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Kinetic analysis of the complete mechanochemical synthesis of a palladium (II) carbene complex

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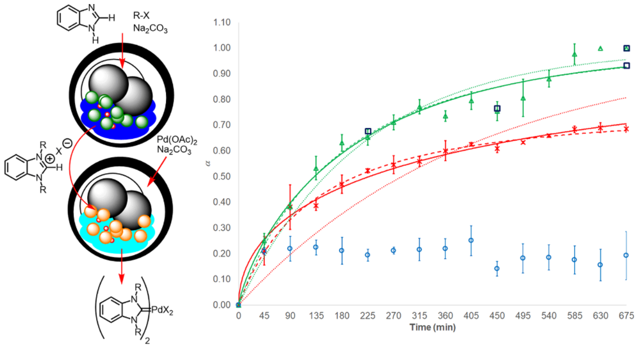
GRAPHICAL ABSTRACT



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ABSTRACT

Benzimidazoline-2-ylidene complexes of palladium(II) were synthesized mechanochemically in a vibratory ball mill. Complete syntheses began with preparation of benzimidiazolium halides from commercially available starting materials. These “greener chemistry” syntheses proceed in high yield and require minimal purification using environmentally benign solvents. Kinetic analysis shows that liquid assisted grinding impedes the production to benzimidazolium halides while enhancing the production of the palladium-carbene complex.

1. Introduction

Mechanochemical reactions involve the use of mechanical energy, often provided by grinding or shaking reagents, rather than thermal or light energy to induce reactions, while using little or no solvent. Along with a move to more environmentally benign solvents [1] when solvent use cannot be avoided, mechanosynthesis can provide a less expensive, greener alternative to solvent-based processes [2–3]; however, work on the preparation of ligands as part of a total mechanosynthesis of organometallic complexes is limited [4–5]. Of the existing types of organometallic mechanosynthesis including (1) ligand exchange/functionalization and/or co-crystallization of organometallic species prepared by non-mechanochemical methods [6–11], (2) preparation of carbonyl complexes, [11–12] and (3) formation of new metal-organic ligand bonds [5,13–24], less than half involve mechanochemical C-H bond activation [5,17–24]. This lack of total syntheses is a problem for widespread adoption of mechanochemistry, as maintaining both solution and mechanochemical systems can be impractical.

Pd-C organometallic species utilized in Heck-type coupling reactions [25–26] have been mechanosynthesized previously [5,20,22].

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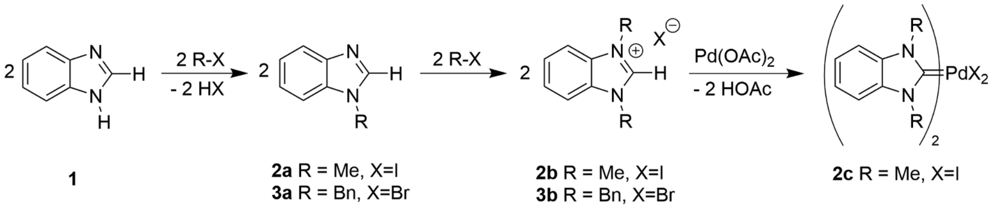

Scheme 1. Mechanochemical synthesis of **2b**, **3b** proceeds through intermediates (**2a**, **3a**). Isolation of **2b/3b** and addition of Na_2CO_3 in each reaction is necessary to maximize yields.

Palladium-imidazoline-2-ylidene complexes have been prepared by mechanochemical transmetallation [24] and in a two-step method via tetrachloropalladate imidazolium salts [27]. However, to the authors' knowledge this is both the first solvent-free preparation to produce a benzimidazoline-2-ylidene Pd-C bond directly and the first kinetic analysis of such a total synthesis (Scheme 1).

