Scheme 3 show that both mechanisms could lead to a first-order dependence on [**1c**] and the oxidant, [O₂] or [BQ] (i.e., when $k_4[\text{O}] \ll k_{-3}$), as has been observed experimentally (cf. Figs. 3 and 4). The “pull” mechanism could exhibit a saturation or zero-order dependence on the oxidant; however, this kinetic regime may not be readily accessible for the reactions described here. In principle, the mechanisms could be distinguished by the kinetic dependence on [OAc] because the “push” and “pull” mechanisms are predicted to exhibit a saturation and first-order kinetic dependence on [OAc], respectively. A saturation kinetic dependence on [OAc] in the presence of O₂ was observed (Figure S5). This result could support a “push” mechanism; however, ¹H NMR spectroscopic studies show that acetate coordinates to the ground-state (π -allyl)Pd^{II} complex (Figure S4), and this equilibrium binding step could explain a saturation kinetic dependence on [OAc], even in the case of a “pull” mechanism. This complexity is compounded by an inability to distinguish between inner-sphere versus outer-sphere C–O reductive elimination (i.e., nucleophilic attack by acetate), which also contributes to the ambiguity of the rate-dependence on [OAc].

Despite the ambiguities associated with the kinetic data, several considerations argue in favor a “pull” mechanism for O₂ and a “push” mechanism for BQ

The acetate scrambling experiments with **1c** show that C–O bond formation is reversible. That this process takes place on a time scale similar to the stoichiometric acetoxylation reaction under O₂ (cf. Table 1 and eq 6) is consistent with O₂ trapping of the Pd⁰ product of the reaction (i.e., a “pull” mechanism). In this case, aerobic allylic acetoxylation reactions (e.g., eqs. 1 and 3) will be effective only with catalyst systems or under reaction conditions that enable C–O reductive elimination in the absence of an oxidant. This conclusion would explain the limited scope of catalytic allylic acetoxylation reactions typically observed when O₂ is used as the oxidant.

The reactions of the “unligated” π -allyl-Pd^{II} complex **1c** with BQ are nearly 10-fold faster than those with O₂ as the oxidant (Figs. 3 and 4). If BQ and O₂ promote the reaction via the same mechanism, this observation would require that (reversible) C–O reductive elimination is much more rapid than the O₂-based turnover rate and that BQ is significantly more effective than O₂ in trapping the Pd⁰ species (k_4 , Scheme 3).¹⁸ Alternatively, BQ could directly promote C–O bond formation in a “push” mechanism (k_1 , Scheme 3). This

possibility could explain the broader scope of catalytic allylic acetoxylation reactions typically observed with BQ as the oxidant.

Several observations from allylic acetoxylation reactions mediated by diazafluorenone (DAF)-Pd^{II} complexes are relevant to the present discussion.¹² π -Allyl-Pd^{II} complexes with DAF and 2,2'-bipyridyl (4,4'-*t*Bu₂bpy) ancillary ligands were compared in stoichiometric acetoxylation and acetate-scrambling experiments, similar to the experiments shown in Table 1 and eq 6. The results, which are summarized in Fig. 6, show that the DAF-ligated π -allyl-Pd^{II} complex forms allyl acetate in the presence of BQ, O₂ and even under N₂, while the *t*Bu₂bpy-ligated complex reacts only in the presence of BQ. The acetate scrambling data show that the DAF-ligated complex undergoes reversible C–O bond formation in the presence of O₂ and under an inert atmosphere, while no acetate scrambling occurs with the *t*Bu₂bpy-ligated complex under any conditions. Taken together, the observations suggest that O₂ can serve as an effective trap for Pd⁰ (“pull” mechanism) upon C–O reductive elimination from Pd^{II}, but it cannot directly promote C–O reductive elimination (“push” mechanism). The ability of BQ to promote allyl acetate formation from the *t*Bu₂bpy complex, which does not undergo reversible C–O reductive elimination, is most readily explained by direct promotion of allyl acetate formation by BQ via a “push” mechanism.

The broad scope of aerobic allylic C–H acetoxylation observed with the DAF/Pd(OAc)₂ appears to reflect, at least in part, the ability of the DAF ligand to facilitate C–O reductive elimination and thereby promote the “pull” mechanism. This property of DAF seems quite unusual, and ongoing studies seek to gain additional insights into the role of DAF in these reactions. Meanwhile, it seems possible that other ligands could be identified to promote a “push”-type mechanism. For example, Mirica and coworkers have shown that certain preorganized tri- and tetradentate ligands can promote stoichiometric oxidation of organopalladium(II) complexes by O₂ and facilitate reductive elimination reactions.¹⁹ Incorporation of such concepts into catalytic allylic acetoxylation reactions could lead to further expansion of the scope of reactions compatible with O₂.

