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Insights into the mechanism of active catalyst generation for the $Pd^{II}(acac)_2/PPh_3$ system in the context of telomerization of 1,3-butadiene†

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The mechanism by which Pd^{II} precursors are reduced to catalytically active low-valent Pd species has been a subject of interest for developing better catalysts. This process is well understood for catalytic systems employing a combination of palladium(II) acetate [$Pd(OAc)_2$] and tertiary phosphines. However, the mechanism of reduction of palladium(II) acetylacetonate [$Pd(acac)_2$] in the presence of phosphines has not been thoroughly investigated. This is especially important in the context of the Pd-catalyzed butadiene telomerization process, which uses a combination of $Pd(acac)_2$ and tertiary phosphines in methanol to produce the commercially valuable precursor 1-methoxyoctadiene (MOD-1). In this work, we elucidate the steps for generating the active Pd^0 species for this reaction using a combination of $Pd(acac)_2$ and triphenylphosphine (PPh_3). The investigations presented in this study provide the following key insights: (a) unification of the steps involved in the generation of the active precatalyst $[Pd^{II}(acac)(PPh_3)_2]^+$; (b) elucidation of the mechanism of reduction of the precatalyst to Pd^0 without MOD-1, which parallels the chemistry of the $Pd(OAc)_2/PPh_3$ system; and (c) the generation of Pd^{II}-octadienyl species from the reaction between the precatalyst and MOD-1, the product of the telomerization reaction. A reversible C–O bond cleavage process was identified that leads to the formation of the Pd^{II} π-octadienyl species as the active catalyst in the commercial telomerization process. These studies provide important insights into the reduction of $Pd(acac)_2$ into active Pd^0 species or Pd^{II} π-allyl species, which have wide implications for both cross-coupling catalysis as well as the telomerization reaction.

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Introduction

Cross-coupling reactions form the cornerstone of modern pharmaceutical and agrochemical industries due to their ubiquity in forging C–C and C–heteroatom bonds. Palladium-catalyzed cross-coupling reactions[1,2] form the most used and well-understood classes of reactions, and were recognized by the 2010 Nobel Prize in Chemistry[3,4] being awarded for the development of this technology. Due to considerations of the ease of use, bench-stable Pd^{II} salts are used, often in conjunction with tertiary phosphines to generate the active catalysts for a plethora of cross-coupling reactions. Significant advancements have been made in attempts to understand the mechanism of generation of these active catalysts, which are often low-valent Pd species that can oxidatively engage with the electrophilic reaction partners. One of the most commonly used Pd^{II} sources is palladium acetate, [$Pd(OAc)_2$], whose reactivity with tertiary phosphines to generate the catalytically active Pd^0 or Pd^I species has been investigated by Amatore and Jutand[5,6] and revisited recently by Fairlamb and coworkers (Fig. 1).[7] An important insight obtained from the latter study was that a complicated Pd speciation involving low-valent dinuclear and trinuclear Pd clusters occurred en route to the generation of [$Pd^0(PPh_3)_n$] and oxidized phosphine species. Thus, understanding the mechanistic intricacies of *in situ* reduction of Pd^{II} sources into catalytically competent, low-valent palladium species is a relevant problem that can give new insights into catalyst design.

Another common source of Pd^{II} is the neutral palladium acetylacetonate [$Pd(acac)_2$], also used in conjunction with tertiary phosphines for various reactions like the hydrogenolysis of allylic formates[8] and carbonates[9] and displacement reactions of vinyl sulfones.[10] One of the foremost industrial uses of the $Pd(acac)_2$/phosphine system is in the telomerization of 1,3-butadiene developed by The Dow Chemical Company. Butadiene telomerization is an important industrial process to

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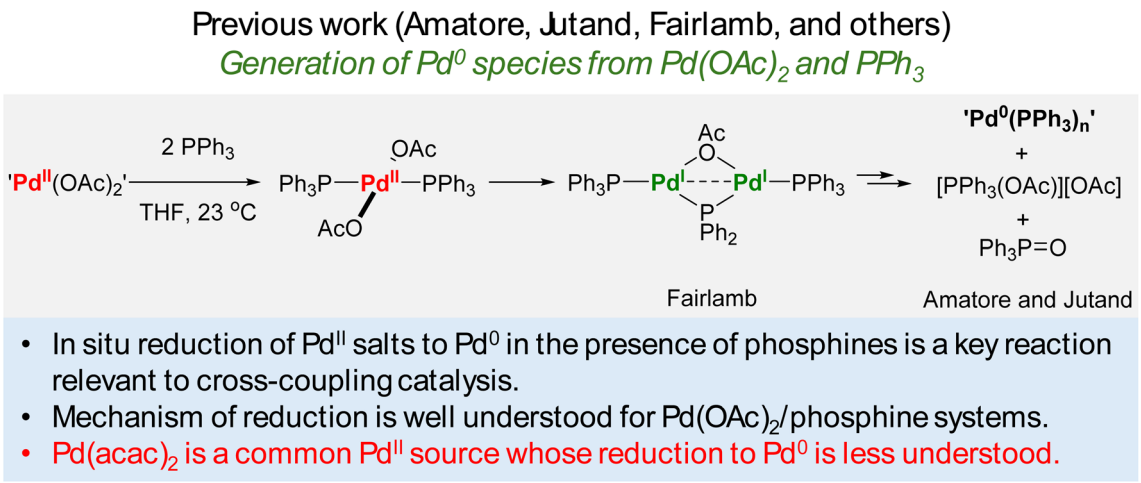


Fig. 1 Summary of key insights obtained in the reduction of the $Pd(OAc)_2/PPh_3$ system to Pd^0 from the work of Amatore, Jutand, and Fairlamb. Unlike this system, the reduction chemistry of $Pd(acac)_2/PPh_3$ is less well understood, which is the subject of the present study.

generate feedstock precursors used in the preparation of polyolefins and linear low density polyethylenes (LLDPE; *via* copolymerization with ethylene).[11] LLDPE is an important material in the commodity world (Fig. 2A), and has one of the largest global demands of any polymeric material.[12] In the Pd-catalyzed telomerization reaction, two equivalents of butadiene are dimerized to generate a Pd-octadienyl species (Fig. 2B). A capping agent (telogen) which is present in the reaction mixture performs a tail-end functionalization of this Pd-octadienyl species and prevents higher order alkene formation.[13,14] This octadiene derivative can further be processed first by hydrogenation to yield the substituted octane, which upon cracking with an alumina catalyst, generates 1-octene (Fig. 2C). It is important to note that the reaction is proposed to be initiated by the coordination of two butadiene units at a monophosphine Pd^0 center, followed by their oxidative dimerization. Yet, there have been no studies which have investigated the mechanism of generation of Pd^0 from the commercially employed $Pd(acac)_2$/tertiary phosphine mixture in the reaction system.

Among telomers, the most common in the literature and the most practical to be used on an industrial scale is methanol. The products of the telomerization reaction are methoxyoctadienes, yet the selective generation of the desired linear isomer 1-methoxy-2,7-octadiene (MOD-1) is not trivial. Other side products can be generated, such as the branched isomer 3-methoxy-1,7-octadiene (MOD-3), generated from alkoxylation at

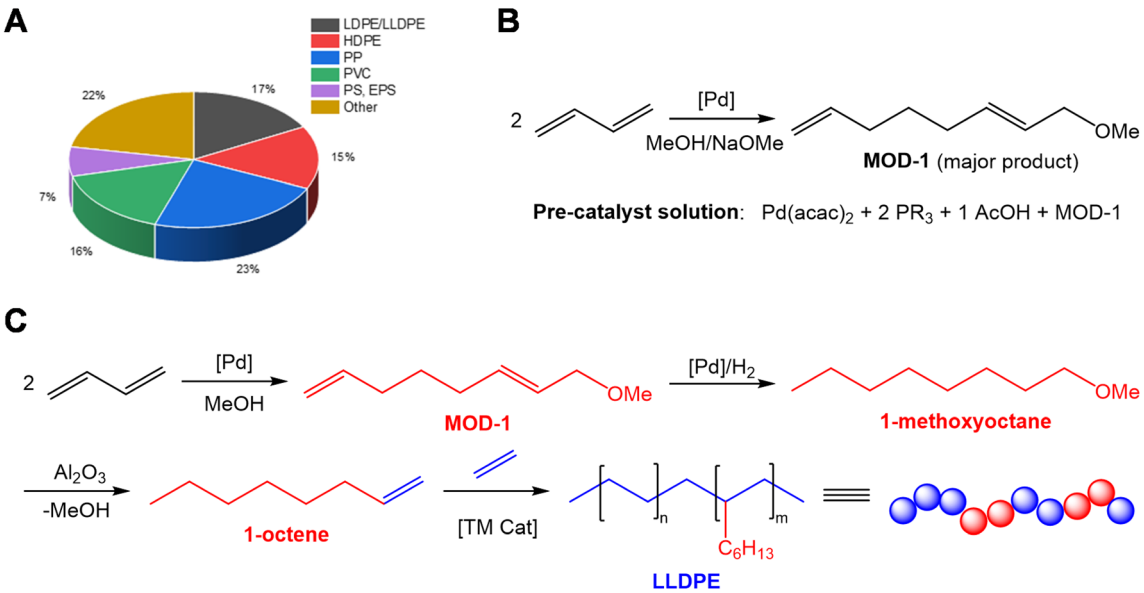


Fig. 2 (A) Global commodity plastics production by type as of 2019;[15] (B) sketch of the butadiene telomerization reaction to form 1-methoxyoctadiene developed by The Dow Chemical Company using the pre-catalyst solution shown; (C) butadiene telomerization reaction and downstream conversion to polymeric materials.