Kinetic understanding of “molecular” mechanochemistry is also in early development, as was first reviewed by Ma and coworkers in 2014 [28]. Since then, work by our group [29–30] and others [31–34] has focused on determining whether or not the models [35] originally developed for the synthesis of inorganic network materials (e.g. metal oxides and nitrides) are applicable to molecular mechanochemistry. Previous research by our group [29–30,36], has shown that the physical properties of a mechanochemical reaction mixture can both aid and retard reaction as those properties change with the reaction mixture composition. Here the effects of liquid assisted grinding (LAG) with a changing η parameter are explored as the alkyl halide in the reaction mixture acts as both a reagent and a modifier of the grinding environment. The parameter, determined as a ratio of μL of liquid to mg of solid, is used to differentiate LAG reactions ($0 < \eta < 2$) from slurrying methods ($2 < \eta < 12$) and solution syntheses ($\eta > 12$) [37–38].

In-situ reaction monitoring via IR [39–40] or Raman [41–44] spectroscopy or X-ray diffractometry [42,45–49] is ideal for mechanochemical preparations; however, inexpensive, readily available ex-situ methods are more likely to be of interest to those for whom mechanochemistry is a cost-saving, low environmental impact means of producing products. For that reason, this and previous work [29–30,36] has focused on analysis of mechanochemically prepared compounds by ^{1}H NMR spectroscopy.

2. Results and discussion

2.1. Benzimidazolium salt preparation

Typical benzimidazolium halide preparation has two steps. The alkyl benzimidazole is prepared from benzimidazole before a second equivalent of alkyl halide is added to prepare the salt [50–52]. Improved single-step syntheses has involved use of a pressure tube and large excesses of alkyl halide [53]. Mechanochemical syntheses of a single benzimidazolium salt [17], *N,N′*-dipicolylbenzimidazolium bromide, has been reported using $NaHCO_3$ as an aid to deprotonation. Modifying that preparation to use Na_2CO_3 gave rapid preparation of **2b** and **3b** with higher conversion (Fig. 1). Details of the synthesis and characterization are provided in the Supporting Information. NMR sample preparation was simplified because no bubbling from the decomposition of carbonic acid was observed. Na_2CO_3 proved such an effective promoter of this reaction that high yields of **2b** can be obtained by simply mixing the reagents and allowing them to sit overnight, if large excesses of methyl iodide are used. Mechanosynthesis was not effective for all alkyl halides, however. Benzyl chloride and butyl iodide were both unreactive with **1** under the reaction conditions, and neither the desired products nor the alkyl-benzimidazole intermediates were observed. This is consistent with the reduced reactivity of benzyl chloride in comparison to benzyl bromide due to the stronger C-X bond. The difference in the reactivities of methyl and butyl iodide is likely caused by steric effects in the solid state not observed in solution synthesis.

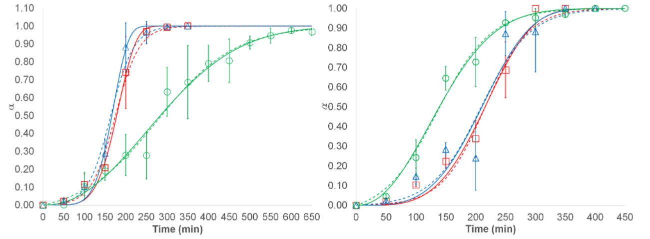

Fig. 1. Kinetic data for the synthesis of **2b** (left) and **3b** (right) using 2 equivalents (□), 3 equivalents (△) and 3 equivalents of RX under LAG conditions (○). The results of JMAYK (solid lines) and FW modeling (dashed lines) are shown.

Using ^{1}H NMR spectroscopy, the relative amounts of **1**, **2a** or **3a**, and **2b** or **3b** were used to determine the reaction coefficient, α, which corresponds to the fraction of complete conversion. Because of the high volatility of the alkyl halides, each reaction mixture could be sampled only once. At least three replicates were analyzed at each time interval, and the average α versus time data for various preparations of **2b** and **3b** are shown in Fig. 1.