Conclusion

Overall, this study highlights both opportunities and constraints on the use of O₂ as an oxidant in Pd-catalyzed oxidation reactions. Mechanistic studies of allylic C–H acetoxylation with “unligated” Pd^{II} complexes and catalysts show that aerobic catalytic turnover is possible when the Pd^{II}/substrate-based intermediate undergoes facile reductive elimination to afford a Pd⁰ intermediate that can react with O₂. When reductive elimination from Pd^{II} is not facile, oxidants other than O₂ (BQ, in the present allylic oxidation reactions) are required to promote product formation via “oxidatively induced” reductive elimination. The identification of ligands, such as 4,5-diazafluorenone, that facilitate reductive elimination from Pd^{II} provides one strategy to expand the scope of Pd-catalyzed aerobic oxidation reactions.

Experimental

All commercially available compounds and deuterated solvents were used as received, and were purchased from Sigma-Aldrich. All NMR experiments were acquired on a Varian INOVA-500 MHz spectrometer. The chemical shifts (δ) of ^1H NMR spectra are given in parts per million and referenced to the residual acetate proton of $\text{AcOH-}d_4$ (2.04 ppm). Unless specified, all experiments used recrystallized 1,3,5-tri-(*tert*-butyl)benzene as the internal standard. All reactions were conducted in J-Young tubes to determine the dependence the initial rate on $[\text{O}_2]$, except for the experiments in Fig. 4B, which were performed in thick-wall flame-sealed NMR tubes.

General Procedure for Synthesis of π -Allyl Palladium Complexes

All π -allyl palladium complexes were prepared according to literature procedures.¹⁴ A representative procedure for the synthesis of cinnamyl derived π -allyl palladium complex **1c** is presented here. To an oven-dried round bottom flask equipped with a magnetic stir bar was added palladium trifluoroacetate (154 mg, 0.5 mmol). The flask was wrapped with aluminum foil, and purged with N_2 . Dry THF (5 mL) and allyl benzene (66 μL , 0.5 mmol) were added via syringe. The solution was stirred for 1 hour at room temperature, followed by addition of tetrabutylammonium chloride (150 mg, 0.55 mmol). The solution was allowed to stir for another 30 min. After the reaction, the mixture was filtered through Celite to remove palladium black. The resulting yellow solid was purified by silica gel column chromatography, and recrystallized from CH_2Cl_2 and hexane. The ^1H NMR spectrum of this compound is consistent with the literature.¹⁴

General Procedure for $\text{Pd}(\text{OAc})_2$ -Catalyzed Aerobic Allylic Acetoxylation of Alkenes

Allylbenzene (132 μL , 1 mmol), LiOAc (130 mg, 3 mmol) and $\text{Pd}(\text{OAc})_2$ (10 mg, 5 mol%) were weighed out in a thick-wall pressure tube. 1.2 ml HOAc and 0.8 ml CH_3CN were then added. The tube was equipped with a pressure regulator. The tube was charged with 60 psi of O_2 following purging and allowed to stir at 80 $^\circ\text{C}$ overnight. The reaction was then cooled to room temperature and trimethoxybenzene (50 mg, 0.3 mmol) was added as an internal standard. Solvent was then removed by rotovap and the sample was analyzed by ^1H NMR spectroscopy. Reactions with other alkene substrates applied the same procedure as allylbenzene.

Reversible Ligand Exchange Reaction

The allyl benzene derived π -allyl palladium complex **1c** (2.2 mg, 4.0 μmol), cinnamyl acetate **2c** (5.5 mg, 5.2 μmol , 31 μmol) and $\text{LiOAc-}d_3$ (2.7 mg, 40 μmol) were added into a J-Young tube. $\text{AcOH-}d_4$ and CD_3CN stock solution were added via gas-tight syringe. The NMR tube was immediately placed in an acetone/dry ice bath. Three freeze-pump-thaw cycles were carried out to degas the solvent. N_2 (1 atm) was introduced to the tube. The probe of the NMR spectrometer was heated to 80 $^\circ\text{C}$. The NMR tube was placed into the INOVA spectrometer and data were acquired over 12 h.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Titration of CH_3CN into a solution of **1c** in AcOH determined by UV-Visible spectroscopy, UV-Visible spectra (A) and the absorption of the peak at 270 nm as a function of $[\text{CH}_3\text{CN}]$ (B). Conditions: $[\mathbf{1c}]_0 = 0.025 \text{ mM}$, solvent = AcOH, 22 °C.

Fig. 2.

The chemical shift of the benzylic proton of **1c** ($[\text{C}_6\text{H}_5\text{CHCHCH}_2\text{PdCl}]_2$) in $\text{AcOH-}d_4$ as a function of $[\text{CD}_3\text{CN}]$ determined by ^1H NMR spectroscopy. The curve fit reflects a nonlinear least-squares fit to a modified hyperbolic function of $[\text{CD}_3\text{CN}]$: $\delta = [\text{CD}_3\text{CN}]/(c_1 + c_2[\text{CD}_3\text{CN}]) + c_3[\text{CD}_3\text{CN}] + \delta_0$. Reaction conditions: $[\mathbf{1c}] = 0.25$ mM, solvent = $\text{AcOH-}d_4$, total solution volume = 0.65 mL, 24 °C.

