A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202001809
Angew. Chem. 10.1002/ange.202001809

Link to VoR: http://dx.doi.org/10.1002/anie.202001809
http://dx.doi.org/10.1002/ange.202001809

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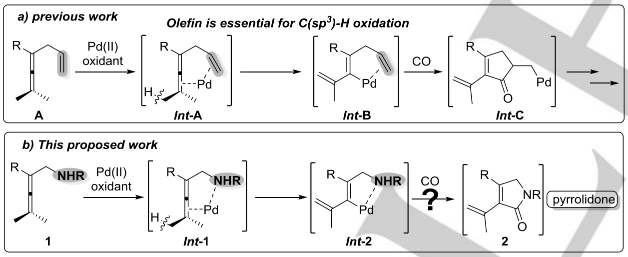
Silver Triggering Activity of Heterogeneous Palladium Catalyst in Oxidative Carbonylation Reactions

Man-Bo Li,[+]* Ying Yang,[+] Abdolrahim A. Rafi, Michael Oschmann, Erik Svensson Grape, A. Ken Inge, Armando Córdova,* and Jan-E. Bäckvall*

Abstract: A silver-triggered heterogeneous Pd-catalyzed oxidative carbonylation has been developed. This heterogeneous process exhibited high efficiency, good recyclability, and was utilized for a one-pot construction of polycyclic compounds with multi-chiral centers. AgOTf was used to remove chloride ions in the heterogeneous catalyst Pd-AmP-CNC, generating a highly active Pd(II), which results in the high efficiency of the heterogeneous catalytic system.

Palladium-catalyzed oxidative carbonylations have been widely used for the introduction of carbonyl groups into organic molecules, which provides the basis for streamlined construction of valuable products from various feedstocks.[1] As a powerful approach towards direct oxidative carbonylations of aliphatic hydrocarbons, these reactions are attractive for applications in industry. A central questions in palladium-catalyzed oxidative carbonylation reactions is the achievement of high palladium efficiency, and at the same time, realizing a well-controlled selectivity and recovery of the metal in the transformations.[2]

During the past six years, our group has developed efficient oxidative carbonylation reactions of enallenes catalyzed by Pd(OAc)$_2$ or Pd(TFA)$_2$.[1j,3] As shown in Scheme 1a, the olefin group of enallene **A** coordinates to Pd(II), triggering the allenic C(sp^3)–H cleavage to give ***Int*-B**. After a carbon monoxide insertion and a subsequent olefin insertion, this reaction allows the construction of a cyclopentenone intermediate (***Int*-C**), which can be transformed to different useful products. In these transformations, the coordination of olefin to Pd(II) is essential for the allenic C(sp^3)–H cleavage, affording ***Int*-B**. Replacement of the olefin group by an alkyl or aryl group completely shuts down the reactivity of the allene.[4] Inspired by these previous studies, we were interested in investigating the oxidative carbonylation of allenes bearing a nitrogen-contained functionality (NHR, Scheme 1b). In this approach the NHR group would trigger the attack of the allene (***Int*-1** to ***Int*-2**) and subsequent carbonylation would give pyrrolidone **2**. In a very recent work we have observed that an amide group can trigger allene attack on Pd(II).[5]



Scheme 1. Previous work on olefin-directed oxidative carbonylation of enallene and this proposed work.