the C3 position, various unfunctionalized octatrienes, and 4-vinylcyclohexene as a Diels–Alder product.[16,17] The use of Pd catalysts supported by phosphine ligands has been extensively studied as a way to improve selectivity and stability over the course of the reaction occurring typically at elevated temperature and pressure (>60 °C and >60 psi).[18–23]

Commercially, this reaction is achieved through the use of $Pd(acac)_2$ as the palladium precursor, in conjunction with a tertiary phosphine such as triphenylphosphine (PPh_3) as the ligand.[24] The consensus mechanism is shown in Fig. 3, and several Pd^{II} species are important intermediates in the butadiene telomerization process.[25] The first compound, abbreviated as **Cat-1** in this study, is a cationic acetylacetonato-bisphosphine Pd^{II} species. The organometallic chemistry of **Cat-1** has been studied by Kawaguchi,[26] Suslov,[27] and others, and serves as the catalyst precursor that enters the catalytic cycle. The second set of compounds, abbreviated as **Cat-2** and **Cat-2′**, are cationic phosphine-ligated Pd^{II}(octadienyl) complexes that are proposed intermediates in the catalytic cycle. **Cat-2** is a monophosphine $Pd^{II}(\eta^3\text{-allyl})(\eta^3\text{-alkenyl})$ compound, while **Cat-2′** is a bisphosphine $Pd^{II}(\eta^3\text{-allyl})$ species. This speciation might be critical, as it has been suggested by Beller and coworkers that the origin of the MOD-1/MOD-3 selectivity is determined by the ligation number of this active catalyst.[16] The monophosphine adduct results in high MOD-1 selectivity, while the bisphosphine adduct leads to an increase in MOD-3 selectivity. It has been shown by researchers from The Dow Chemical Company that using a MOD-1 modified pre-catalyst solution eliminates an induction period in catalysis (Fig. 2B).[28] It is plausible that the induction period originates from facile generation of the proposed active Pd^0 complex from the Pd^{II} precursor, and it has been proposed that on-cycle species such as **Cat-2** and **Cat-2′** generated *in situ* eliminate this induction period. However, the mechanism of the generation of these Pd^{II} species from a reaction between **Cat-1** and MOD-1, presumably *via* coordination of olefinic species to low-valent Pd species, has not been studied in detail.

In this study, we use the combination of $Pd(acac)_2$ and PPh_3 as a model system to address some of the gaps in knowledge in the context of the aforementioned chemistry (Fig. 4). First, we build on the foundational studies from Kawaguchi *et al.*[26] to validate the mechanism of generation of **Cat-1** from $Pd(acac)_2$ and PPh_3, which is not a simple, one-step reaction. We use a combination of multinuclear NMR spectroscopies and X-ray crystallography to elucidate this set of reactions and uncover a solvent dependence on the major products formed. We then provide definitive evidence of the generation of Pd^0 by the *in situ* reduction of this Pd^{II} species,[29,30] which has broader thematic relevance in the context of Pd-catalyzed reactions which make use of $Pd(acac)_2$/phosphine systems. Finally, we show that in the presence of MOD-1, the product of the telomerization reaction, the formation of Pd^{II} octadienyl species like **Cat-2** and **Cat-2′** occurs from **Cat-1** *via* a series of steps. These include the reduction of Pd^{II} to Pd^0, followed by a reversible cleavage of the C–OMe bond in MOD-1 to generate the Pd^{II}-octadienyl species **Cat-2** and **Cat-2′**. The existence of **Cat-2** and **Cat-2′** has been widely noted, but the pathway of generating them from the product of the telomerization reaction has never been investigated. While this reaction is specific for telomerization chemistry, the generation of Pd^{II}-allyl species from a mixture of $Pd(acac)_2$, phosphines, and an allylic group has broader relevance as Pd^{II}-allyl compounds are privileged precatalysts for various cross-coupling reactions.[31]

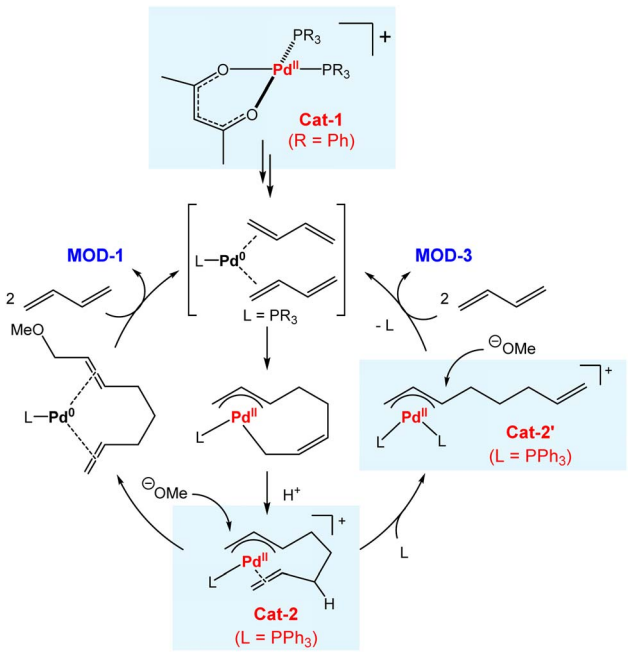


Fig. 3 Proposed catalytic cycle for butadiene telomerization using $Pd(acac)_2$ and tertiary phosphines. The key complexes that are discussed herein are highlighted in blue.

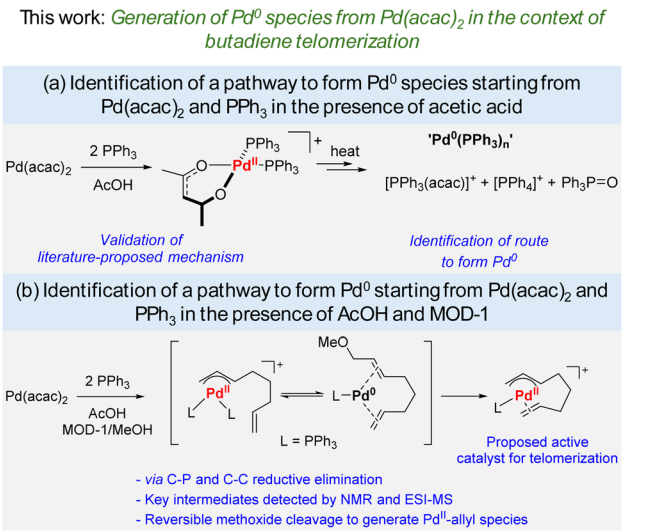
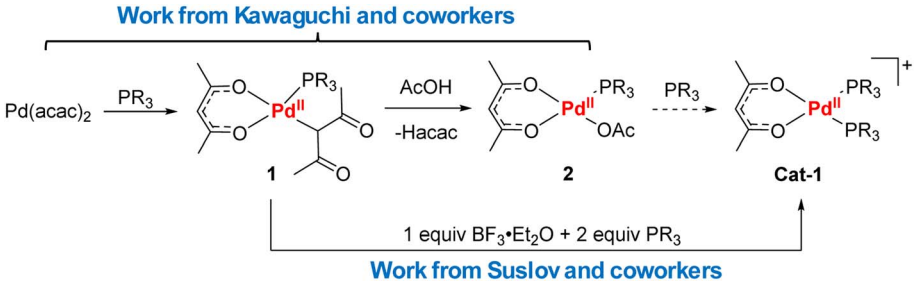


Fig. 4 The context of the present study: (a) validation of the mechanism of generating **Cat-1** and unraveling its mechanism to form Pd^0 phosphine species; (b) elucidation of the mechanism of formation of the octadienyl Pd^{II} precatalysts **Cat-2** and **Cat-2′** when the $Pd(acac)_2$/PPh_3 system is treated with MOD-1.