This kinetic analysis is somewhat unique because the synthesis of a well-defined intermediate can be simultaneously tracked as shown in Fig. 2. The relative amount of intermediate that builds up in the reaction mixture relates directly to the amount of liquid, MeI or $CDCl_3$, present in the reaction mixture, implying that the intermediate may be stabilized. However, the possibility that the increased η parameter merely decreases the availability of intermediate and effectiveness of the milling impacts cannot be discounted.

2.2. Benzimidazoline-2-ylidene complex preparation

The literature preparation [25] of these complexes requires heating $Pd(OAc)_2$ and the desired benzimidazolium salt in DMSO. Presumably due to the dilution and stabilization of the resulting acetic acid byproduct by the solvent, high yields are obtained. In the case of mechanochemical reaction, acetic acid does inhibit the reaction, but addition of Na_2CO_3 gives complete conversion. Initial experiments focused on neat reaction as shown in Fig. 3; however, these reactions did not near complete conversion in a reasonable timeframe. Both toluene-d_8 and $CDCl_3$ were tried as LAG solvents, but toluene-d_8 did not improve results over neat reactions. By adding $CDCl_3$ for a LAG

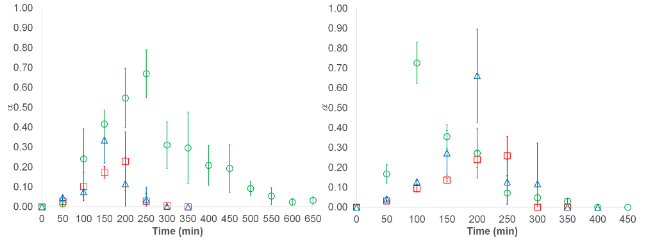

Fig. 2. Kinetic data for the synthesis of intermediates **2a** (left) and **3a** (right) using 2 equivalents of RX (□), 3 equivalents of RX (△) and 3 equivalents of RX under LAG conditions (○).

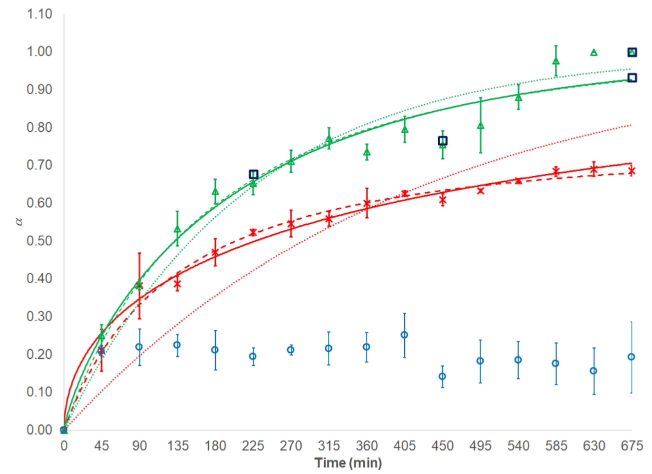

Fig. 3. Kinetic data for the synthesis of **2c** neat (×) and under LAG conditions with (○) and without (△) added KI. To check that repeated sampling did not affect results, single sample trials were also carried out (□). The results of JMAYK (solid lines), FW modeling (dashed lines), and FW modeling with variables restricted to positive values (dotted lines) are shown.

reaction, complete conversion could be reached in 630 min. As with the LAG preparation of the benzimidazolium salts, deuterated LAG solvents were utilized to simplify the NMR analysis by minimizing the appearance of solvent signals. To check that sampling the reaction mixtures multiple times was not changing the conversion, single-sample trials were also performed at 180, 450, and 675 min. The analysis at 675 min was repeated three times because on the first trial the ball became stuck, leading to a reduced conversion. The two other trials both reached complete conversion. This is the main difference between sampling the reaction mixture at multiple time intervals and only once. Any problems with bulk mixing due to a compaction of the reaction mixture and the ball are avoided by manually checking the reaction mixture.