We initiated our proposal by using allene **1fa** (R = Ph) as the starting material in the presence of Pd(TFA)$_2$, BQ, CHCl$_3$ and 1 atm of CO at room temperature (For details, see Supporting Information, p. S8). **1fa** was very reactive and it was consumed completely under the reaction conditions. However, only dihydropyrrole **3** was observed as the sole product, which was generated from Pd-catalyzed intramolecular aminopalladation (***Int*-D**). In contrast, treatment of allene **1f** (R = Ts) under the same reaction conditions resulted in the recovery of the starting material. At 60^{o}C a similar aminopalladation product **3** was isolated in 89% yield, while, to our delight, the desired product **2** was observed in 8% yield. These results demonstrated that 1) allene amine (**1fa**) and allene amide (**1f**) are reactive with Pd to be cyclized via intramolecular aminopalladation;[6] 2) the reactivity of allene amide (**1f**) can be partially switched to proceed with Pd-catalyzed oxidative carbonylation, giving desired product pyrrolidone **2**.[7]

Based on the initial results, we tried to improve the selectivity of the reaction by using allene amide **1a** as the starting material at room temperature, producing pyrrolidone **2a**. Different variants of homogeneous palladium catalysts, solvents or oxidants did not give any desired product. Instead allene **1a** was recovered in these cases (For details on optimization of reaction conditions, see Supporting Information, p. S9). Very recently, our group has developed an efficient heterogeneous palladium catalyst immobilized on amino-functionalized siliceous

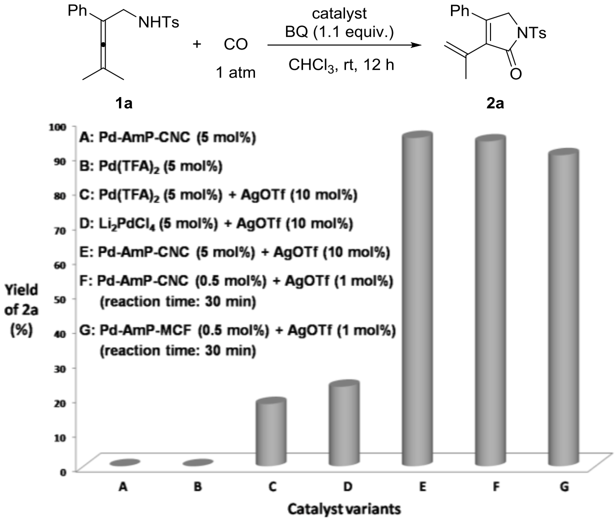


Figure 1. Comparison of different catalyst variants.

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mesocellular foam (Pd-AmP-MCF) for oxidative cyclizations of enallenols.[8] In these transformations, Pd-AmP-MCF showed higher catalytic activity as well as stability compared to the corresponding homogeneous palladium catalysts such as $Pd(OAc)_2$ or $Pd(TFA)_2$. By using an eco-friendly nanocellulose as the support, herein we also prepared a heterogeneous palladium catalyst immobilized on renewable amino-functionalized crystalline nanocellulose foam (Pd-AmP-CNC).[9] To improve the activity and selectivity of the Pd-catalyzed oxidative carbonylation of allene **1**, we turned our attention to the heterogeneous catalysts. Initially, none of desired product was isolated by using 5 mol% of Pd-AmP-CNC as the catalyst (Figure 1, A). However, surprisingly, when we added catalytic amounts of AgOTf (10 mol%) to the heterogeneous system, a highly improved activity and selectivity of Pd-AmP-CNC was observed, and pyrrolidone **2a** was obtained in 95% yield at room temperature in 30 minutes (Figure 1, E). In contrast, the homogeneous catalytic system did not give satisfactory results (Figure 1, B, C and D).[10] To be noted, the heterogeneous system is highly efficient: the catalyst and AgOTf loading can be reduced to 0.5 mol% and 1 mol%, respectively, producing pyrrolidone **2a** in >90% yields within 30 minutes (Figure 1, F). Another heterogeneous palladium catalyst Pd-AmP-MCF also showed the similar “additive-effect” (Figure 1, G).