Scheme 1 Prior work from the Suslov and Kawaguchi groups in identifying the intermediates leading to the formation of **Cat-1**.

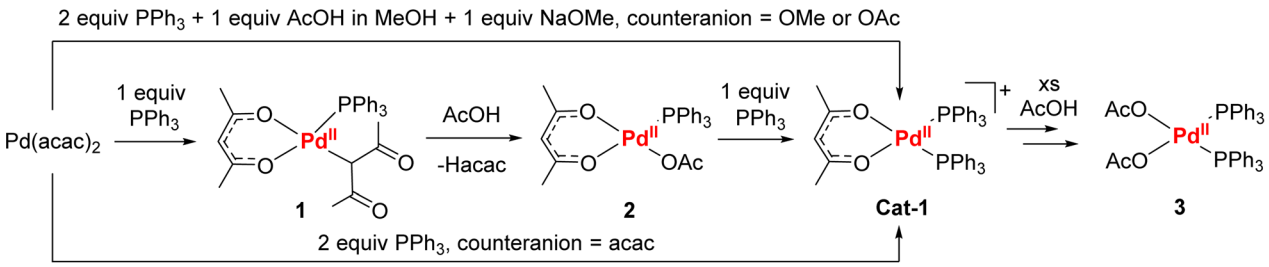
Results and discussion

Validation of the mechanism of formation of [(acac)$Pd^{II}(PPh_3)_2]^+$ (Cat-1)

The reaction of $Pd(acac)_2$ with triarylphosphines in the presence of acetic acid and Lewis bases has been studied extensively by Kawaguchi[26] and Suslov,[27] respectively (Scheme 1). In this context, we set out to investigate the entire set of reactions involved in the proposed generation of $[(acac)Pd^{II}(PPh_3)_2]^+$ (**Cat-1**) from $Pd(acac)_2$. The first step is the addition of one equivalent of phosphine to $Pd(acac)_2$, leading to the linkage isomerization of one bound acac ligand from the κ^2-*O*,*O* to the κ^1-C_γ binding mode and formation of compound **1**, which was crystallographically characterized by Kawaguchi and coworkers.[26] The preference of the κ^1-C_γ binding is governed by the relative stabilities of the keto *versus* enol forms of the β-dicarbonyl compounds and has been reviewed extensively by Kawaguchi.[32]

In the presence of acetic acid, the formation of **2** can be readily explained by the protodemetalation of the κ^1-C_γ-bound acac to release one equivalent of free Hacac and subsequent κ^1-*O* coordination of the acetate.[26,33] This compound has been characterized by NMR and IR spectroscopy by the Kawaguchi group, but no crystallographic evidence was presented. The final step is the ligand substitution of the acetate by another equivalent of phosphine to generate **Cat-1**.[33] An analogous reaction has been reported by Suslov and coworkers,[27] whereby **Cat-1** was prepared and crystallographically characterized from the reaction of **1** with two equivalents of the Lewis acid boron trifluoride etherate ($BF_3 \cdot OEt_2$) and one equivalent of phosphine. To the best of our knowledge, the sequence of reactions to get from $Pd(acac)_2$ to **Cat-1** in the presence of acetic acid and PPh_3 has never been consolidated into a single, contiguous set of reactions. During our efforts to do so, we also crystallized several Pd–phosphine species that are along the reaction pathway in Scheme 1 and an off-pathway *cis*-$(PPh_3)_2Pd^{II}(OAc)_2$ byproduct that is in contrast to the expected product from ligand *trans* influence. Scheme 2 summarizes the key ^{31}P NMR signatures observed experimentally in our studies.

In the context of butadiene telomerization, **Cat-1** is usually prepared directly by mixing $Pd(acac)_2$ with 2 equivalents of PPh_3



Compound/Rxn mixture (R = PPh_3)	1	2	Cat-1	3
δ_P (CD_2Cl_2) of sequential reactions	33.5 ppm	23.7 ppm	30.5, 36.3 ppm	-
δ_P (CD_3OD) of sequential reactions	36.5, 33.5 ppm + (**1**) as precipitate	36.5, 23.6 ppm + (**2**) as precipitate	36.5 ppm	-
δ_P of isolated product (solvent)	33.5 ppm (toluene)	23.7 ppm (toluene)	36.5 ppm (MeOH, $CDCl_3$)	28.3 ppm ($CDCl_3$)
Solid-state structure	with $PPh(^{2\text{-}OMe}Ph_2)$ this work	This work	with BF_4^- (Suslov)	This work

Scheme 2 Key ^{31}P NMR signatures for identifying the intermediates leading to the formation of **Cat-1** in CD_2Cl_2 and CD_3OD described in this study.

and 1 equivalent AcOH in methanol.[28] This solution exhibits a single resonance of 36.5 parts per million (ppm) in the ^{31}P NMR spectrum in $CDCl_3$ (Fig. S1†). ESI-MS analysis of the methanolic solution reveals a peak at $m/z = 729.1317$, which corresponds to the mass of the cationic species **Cat-1**. In order to understand the solution speciation of the sequence of reactions described above, we conducted stepwise reactions shown in Scheme 2. The reaction mixture was monitored by ^{31}P and ^{1}H NMR spectroscopy in CD_3OD (the solvent used for telomerization) and CD_2Cl_2 (a less polar, aprotic solvent). As shown in Fig. 5A (top), addition of one equivalent of PPh_3 to $Pd(acac)_2$ in CD_2Cl_2 leads to a single peak in the ^{31}P NMR spectrum at 33.5 ppm and characteristic shifts for the methine protons of the κ^2-*O*,*O* and κ^1-C_γ bound acac (Fig. S16†). This compound corresponds to the Pd^{II} species with the κ^1-C_γ acac in the ^{1}H NMR spectrum (**1**), and it has been crystallized before by Kanda and coworkers.[26] During the course of our studies, an analog of **1** was crystallized through the use of a bis-(2-methoxyphenyl) phenylphosphine ligand – labelled **1-PPh$^{2\text{-OMe}}$Ph$_2$** (Fig. 7). On adding one equivalent acetic acid to the solution of **1** in CD_2Cl_2, the major species seen in the ^{31}P NMR spectrum is a peak at 23.7 ppm (Fig. 5A, middle), which is attributed to **2** in the ^{1}H NMR spectrum. The disappearance of the methine and methyl protons corresponding to the κ^1-C_γ acac was observed, along with the appearance of the characteristic protons of free Hacac (Fig. S17 and S18†), thus confirming the replacement of the κ^1-C_γ bound acac with κ^1-*O* bound acetate. This was a fast reaction, and no intermediates were observed in the NMR timescale, suggesting that the formation of **2** from **1** is a simple ligand substitution reaction. An independent synthesis of the same compound in toluene showed the same ^{31}P NMR shift (Fig. S2†). We were able to grow single crystals by the diffusion of diethyl ether into a toluene solution of **2**, and the solid-state structure confirms the proposed identity of **2**.

Interestingly, when the same set of reactions were carried out in CD_3OD, the importance of solvent polarity became apparent. Addition of one equivalent of PPh_3 to $Pd(acac)_2$ led to the precipitation of a small amount of yellow solid from the solution mixture. The ^{31}P NMR of the solution showed two peaks, an intense peak at 36.5 ppm (**Cat-1**) and a less intense peak at 33.5 ppm (**1**, Fig. 5B, top). Adding 1 equivalent of AcOH to the reaction mixture led to the appearance of a peak at 23.6 ppm (**2**) with the concomitant formation of insoluble yellow solids, but the major species was still retained at 36.5 ppm. The yellow precipitate in these two reactions, which are formed in miniscule amounts, are **1** and **2**, along with other minor species (Fig. S19 and S20†). These observations are consistent with the neutral compounds **1** and **2** being soluble in a relatively less polar solvent (CD_2Cl_2) and sparingly soluble in a polar solvent like CD_3OD. Interestingly, some of the monocationic **Cat-1** forms even during the first step in methanol, while the formation of **Cat-1** is incomplete even after the addition of one equivalent of PPh_3, AcOH, and a further equivalent of PPh_3 to $Pd(acac)_2$ in dichloromethane (*vide infra*).