Mechanochemical preparation of the imidazoline-2-ylidene palladium complex $Pd(IBz)_2Cl_2$ from reaction of HIBzCl and K_2PdCl_4 in the presence of KOH has been shown to initially form $(HIBz)_2[PdCl_4]$, and the byproduct KCl must be removed before the $(HIBz)_2[PdCl_4]$ can be further ground to produce $Pd(IBz)_2Cl_2$ [27]. Unlike that preparation, either a one-pot or "shotgun" style reaction where reagents are added in multiple steps will produce **2c**; however, the reactions do not proceed cleanly, and yields are low. This is attributed to the inhibition of the desired reaction by excess iodine salt. Addition of KI in the LAG synthesis of **2c** inhibits reaction after the initial mixing period (Fig. 3). PdI_2 does not react with **2b** under the conditions employed here.

2.3. Kinetic analysis

Based on the sigmoidal nature of the α versus time curves (Fig. 1), two different kinetic models were utilized to fit the data, the Johnson-Mehl-Avrami-Yerofeev-Kolmogrov (JMAYK, Equation (1)) and Finke-Watzky (FW, Eq. (2)) [54] models using the form of the JMAYK model proposed by Finney and Finke [55]. In those equations, k, k_1, and k'_2 are rate related parameters where k'_2 is dependent on initial concentration according to $k'_2 = k_2[A]_0$, where t is time, and n is the Avrami exponent. Both models are based on a process of nucleation and autocatalytic growth. The JMAYK model is an empirical method, and Finney and Finke [55] have pointed out that this model combines both nucleation and growth under a single rate related parameter (k). Their model has separate rate related parameters k_1 and k_2 for nucleation and autocatalytic growth.

$$\alpha = 1 - e^{-(kt)^n} \tag{1}$$

Table 1
Results of kinetic modeling, where parameters are defined as in Eqs. (1)–(3).

	Cond.	JMAYK	FW	*ER*
2b	3 MeI neat	$k = 5.644 \times 10^{-3}$ $n = 5.904$ $R^2 = 0.9951$	$k_1 = 1.028 \times 10^{-4}$ $k'_2 = 3.562 \times 10^{-2}$ $R^2 = 0.9882$	34.68
	3 MeI LAG	$k = 2.981 \times 10^{-3}$ $n = 2.171$ $R^2 = 0.9834$	$k_1 = 5.225 \times 10^{-4}$ $k'_2 = 1.020 \times 10^{-2}$ $R^2 = 0.9845$	0.6354
	2 MeI neat	$k = 5.246 \times 10^{-3}$ $n = 5.366$ $R^2 = 0.9939$	$k_1 = 8.271 \times 10^{-5}$ $k'_2 = 3.438 \times 10^{-2}$ $R^2 = 0.9912$	4.382
3b	3 BnBr neat	$k = 4.305 \times 10^{-3}$ $n = 3.705$ $R^2 = 0.9445$	$k_1 = 1.530 \times 10^{-4}$ $k'_2 = 2.4078 \times 10^{-2}$ $R^2 = 0.9464$	0.8501
	3 BnBr LAG	$k = 6.075 \times 10^{-3}$ $n = 2.180$ $R^2 = 0.9902$	$k_1 = 1.056 \times 10^{-3}$ $k'_2 = 2.0962 \times 10^{-2}$ $R^2 = 0.9890$	1.758
	2 BnBr neat	$k = 4.226 \times 10^{-3}$ $n = 3.956$ $R^2 = 0.9826$	$k_1 = 7.160 \times 10^{-5}$ $k'_2 = 2.7519 \times 10^{-2}$ $R^2 = 0.9801$	1.732
2c	neat	$k = 2.186 \times 10^{-3}$ $n = 0.5221$ $R^2 = 0.9887$	$k_1 = 6.113 \times 10^{-3}$ $k'_2 = -8.3542 \times 10^{-3}$ $R^2 = 0.9905$	0.2438
			$k_1 = 2.442 \times 10^{-3}$ $k'_2 = 0$ $R^2 = 0.7672$	
	LAG	$k = 4.837 \times 10^{-3}$ $n = 0.8147$ $R^2 = 0.9673$	$k_1 = 6.330 \times 10^{-3}$ $k'_2 = -3.593 \times 10^{-3}$ $R^2 = 0.9663$	1.278
			$k_1 = 4.612 \times 10^{-3}$ $k'_2 = 0$ $R^2 = 0.9521$	

$$\alpha = 1 - \frac{k_1 + k_2^{'}}{k_2^{'} + k_1 e^{(k_1 + k_2^{'})t}} \tag{2}$$