Fig. 3.

Kinetic orders of O_2 -promoted acetoxylation of **1c**: dependence of the initial rate on $[1c]$ (A) and $[O_2]$ (B). Reaction conditions: $AcOH-d_4 = 0.4$ mL, $CD_3CN = 0.25$ mL, $80^\circ C$, $[LiOAc] = 30$ mM, (A) $[O_2] = 13$ mM and (B) $[1c]_0 = 1.5$ mM.

Fig. 4.

Kinetic orders of BQ-promoted acetoxylation of **1c**: dependence of the initial rate on **[1c]** (A) and **[BQ]** (B). Reaction conditions: $\text{AcOH-}d_4 = 0.4$ mL, $\text{CD}_3\text{CN} = 0.25$ mL, 80°C , (A) $[\text{LiOAc}] = 12$ mM, $[\text{BQ}] = 30$ mM (B) $[\text{LiOAc}] = 30$ mM, $[1c]_0 = 1.5$ mM.

Fig. 5.

Hammett plot of the acetoxylation of *p*-substituted π -allyl-PdCl complexes in the presence of BQ (A) and O₂ (B). Reaction conditions: [Pd]₀ = 3 mM, [LiOAc] = 30 mM, AcOH-*d*₄ = 0.4 mL, CD₃CN = 0.25 mL, 80 °C, (A) BQ = 30 mM; (B) [O₂] = 13 mM.

Stoichiometric Allyl Acetate Formation (cf. Table 1)

[(DAF)Pd(allyl)]⁺	[(<i>t</i>Bu₂bpy)Pd(allyl)]⁺
88% (BQ, 1 h)	88% (BQ, 24 h)
90% (O ₂ , 3 h)	0% (O ₂ , 24 h)
70% (N ₂ , 24 h)	0% (N ₂ , 24 h)

Acetate Scrambling (cf. eq 6)

[(DAF)Pd(allyl)]⁺	[(<i>t</i>Bu₂bpy)Pd(allyl)]⁺
0% (BQ)	0% (BQ)
33% (O ₂ , 1 atm)	1% (O ₂ , 3 atm)
76% (N ₂)	4% (N ₂)

Fig. 6.

Comparison between the reactivity of DAF- and *t*Bu₂bpy-ligated π-allyl-Pd^{II} complexes in the presence of O₂ and BQ reported in ref. 12.

Scheme 1.

Pd-Catalyzed Oxidative Allylic Acetoxylation Reactions

Scheme 2.

"Push" versus "Pull" Mechanisms to Account for the Promotion Effect of BQ in Pd-Catalyzed Acetoxylation of Allylic C–H Bonds.

"Push" Mechanism: Oxidatively-Induced Reductive Elimination **"Pull" Mechanism: Trapping of Pd⁰ by the Oxidant** **Scheme 3.**

Possible Pathways for Oxidant-Promoted Acetoxylation of π -allyl-Pd Complexes, [O] = BQ or O₂.

Table 1Acetoxylation of π -Allyl-Pd Complexes in the Presence of BQ and O₂.^a

NMR yield (%)				
Entry	π -allyl Pd complex	[O]	<i>trans</i> -2	<i>cis</i> -2
1		BQ	69	0
2		O ₂	2	0
3		None	1	0
1a				
4		BQ	93	7
5		O ₂	94	6
6		None	19	0
1b				
7		BQ	96	0
8		O ₂	31 ^b	0
9		None	1	0
1c				

^a Reactions were performed in NMR tubes and monitored by ¹H NMR spectroscopy with 1,3,5-tri-*tert*butylbenzene as the internal standard. Reaction conditions: [Pd]₀ = 2.5 mM, [LiOAc]₀ = 12 mM, [O] = 30 mM, AcOH-*d*₄ = 0.4 mL, CD₃CN = 0.25 mL, reaction time = 12 h.

^b Unidentified by-product started to form at 31% conversion, at which point the formation of cinnamyl acetate stopped.

Table 2Pd(OAc)₂-Catalyzed Aerobic Allylic Acetoxylation Reactions.^a

$$\text{R}^1\text{-CH=CH}_2 \xrightarrow[\text{AcOH, CH}_3\text{CN}]{\text{Pd(OAc)}_2 \text{ (5 mol\%), LiOAc (2 equiv), O}_2 \text{ 60 psi, 80 }^\circ\text{C, 24 h}} \text{R}^1\text{-CH=CH-CH}_2\text{OAc}$$

Entry	Substrate	Product	yield ^b
1			0% ^c
2			75%
3			67%
4			30%

^aReaction conditions: [substrate]₀ = 0.5 M, [LiOAc] = 1 M, AcOH-*d*₄ = 2 ml, CD₃CN = 1.2 ml.^bYields were determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as the internal standard. Only the *trans* alkene isomer was obtained.^cDouble bond migration was observed.