Finally, the last step in the reaction to generate **Cat-1** is the replacement of the inner-sphere acetate by a second equivalent of PPh_3. Accordingly, the addition of one equivalent of PPh_3 to the reaction mixture containing **2** in CD_2Cl_2 led to the formation of two new species in the ^{31}P NMR (Fig. 5A, bottom). One of them was readily identified as the cationic **Cat-1** (36.5 ppm) and a second unidentified species was seen at 30.5 ppm. Our hypothesis about the identity of this species is a bridged Pd^{II}-acetate compound, which has been discussed later (*vide infra*). As expected, the same reaction in CD_3OD led to the clean formation of a single peak at 36.5 ppm (Fig. 5B, bottom), confirming that the more polar solvent helps stabilize the cationic species **Cat-1**. In order to verify this hypothesis, we reasoned that the formation of the cationic species may not need AcOH, as the acac itself can act as the counteranion. Indeed, when two equivalents of PPh_3 are added to $Pd(acac)_2$ in CD_3OD, clean formation of **Cat-1** at 36.5 ppm is observed (Fig. 6A, top). When the same reaction is performed in CD_2Cl_2, the major peak corresponding to **1** is seen at 33.5 ppm, along with free PPh_3 at −4.5 ppm (Fig. 6A, bottom). It has been previously noted by Kawaguchi and coworkers that **1** is formed even when two equivalents of phosphine (or other Lewis bases) are reacted with $Pd(acac)_2$.[33] The ^{1}H NMR also verifies the

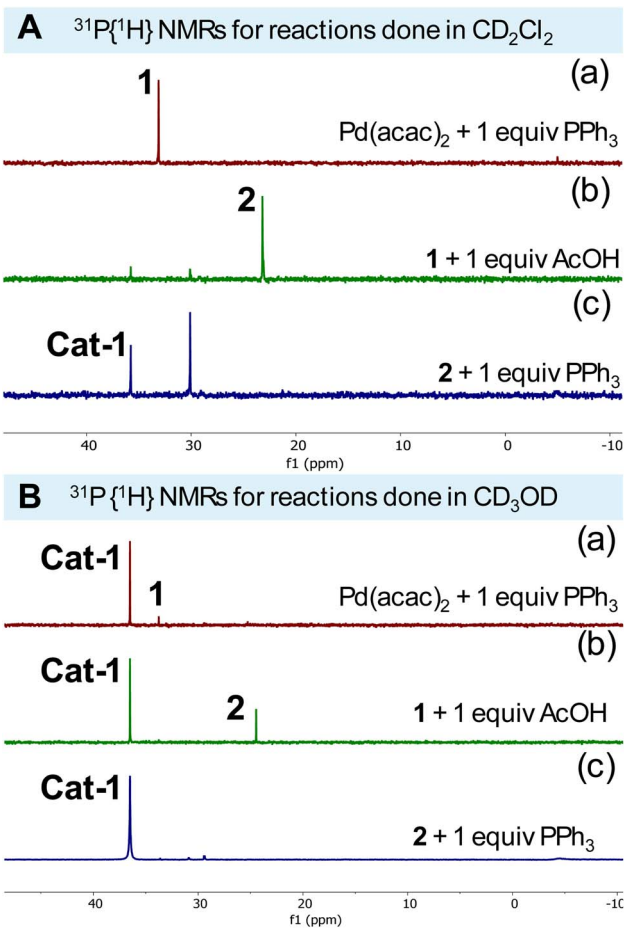


Fig. 5 (A) ^{31}P NMR (202 MHz) spectra of the contiguous set of reactions starting from $Pd(acac)_2$ and leading to **Cat-1** in CD_2Cl_2; (B) ^{31}P NMR (202 MHz) spectra of the contiguous set of reactions starting from $Pd(acac)_2$ and leading to **Cat-1** in CD_3OD. For panels (A) and (B), the sequence of reactions is as follows: (a) $Pd(acac)_2$ + 1 equiv. PPh_3 (top), (b) reaction mixture of (a) + 1 equiv. AcOH, and (c) reaction mixture of (b) + 1 equiv. PPh_3.

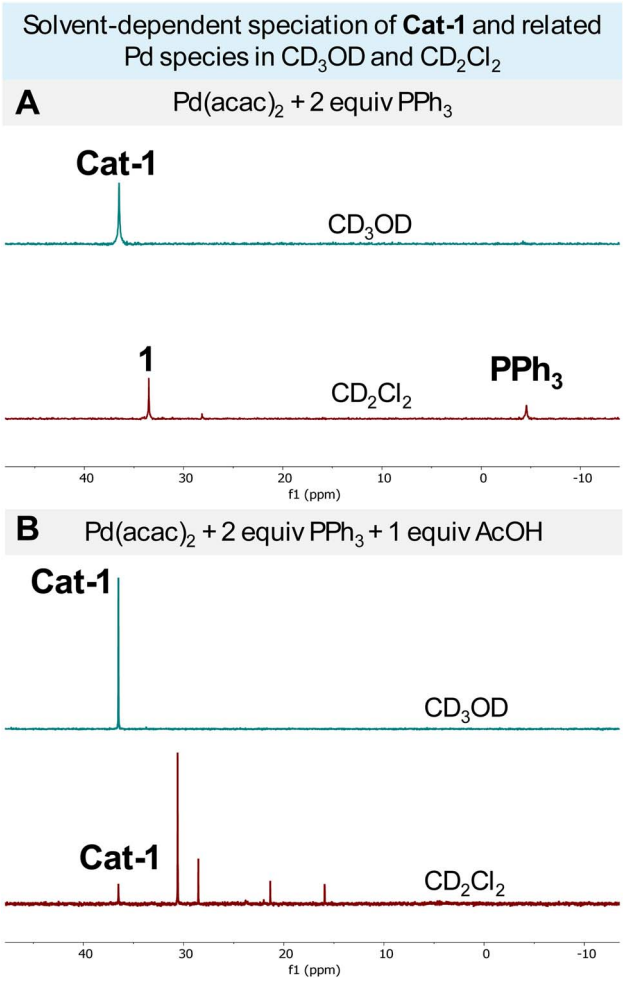


Fig. 6 (A) ^{31}P NMR (202 MHz) spectra of the reaction between $Pd(acac)_2$ and two equivalents of PPh_3 performed in CD_3OD (top) *versus* CD_2Cl_2 (bottom); (B) ^{31}P NMR (202 MHz) spectra of the reaction between $Pd(acac)_2$, one equivalent acetic acid, and two equivalents of PPh_3 performed in CD_3OD (top) *versus* CD_2Cl_2 (bottom).

identity of the species in solution as **1** along with free PPh_3 being formed (Fig. S23†).[33] When the precatalyst solution is prepared in one pot by mixing $Pd(acac)_2$, one equivalent of AcOH, and two equivalents PPh_3 in CD_2Cl_2, several signals are seen in the ^{31}P NMR spectrum (Fig. 6B, bottom). Only a small peak is seen at 36.5 ppm, which stands in contrast to the clean formation of **Cat-1** in a methanolic solution (Fig. 6A, top, and also confirmed by ^{1}H NMR, Fig. S26†). Taken together, these results demonstrate the importance of methanol in stabilizing the cationic **Cat-1** species.

Some general observations can be made about the differences in reactivity between the two solvents. It is likely that compounds **1**, **2**, and **Cat-1** exist in equilibrium with one another. In CD_2Cl_2, a salt like **Cat-1** may form immediately but is unlikely to be stable. In such a case, the outer-sphere counteranion would preferentially displace one of the PPh_3 ligands to form either **1** or **2** from acac or $^-$OAc counteranions. On the other hand, methanol will likely preferentially stabilize the charge separated **Cat-1** more strongly than **1** or **2**. This is particularly evident in the NMR comparison shown in Fig. 6B.