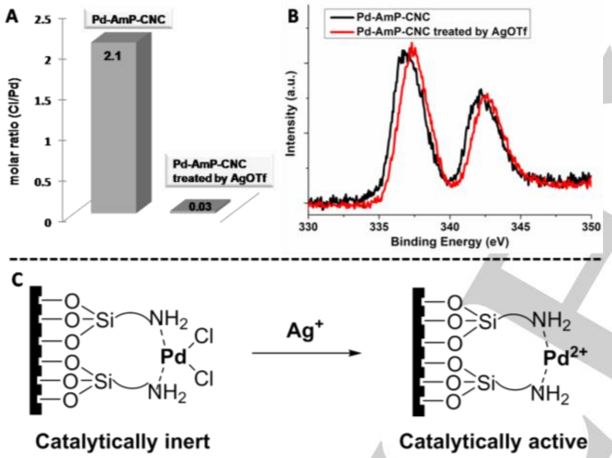
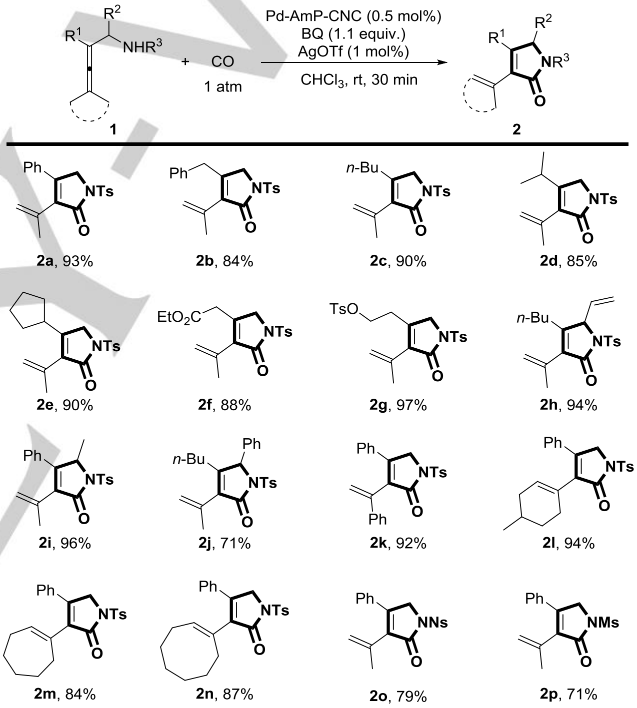


Figure 2. Molar ratios of Cl/Pd (**A**) and Pd3d XPS spectra (**B**) of Pd-AmP-CNC and Pd-AmP-CNC treated by AgOTf. **C**: An illustration of Ag^+-triggered generation of catalytic active cationic palladium in Pd-AmP-CNC.