The models were evaluated for their fit to the data based on coefficients of determination (R^2 values); however, to compare the utility of the two models to each other, evidence ratios (*ER*) were utilized. Calculated from Akaike weights (*w*, which vary from 0 to 1 based on the how strongly one model fits the data compared to others), $ER \geq 10^4$ show the JMAYK model is significantly better, while $ER \leq 10^{-4}$ show that the FW model is better (Eq. (3)). These values for determining significant *ER* were originally proposed by Finney and Finke [55]. More information on the determination of *w* and *ER* is provided in the Supporting Information and in previous work, as well as tables of all calculated values [30]. The results of kinetic analysis show that both models provide good fits to the data, and neither model is preferable based on the *ER* values (Table 1).

$$ER = \frac{w_{JMAYK}}{w_{FW}} \tag{3}$$

Because the FW model has separate parameters for nucleation and autocatalytic growth, it is the simpler model to use in examining the effects of reaction parameters. In the synthesis of **2b** and **3b**, significant amounts of the intermediates **2a** and **3a** build up in the reaction mixture and reaction does occur in the absence of added Na_2CO_3, so the rate limiting step would seem to involve the alkyl-benzimidazole species. That increasing the amount of RX added does not significantly alter the rate points to alkyl-benzimidazole based nucleation sites. Using 2 equivalents of both MeI and Na_2CO_3, the reaction begins as a LAG process with an η parameter of 0.38 based on the average volumes and masses of reagents used for the kinetic studies (see Supporting Information). Over the course of the reaction, this drops to zero and the reaction mixture becomes a compacted, dry powder. Addition of an extra equivalent of MeI modified the initial and final η parameters to 0.56 and 0.10, respectively. The lack of significant changes to the kinetics of the reaction, means that LAG reactions cannot be thought of solely in terms of the physical effects of increasing η.

The effect of using $CDCl_3$ as a LAG solvent is to increase nucleation, as reflected in increased k_1, while autocatalytic growth remains constant or decreases. This gives an initially faster rate compared to neat reactions, but a slower time to complete conversion (Fig. 1). The η parameter varies from 1.53 to 0.63 over the course of the reaction.

In the synthesis of **2c**, nucleation remains constant when the LAG solvent is added, but the parameter for autocatalytic grown, k'_2, increases. Because the k'_2 values obtained without restricting modeling were negative, and the values obtained restricting values to physically relevant positive values gave poor fits, the JMAYK model, although empirical, seems more practical here. In this case, the breakdown of the Avrami exponent according to Eq. (4) [56] where a is the nucleation term ($a = 0$ for pre-existing sites, $a = 1$ for instantaneous nucleation, b is the dimensionality of growth, and p is the growth mechanism ($p = 1$ for interfacial and $p = 1/2$ for parabolic) is useful. Due to the low values of the n, pre-existing nucleation sites and parabolic growth are selected. The change upon adding the LAG solvent is then to increase the dimensionality of growth.

$$n = a + bp \tag{4}$$

3. Conclusions

Complete mechanochemical preparation of palladium-carbene complexes can be achieved through judicious selection of base and reaction conditions; however, isolation of the benzimidazolium salt is necessary to maximize yields, and not all alkyl halides are sufficiently reactive for this “gentle” methodology. Kinetic analysis shows that both the JMAYK and FW models are applicable to the preparations of both the benzimidazolium salts and a palladium-carbene species. However, LAG conditions can hinder the production of benzimidazolium salts while enhancing production of the palladium-carbene.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2019.107622. Supporting information to this article including details of synthesis and characterization for all compounds discussed, parameters for kinetic studies, and calculations of statistical parameters and η can be found online.

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