We then set out to connect the aforementioned chemistry with the $Pd(OAc)_2/PPh_3$ system, and probe whether we could access similar Pd species starting from $Pd(acac)_2$. Upon addition of excess AcOH to the reaction mixture in methanol (5 equivalents instead of 1 equivalent), we were able to synthesize and crystallographically characterize an unusual compound *cis*-$(PPh_3)_2$-$Pd^{II}(OAc)_2$ (**3**) that has a characteristic ^{31}P NMR peak of 28.3 ppm in $CDCl_3$. While **3** does not directly fall along the reactivity scheme, we hypothesize that its formation occurs *via* a repeat of the earlier reaction steps on **Cat-1**. The first step is the κ^2-*O*,*O* to κ^1-C_γ isomerization of the acac ligand, followed by a protodemetalation with a second equivalent of acetic acid, and then coordination of both acetate anions. We propose that this compound links the more well understood $Pd(OAc)_2/PPh_3$ with the $Pd(acac)_2/PR_3$ chemistry discussed here. It is known that $Pd(OAc)_2$ reacts with two equivalents of triphenylphosphine at room temperature to form *trans*-$(PPh_3)_2Pd^{II}(OAc)_2$, which was shown to undergo a phosphine-acetate reductive elimination by Amatore and coworkers to eventually reduce to a $[Pd^0(PPh_3)_n]$ species and an oxidized phosphine product. In our case, the *cis* configuration of all compounds shown in Scheme 2 is enforced from the start by the *cis*-chelating acac ligand. The proposed PPh_3-OAc reductive elimination in the *trans* isomer to generate the Pd^0 species relies on the formation of a chelate ring between

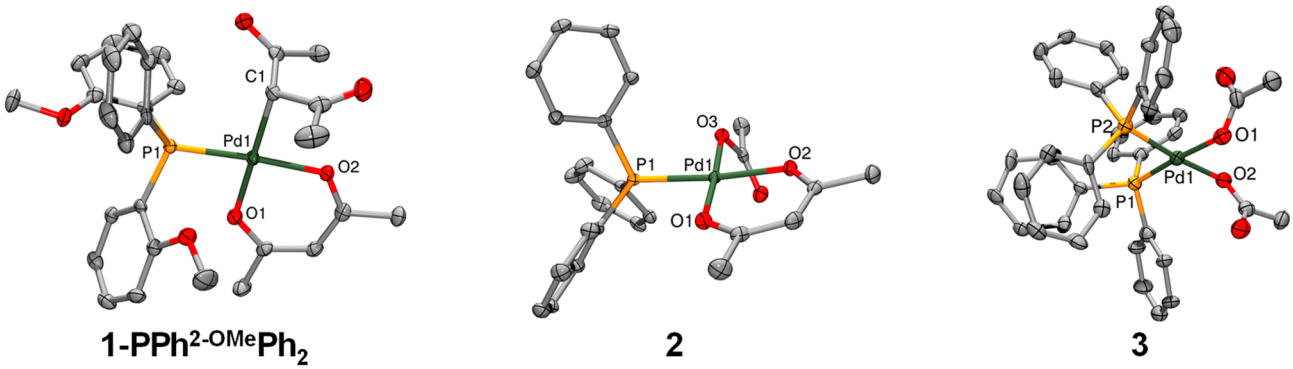
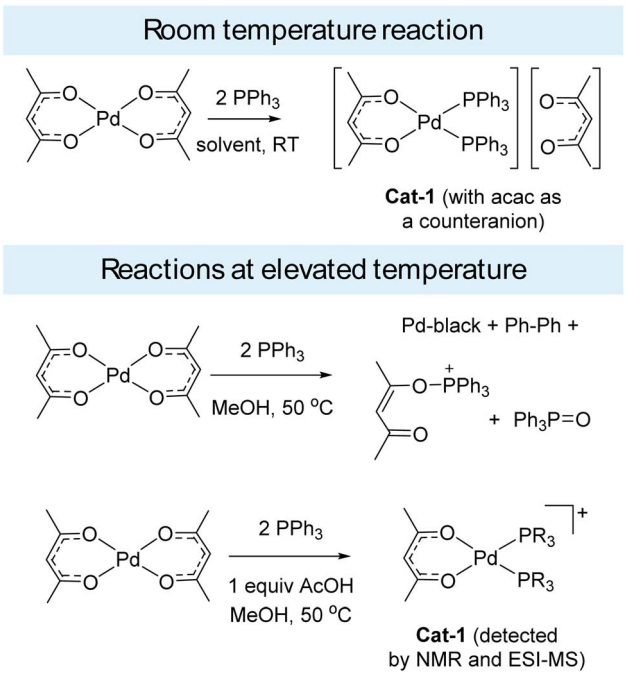


Fig. 7 Oak Ridge Thermal Ellipsoid Plots (ORTEPs) of complexes **1-PPh$^{2\text{-OMe}}$Ph$_2$**, **2**, and **3**, shown at 50% probability and with H atoms omitted for clarity. Selected bond distances (Å) for **1-PPh$^{2\text{-OMe}}$Ph$_2$**: Pd1–P1: 2.2598(8); Pd1–C1: 2.104(3); Pd1–O1: 2.060(2); Pd1–O2: 2.058(2); **2**: Pd1–P1: 2.2466(3); Pd1–O1: 1.9915(9); Pd1–O2: 2.0531(9); Pd1–O3: 2.0095(9); and **3**: Pd1–P1: 2.255(4); Pd1–P2: 2.288(4); Pd1–O1: 2.058(10); Pd1–O2: 2.068(10).



Scheme 3 Key reactions involved in the generation of **Cat-1** and Pd^0 species from $Pd(acac)_2/PPh_3$, both at room temperature and elevated temperature in methanol.

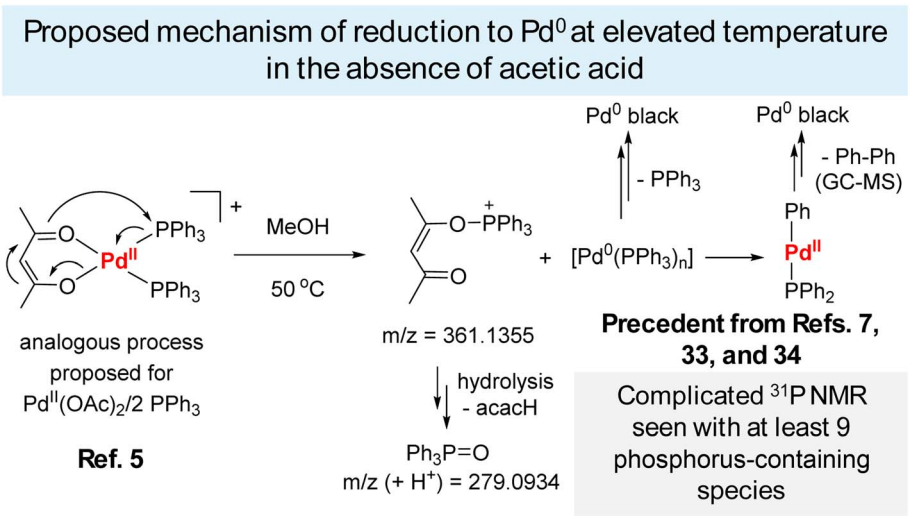
PPh_3 and the bound acetate.[7] In contrast, the *cis* configuration of the acetate ligands may be primed for hydrogen bonding with protic solvents or water, as seen in the solid-state structure of **3** (Fig. S43†). This may prevent the formation of a chelate with PPh_3 and hence prevent reductive elimination with PPh_3 at room temperature, which is consistent with the lack of $[Pd^0(PPh_3)_n]$ or Pd black formation in this reaction system.

The solid-state structures shown in Fig. 7 merit some discussion. All complexes demonstrate square planar geometries, with geometry index τ_4' values of 0.046, 0.053, and 0.070, respectively, as expected for 4-coordinate Pd^{II} complexes. Complexes **1-PPh$^{2\text{-OMe}}$Ph$_2$**, **2**, and **3** show Pd–P bond lengths of 2.260, 2.247, and a Pd–P_{ave} bond length of 2.275 Å (values ranging from 2.255 to 2.289 Å, two molecules of **3** per asymmetric unit), respectively. Complex **1-PPh$^{2\text{-OMe}}$Ph$_2$** also shows longer average Pd-acac bond lengths as compared to **2** (2.059 *vs.* 2.022 Å) due to a stronger *trans* influence from the κ^1-C_γ binding mode of the acac ligand and more electron-donating phosphine ligand. Furthermore, the asymmetry of the Pd–O bond lengths in the Pd-acac moiety is significantly larger in complex **2** compared to **1-PPh$^{2\text{-OMe}}$Ph$_2$** due to disparity in the *trans* influence going from a C-bound acac to an acetate ligand (**1-PPh$^{2\text{-OMe}}$Ph$_2$**: 2.060 & 2.058 Å; **2**: 1.992 & 2.053 Å). It is also worth noting that **3** has shorter Pd–P_{ave} distances (*cis*: 2.27 Å, *trans*: 2.33 Å) and longer Pd–O bond lengths (*cis*: 2.06 Å, *trans*: 2.03 Å) than the *trans* isomer,[7] due to the stronger *trans* influence of PPh_3.