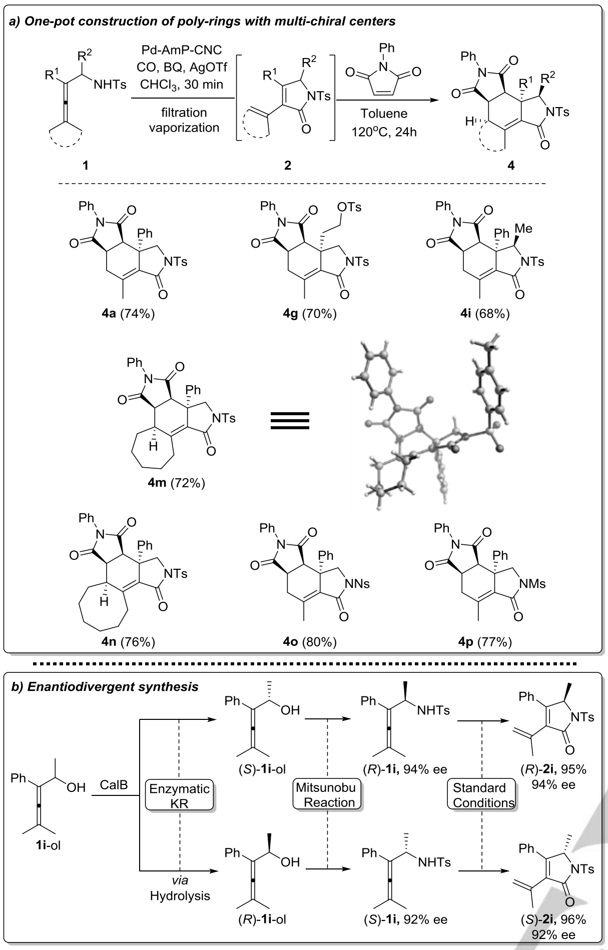
To determine the origin of the “additive-effect” in the heterogeneous Pd-catalyzed oxidative carbonylation of allene amide, we conducted several control experiments (see Supporting Information, p. S9, Table S1, entries 17-24). First, we checked three other $M(OTf)_n$ salts ($M = Cu^{2+}$, Fe^{3+}, Zn^{2+}) as the additives. However, none of these salts improved the transformation of **1a** to **2a**. Second, we checked different silver salts and it was found that $AgPF_6$ and $AgSbF_6$ also improved the yield of **2a** to >90% yields. These results suggest that the “additive-effect” could be credited to the removal of chloride ions by the Ag salt, generating cationic Pd(II)[11] with high catalytic activity for the oxidative carbonylation reaction. To verify our assumption, we compared the Cl/Pd molar ratios of the heterogeneous catalyst before and after treatment by AgOTf. These ratios were determined by elemental analysis and the Mohr titration method and were found to be 2.1/1 and 0.03/1 before and after treatment by AgOTf, respectively (Figure 2A). This result confirms that the chloride on the palladium of Pd-AmP-CNC had been removed by the silver salt. Moreover, the Pd3d XPS spectrum of Pd-AmP-CNC treated by AgOTf showed a slightly higher binding energy than that of Pd-AmP-CNC (Figure 2B), which supported the generation of highly active cationic palladium (Figure 2C).

Under the optimized reaction conditions (Figure 1, F), we explored the substrate scope for the oxidative carbonylation of allene **1** at room temperature (Scheme 2). Substituents including various aryl and alkyl groups (cyclic or acyclic) on R^1, R^2, R^3 and on the terminal positions of allene **1** worked well to give pyrrolidone **2** in excellent yields. Different functional groups such as EtO_2C, TsO, Ns, and Ms were tolerated in the oxidative carbonylation reactions. To be noted, the catalytic system is highly efficient. For all of the substrates, only 0.5 mol% of Pd-AmP-CNC and 1 mol% of AgOTf were used, and the reactions were completed within 30 minutes.



Scheme 2. Substrate scope of the Pd-AmP-CNC-catalyzed oxidative carbonylation of allenic amides to pyrrolidones.

Bearing a 1,3-diene moiety in the oxidative carbonylation products **2**, an efficient one-pot-two-step reaction was developed for the construction of polycyclic compounds **4** with multi-chiral centers (Scheme 3a). This strategy provides an atom- and step-economic procedure for the construction of cyclohexenyl-γ-lactam based polycyclic compounds[12] in high yield and stereoselectivity, which will be beneficial in synthetic chemistry. An enantiodivergent synthesis of pyrrolidones (*R*)-**2i** and (*S*)-**2i** with high yields and enantioselectivity was realized starting from allenic alcohol **1i**-ol (Scheme 3b), followed by an enzymatic kinetic resolution, Mitsunobu reaction, and the standard reaction conditions of Pd-AmP-CNC-catalyzed oxidative carbonylation.



Scheme 3. Applications of the heterogeneous process. KR = kinetic resolution, Standard Conditions = Pd-Amp-CNC, CO, BQ, AgOTf, $CHCl_3$, 30 min.