Conversion of Cat-1 to Pd^0 species

As alluded to in the previous sections, the mechanism of Pd^{II} reduction in the $Pd(OAc)_2/PPh_3$ catalytic system has garnered significant interest, yet little work has been done in investigating the mechanism of reduction of the $Pd^{II}(acac)_2/PPh_3$ catalytic system. During the course of our studies, we found that reduction of the Pd^{II} to Pd^0 did not happen at room temperature, yet it was facile at higher temperatures in the absence of acetic acid. This section deals with the mechanistic insights we obtained in this regard, with the key findings being summarized in Scheme 3.

As noted previously, when a methanolic solution of $Pd(acac)_2$ is treated with 2 equiv. PPh_3 in the absence of acetic acid, formation of **Cat-1** was observed in the ^{31}P NMR and **1** crashed out of the solution (Fig. S29†). However, on heating the same reaction mixture up to 50 °C, significant formation of Pd^0 black was observed. ESI-MS analysis (Fig. S27 and Table S1†) of the organic fraction revealed mass fragments for $[(acac)\text{-}PPh_3]^+$ and O=PPh_3, providing strong evidence of reductive elimination of (acac) and PPh_3 from Pd^{II} to generate Pd^0 species (Scheme 4). This would presumably proceed similarly to the mechanism



Scheme 4 Proposed mechanism of the generation of Pd^0 species from $Pd(acac)_2/PPh_3$ at elevated temperature.

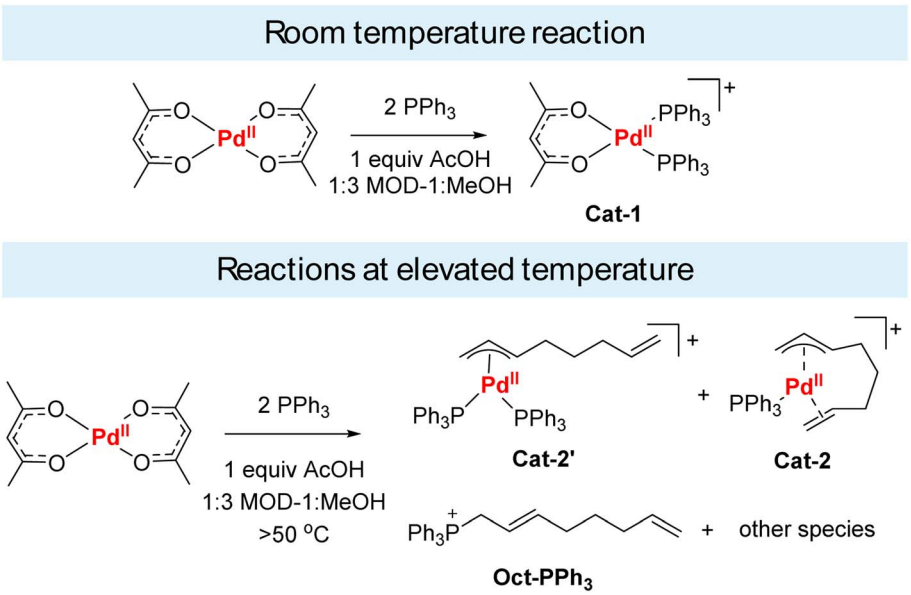
proposed by Amatore and Jutand[6,34] for the reductive elimination of Pd^{II} bound acetate and triphenylphosphine. The generation of O=PPh_3 can be rationalized by the hydrolysis of $[(acac)\text{-}PPh_3]^+$, which can be generated from trace water in methanol or in the solution used for mass spectrometry analysis. The ^{31}P NMR of this solution showed the peak corresponding to **Cat-1**, along with the formation of a bisphosphine species. This was evident from the appearance of two equal intensity doublets (J = 32 Hz). In the absence of other evidence, we cannot confirm the exact identity of this species (Fig. S30†). We hypothesize that this is an intermediate that decomposes by reductive elimination. GC-MS analysis of the organic fraction of this reaction mixture shows stoichiometric biphenyl formation (integrated relative to PPh_3), which suggests P–C_{aryl} bond cleavage of PPh_3 (Fig. S32†). This process has precedence from the work of Hursthouse and coworkers,[35] who reported the synthesis and characterization of a Pd^{II} dimer formed by the cleavage of the P–C_{aryl} bond – $[Pd^{II}_2(\mu\text{-}OAc)_2Ph_2(PPh_3)_2]$ in 41% yield when $Pd(OAc)_2$ is refluxed with excess PPh_3 in methanol. Interestingly, formation of biphenyl was observed by Fairlamb and coworkers[7] in a crude reaction mixture containing the Pd^{I} dimer shown in Fig. 1, indicating that such intermediates may be accessed in the $Pd(acac)_2$/2 PPh_3 system as well. Based on this evidence, we propose that Pd^{II}(acac)-derived precursors may undergo the same types of reductive transformations as the more ubiquitous $Pd(OAc)_2/PPh_3$ systems.[7]

In the presence of acetic acid, the solution chemistry of $Pd(acac)_2/PPh_3$ is remarkably different. Addition of 1 equivalent AcOH to this reaction at 50 °C does not result in any new reactivity, only **Cat-1** being formed, as observed by ^{31}P NMR and ^{1}H NMR (Fig. S33–S35†). The main differentiating factor, however, is that Pd black is not observed in any reaction when AcOH is added, even at elevated temperatures (80 °C) or longer reaction times (16 hours). Critical evidence was obtained from ESI-MS studies (Fig. S28†), which notably showed only trace triphenylphosphine oxide and no evidence of $[(acac)\text{-}PPh_3]^+$. This indicates an absence of reductive elimination pathways. Instead, new Pd-based mass fragments were seen, which could be assigned to **Cat-1** and other Pd^{II} species. Possible explanation for the lack of Pd^{II} reduction could be the reoxidation of any Pd^0 species being formed by acetic acid, which can react further with free acac and PPh_3 to form **Cat-1**. It is interesting to note that this pattern of reactivity is completely divergent from the facile, room-temperature reduction of the *trans*-$(PPh_3)_2$-$Pd^{II}(OAc)_2$ generated when $Pd(OAc)_2$ reacts with 2 equivalents of PPh_3.[5]

Conversion of Cat-1 to Cat-2 and Cat-2′ in the presence of MOD-1 *via* Pd^0 intermediates

Having established the reductive chemistry of the $Pd(acac)_2$/2 PPh_3 system without MOD-1, we then investigated the steps to generate the Pd^{II}-octadienyl intermediates **Cat-2** or **Cat-2′** in the presence of MOD-1. It must be mentioned that significant prior work by Jolly and Beller has focused on the investigation of the solution-state speciation of the intermediates involved in Pd-catalyzed reactions of 1,3-dienes.[36–39] Yet there has been no investigation into the generation of these Pd^{II}-octadienyl species when there is no butadiene in the reaction mixture, and the sole source of the octadiene is in fact MOD-1, the product of the butadiene telomerization reaction with methanol. In this section, we provide evidence for the C–O bond cleavage of the allyl ether and propose feasible routes for the generation of **Cat-2** and **Cat-2′** from $Pd(acac)_2$, PPh_3, AcOH, and MOD-1 (Scheme 5).

At temperatures below 50 °C for the reaction between $Pd(acac)_2$, 2 equivalents PPh_3, and 1 equivalent AcOH in the presence of excess MOD-1, no formation of **Cat-2** is observed by ^{31}P NMR spectroscopy (Fig. S34†). Since the formation of **Cat-2**



Scheme 5 Key reactions involved in the attempted generation of Pd^{II}-octadienyl species from $Pd(acac)_2/PPh_3$ at room temperature and elevated temperature in the presence of MOD-1 in methanol.

from MOD-1 would involve oxidative addition to an allyl ether, it is likely that a low-valent Pd species must be generated *via* a C–P reductive elimination as highlighted in the previous section. This is not observed at lower temperatures, which can be attributed to slow oxidative addition of the octadienyl ether or slow acac dissociation from **Cat-1**. However, when the same reaction mixture is heated at 70 °C, a complicated mixture of species is observed (Fig. 8, bottom panel). Most of the characteristic ^{31}P signals were identified by comparison with independently synthesized compounds or literature precedents, which helped us assign most of the major species in solution. The most characteristic set of peaks was a set of two doublets at 25.6–26.3 ppm (J = 41.1 Hz) which are assigned to the bisphosphine species **Cat-2′** (confirmed by independent synthesis, Fig. 8, middle panel). In addition, a singlet could be identified at 26.05 ppm which was confirmed to be **Cat-2** (Fig. 8, top panel) by independent synthesis following the protocol reported by Weckhuysen *et al.*[40] By fitting the peaks an approximate ratio of 1 : 3 can be identified for **Cat-2 : Cat-2′** in the reaction mixture (Fig. S36†). ESI-MS analysis of this reaction mixture shows two major organic products at m/z = 279.0936 and m/z = 371.1921 (Fig. S38 and Table S4†), which can be assigned to triphenylphosphine oxide and an octadienylphosphonium (**Oct-PPh$_3$**) salt, respectively. The latter has been reported[24] to be a decomposition product in butadiene telomerization reactions, and the former is known to be a hydrolysis product of **Oct-PPh$_3$**. Moreover, we could also identify the octadienylphosphonium salt in the ^{31}P NMR spectrum that reveals a singlet at 21.6 ppm.[41,42] Other key ^{31}P NMR signals were attributed to **3** (28.6 ppm) and the bridging Pd^{II} species arising from C–P bond cleavage (30.5 ppm), as observed by Hursthouse when Pd(OAc)$_2$ reacts with PPh$_3$ in methanol (*vide supra*).[35] Control experiments mimicking the generation of a MOD-1 bound Pd^0 PPh$_3$ compound (Fig. S37†) suggest that the peak at 32.5 ppm may be (PPh$_3$)Pd^0(MOD-1), which we also see in the ESI-MS of the reaction mixture.

With the NMR and ESI-MS evidence in hand and based on our knowledge from the works of Jolly, Beller, and others, we propose the simplified mechanism outlined in Scheme 6. Importantly, this work focuses on how **Cat-2** or **Cat-2′** can be generated starting from the precatalyst solution used in the commercial process of the Dow Chemical Company, in order to eliminate induction period in the Pd-catalyzed telomerization reactions.[28] In summary, we know that heating **Cat-1** in the absence of acetic acid produces Pd^0 species, which are presumably reoxidized in the presence of acetic acid. However, in the presence of a large excess of MOD-1 this putative phosphine-ligated Pd^0 species can bind to a molecule of MOD-1 to generate [**LPd^0(MOD-1)**], whose protonated adduct was detected by ESI-MS. This can then oxidatively add to the allyl ether bond where the methoxy group acts as a leaving group to generate the monophosphine Pd^{II} octadienyl species **Cat-2**, detected in both ESI-MS and ^{31}P NMR. Key evidence for this step was obtained from the reaction of Pd^{II}(acac)$_2$ with 2 equiv. PPh$_3$ and 10 equiv. MOD-1 in CD$_3$OH in the absence of acetic acid. GC-MS analysis of the reaction mixture shows the incorporation of 3 deuterium atoms into MOD-1 with no observed formation of octadienes, which indicates that C–O bond cleavage is reversible under these conditions and the exchange of the methoxy group with the deuterated methanol solvent is occurring during this process (Fig. S39†).

While the above discussion implies that the Pd center is cleaving the C–O bond that it forms during the catalysis, it is important to note that the catalytic reaction is initiated with a large excess of butadiene relative to the palladium catalyst. All experimental data presented in this study consider reaction conditions in which butadiene is not involved. In addition,

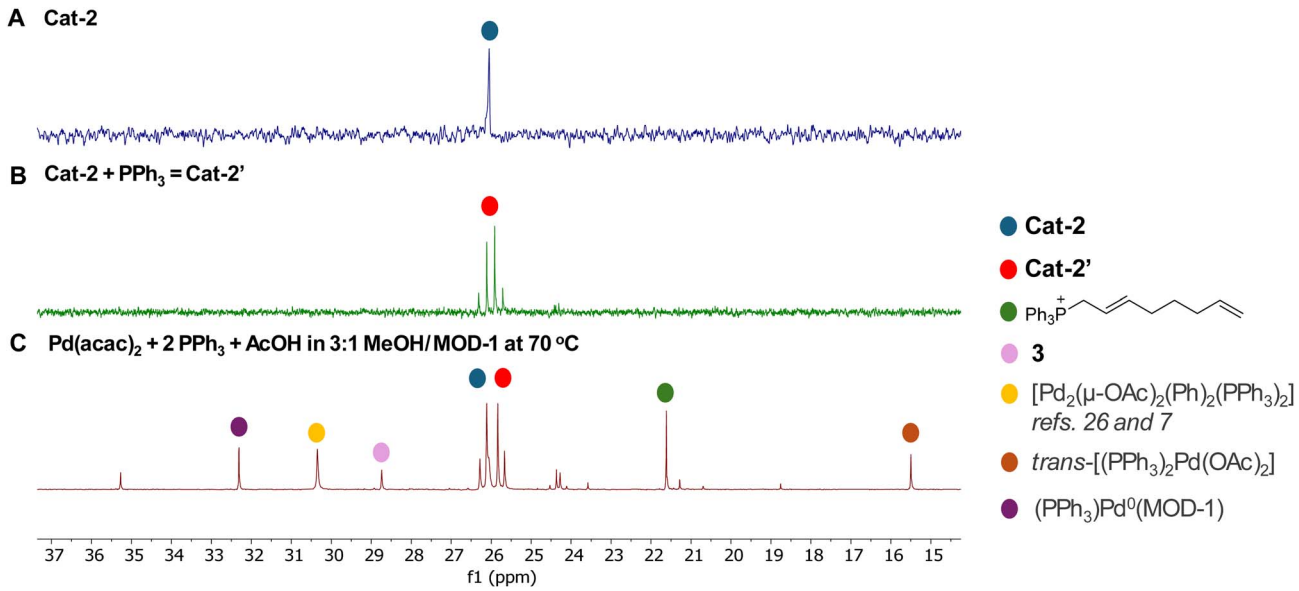
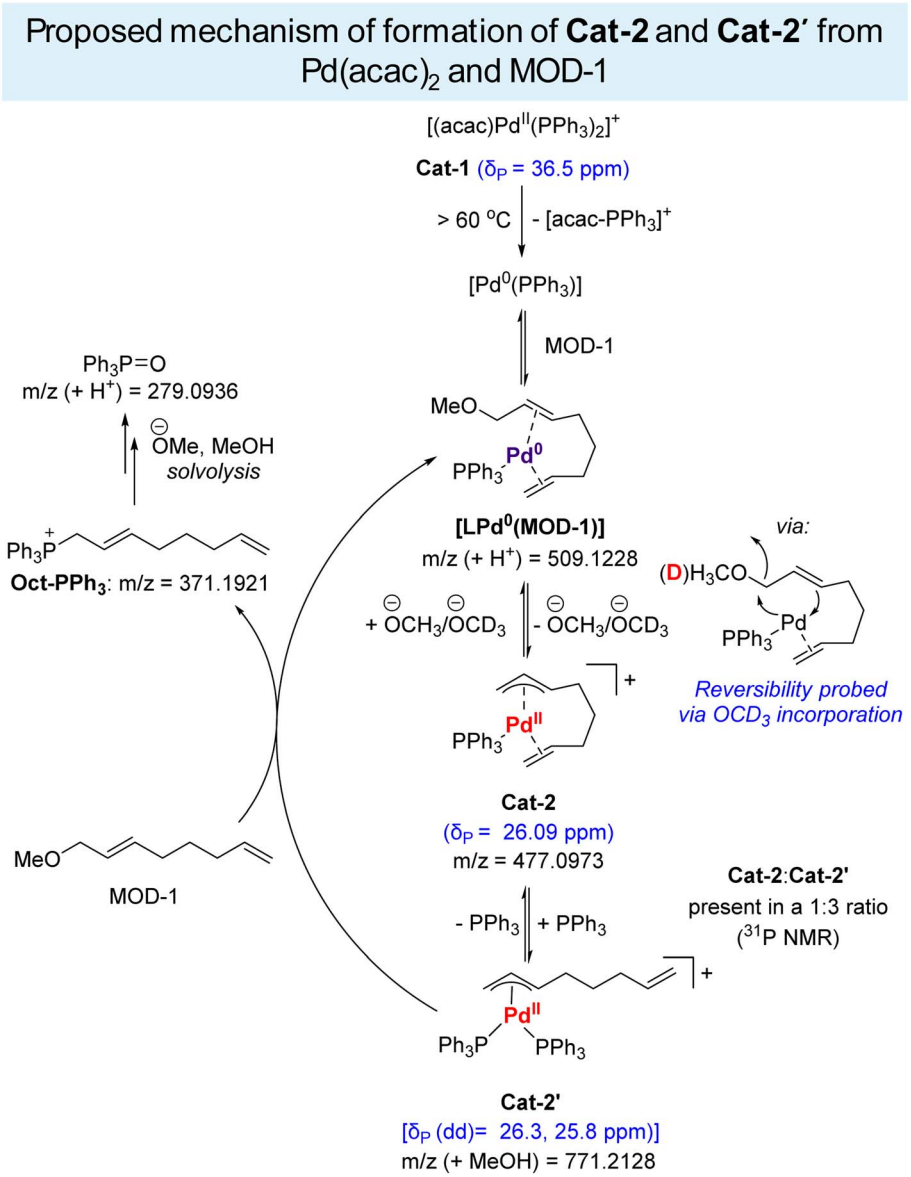


Fig. 8 ^{31}P NMR (202 MHz) spectra related to the generation of **Cat-2** and **Cat-2′**. (A) ^{31}P NMR spectrum of **Cat-2** synthesized by the method reported by Weckhuysen *et al.*; (B) ^{31}P NMR spectrum obtained on adding one equivalent PPh$_3$ to **Cat-2** to generate **Cat-2′**; (C) crude ^{31}P NMR spectrum of Pd(acac)$_2$, PPh$_3$, AcOH heated to 70 °C in 3 : 1 MeOH/MOD-1.