To further verify the efficiency of the heterogeneous Pd catalyst in the oxidative carbonylations, we conducted catalyst recycling experiments and a hot filtration test. The recycling experiments revealed that the efficiency of Pd-AmP-CNC was maintained from the first to ninth runs (Figure 3A). Pd3d XPS spectra and TEM images of Pd-AmP-CNC after the 1st and 9th run showed no detectable change of the catalyst (Figure 3B, 3C and 3D). Both TEMs in Fig. 3 showed a nanoparticle size of 1-2 nm and the deconvoluted XPS (see Supporting Information, p, S24) had a ratio Pd(0)/Pd(II) of about 20/80 after the 1st and 9th run.[13] These results demonstrate that the heterogeneous palladium catalyst is robust, recoverable and recyclable during the oxidative carbonylation. To be noted, the addition of 1 mol% of AgOTf is necessary in each cycle for triggering the activity of the heterogeneous Pd catalyst.[14] Pd leaching was not observed based on a hot filtration test (For details, see Supporting Information, p. S25), which excludes that the reaction proceeds through a homogeneous pathway.

To gain a deeper insight into the mechanism of the Pd-AmP-CNC-catalyzed oxidative carbonylation, we performed deuterium kinetic isotope effect (KIE) studies (For details, see Supporting Information, p. S26-S28). An intermolecular competitive experiment was conducted by using a 1:1 mixture of **1a** and**1a**-d_6 at 0 °C. The product ratio **2a**:**2a**-d_5 measured at 8% conversion was 5:1. From this ratio and the conversion, the competitive KIE value was determined to be k_H/k_D = 5.4. Furthermore, the parallel KIE experiments afforded k_H/k_D = 3.9. These results indicate that in the heterogeneous process, the simultaneous coordination of the sulfonamide group (NHTs) and the allene unit to the Pd(II) center does trigger the allenic C(sp^3)–H bond cleavage of **1** (***Int*-1** in Scheme 1) to initiate the oxidative carbonylation reaction, and this initial step is rate limiting as well as the first irreversible step of the reaction.

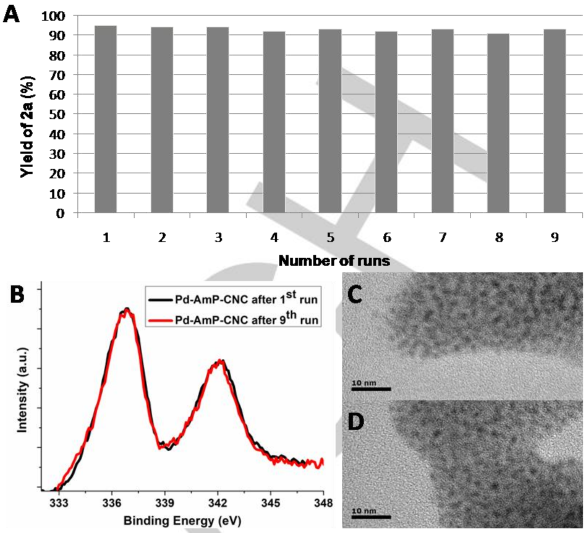
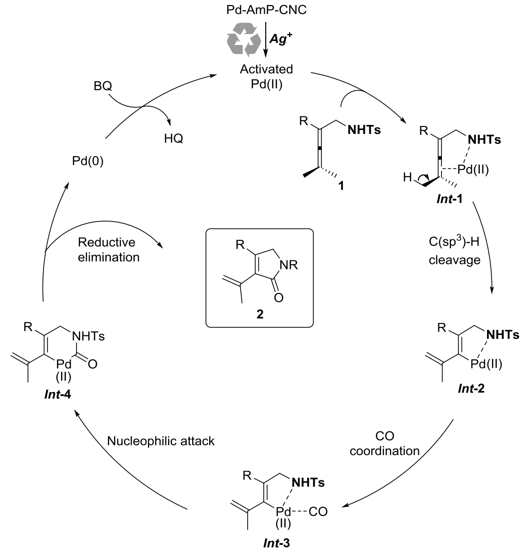


Figure 3. Recycling experiments (**A**), Pd3d XPS spectra (**B**) and TEM images of Pd-AmP-CNC after the first run (**C**) and the ninth run (**D**).