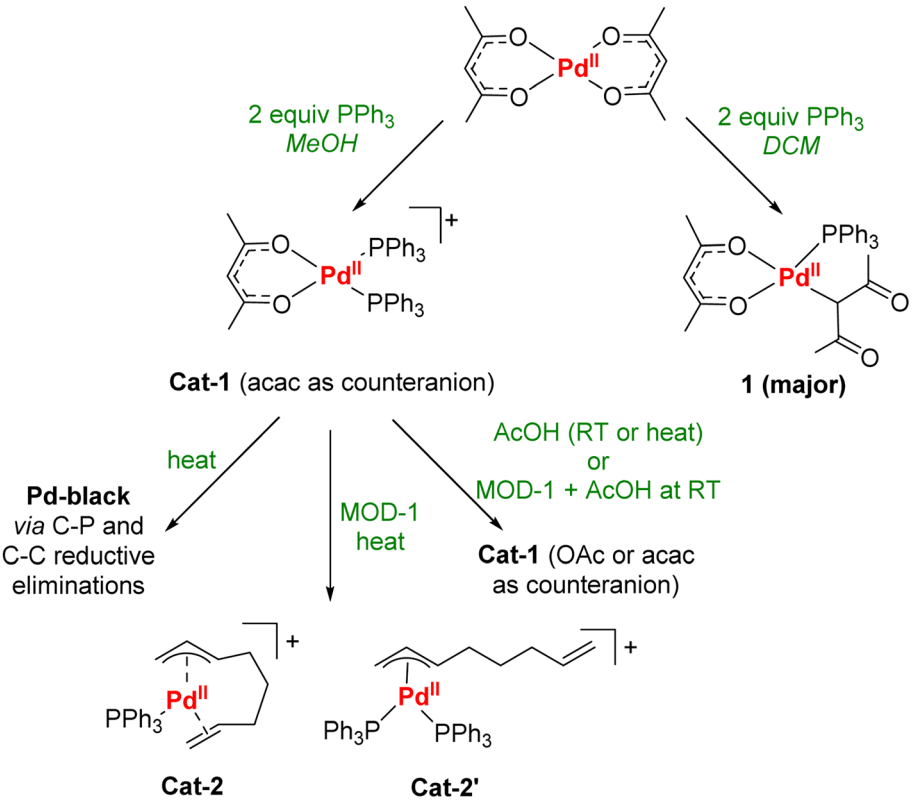
Scheme 6 Proposed mechanism of the generation of **Cat-2** and **Cat-2′** species from $Pd(acac)_2/PPh_3$ at elevated temperature in the presence of MOD-1. The ^{31}P NMR shifts of the relevant species in methanol and the observed *m/z* values from ESI-MS are given as well.[41]

typical reaction times tend to be quite short – usually two hours.[24] Thus, it is expected that the oxidative dimerization of two butadiene molecules at Pd^0, followed by nucleophilic attack of methoxide should still be the predominant reaction pathway under normal telomerization reaction conditions.

While **Cat-2** is the critical selectivity-determining intermediate for the formation of MOD-1, we also see NMR and ESI-MS evidence of a bisphosphine species. This can be readily explained by a reversible addition of a further equivalent of PPh_3 to **Cat-2**, to generate **Cat-2′**. In fact, this is the major species we see in solution and also has precedent. It has been shown that less sterically demanding phosphines, without an *ortho* substituent leads to the formation of bisphosphine species. Finally, to account for the formation of octadienyl-phosphonium species detected in the ^{31}P NMR and ESI-MS, we propose two possible pathways. One possibility is the reductive elimination of a molecule of PPh_3 with the octadienyl species which can regenerate the Pd^0 species [**LPd^0(MOD-1)**]. Another route for generating the octadienyl-phosphonium salt is the nucleophilic attack of a free phosphine on the π-allyl system of the octadienyl ligand bound to **Cat-2**, which would also generate a putative monophosphine-Pd^0 species that can participate in downstream reactivity; a step that has been investigated by Weckhuysen and coworkers.[24,30,41]

Conclusions

In this study, we have undertaken a systematic investigation of the chemical steps involved in the generation of the $[(PPh_3)_2Pd^{II}(acac)]^+$ species starting from $Pd(acac)_2$. The summary of the key Pd species and the conditions under which they are generated has been shown in Scheme 7. We have also uncovered a solvent-



Scheme 7 Summary of overall palladium reactivity for the $Pd(acac)_2$/2 PPh_3 system in the context of precatalyst speciation for butadiene telomerization. Reaction conditions are shown in green.

dependent speciation for this process, whereby a polar protic solvent (methanol) can stabilize the cationic species better than a polar aprotic solvent (dichloromethane). In addition, we provided the first structural evidence for one of the intermediates (**2**) involved in the generation of $[(PPh_3)_2Pd^{II}(acac)]^+$ and isolated a rare *cis*-$[(PPh_3)_2Pd^{II}(OAc)_2]$ (**3**) during these investigations. Then we sought to understand the mechanism of reduction of the Pd^{II} species to generate Pd^0. We found that in the absence of acetic acid, this process is facilitated by an acac-PPh_3 reductive elimination, akin to the OAc-PPh_3 reductive elimination seen in the $Pd(OAc)_2$/PPh_3 system. Importantly, this study provides strong support for the potential use of $Pd(acac)_2$/triarylphosphine systems as a precatalyst combination for traditional Pd-catalyzed reactions. This is especially relevant as the $Pd(OAc)_2$/PPh_3 system tends to form more complicated mixtures of Pd species. One surprising departure from the $Pd(OAc)_2$/PPh_3 system was the finding that adding AcOH to the $Pd(acac)_2$/PPh_3 system prevents the formation of Pd^0 species, even at higher temperatures.

Finally, in the context of butadiene telomerization, we have provided a mechanistic explanation for how this precatalyst system can react with MOD-1 to generate on-cycle intermediates such as **Cat-2** and **Cat-2′**, or "naked" $[Pd^0(PPh_3)_n]$ species that skip the induction period typically observed during catalysis with **Cat-1**. This is somewhat counterintuitive, as MOD-1 is the major product of the telomerization reaction. However, the precatalyst solution is generated separately, without any butadiene present, which aids the formation of on-cycle species like **Cat-2** and **Cat-2′**. The key new finding is the direct observation of the reversible C–O bond cleavage of the methoxy-octadiene fragment to generate a π-allyl species, a step that mimics the formation of Pd^{II} π-allyl compounds in Tsuji–Trost reactions. We anticipate that these insights will facilitate the design of more active catalytic systems for this important reaction. Overall, these results map an underused catalytic system – the combination of $Pd(acac)_2$ with triarylphosphines, into the broader context of Pd catalysis by examining the mechanism and conditions for the generation of catalytically active Pd^0 and Pd^{II}-octadienyl compounds in protic solvents.[30]

Data availability

Experimental details of the synthesis of new compounds (**3** and **1-PPh$^{2\text{-OMe}}$Ph$_2$**), NMR and ESI-MS of reaction mixtures, additional characterization data including ^{1}H, ^{13}C, and ^{31}P NMR spectra, and crystallographic information are available in the ESI.† The deposition numbers CCDC 2376744–2376746 at the Cambridge Crystallographic Data Centre (CCDC) contain the crystallographic data for compounds **1-PPh$^{2\text{-OMe}}$Ph$_2$**, **2**, and **3**. These data are provided free of charge by the CCDC (https://www.ccdc.cam.ac.uk/).

Author contributions

BSB, DYB, SC, MR, RDK, and LMM designed the experiments. Experimental work and data analysis were performed by SC,

DYB and BSB. The manuscript was written through the contributions of all authors.

Conflicts of interest

The authors have no conflicts to declare.

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