Based on the experimental results, we propose a mechanism for the Pd-AmP-CNC-catalyzed oxidative carbonylation triggered by silver salt (Scheme 4). Initially, Ag^+ would activate Pd-AmP-CNC to generate highly active Pd(II). Simultaneous coordination of the sulfonamide group (NHTs) and the allene unit to the Pd(II) center (***Int*-1**) would promote the allenic C(sp^3)–H cleavage to form ***Int*-2**. Coordination of CO to palladium leads to ***Int*-3**, which would undergo a nucleophilic attack by NHTs on the coordinated CO, affording ***Int*-4**. Reductive elimination of ***Int*-4** would give the final carbonylative product **2** and the released Pd(0) is reoxidized to Pd(II) by BQ.



Scheme 4. Proposed mechanism.

In conclusion, we have developed a highly efficient heterogeneous catalytic system for oxidative carbonylation reactions. The heterogeneous Pd (Pd-AmP-CNC), which is activated by Ag$^+$, catalyzes the transformation of allene amide to pyrrolidone **2** in 30 minutes at room temperature. This heterogeneous process can be applied for a one-pot-two-step construction of polycyclic systems with multi-chiral centers. The high efficiency of the heterogeneous catalytic system originates from the removal of Cl in Pd-AmP-CNC by a silver salt, generating highly active Pd(II). The heterogeneous catalyst is robust in oxidative carbonylations, and can be recycled at least 9 runs without loss of activity. This heterogeneous catalytic system may open up new opportunities in oxidative carbonylation reactions, and stimulate more research on the development of heterogeneous transition metal catalysts with high activity and selectivity.

Acknowledgements

Financial support from the Swedish Research Council (2016-03897) and (2018-04425), the Foundation Olle Engkvist Byggmästare, the European Union and the Knut and Alice Wallenberg Foundation (KAW 2016.0072) is gratefully acknowledged. This research has been supported by Treesearch.se.

Keywords: heterogeneous palladium • silver triggering • crystalline nanocellulose • polycyclic compounds with multi-chiral centers

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[13] The deconvoluted Pd3d XPS spectra before and after the reaction (Supporting Information, Fig. S2 and S4) showed that the ratio of Pd(0)/Pd(II) was increased from about 5/95 to 20/80 after the first run, and this ratio was maintained in the recovered catalyst for all runs. This increase could be explained by the partial reduction of Pd(II) in the reaction system.

[14] If AgOTf is not added in the next run, the yield of **2a** is only 59%.

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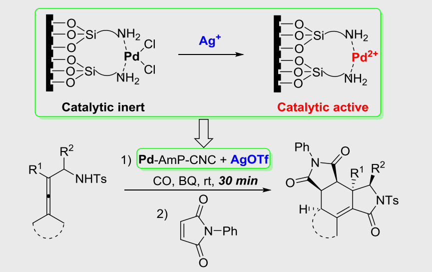
Layout 1:

COMMUNICATION

A silver-triggered heterogeneous palladium-catalyzed oxidative carbonylation of allene amide is developed for the construction of pyrrolidones and polycyclic compounds with multi-chiral centers. The heterogeneous catalyst (Pd-AmP-CNC) employed can be recycled at least 9 runs without loss of activity. It is revealed that the Ag salt removes Cl, generating highly active Pd(II), which results in the high efficiency of the heterogeneous catalytic system.



- Ag$^+$ trigerred generation of highly active Pd^{2+} with recyclability
- Heterogeneous Pd-catalyzed oxidtive carbonylations in 30 mins
- One-pot construction of poly-rings with multi-chiral centers

Man-Bo Li, Ying Yang, Abdolrahim A. Rafi, Michael Oschmann, Erik Svensson Grape, A. Ken Inge, Armando Córdova* and Jan-E. Bäckvall**

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