Solventless Cross-Coupling

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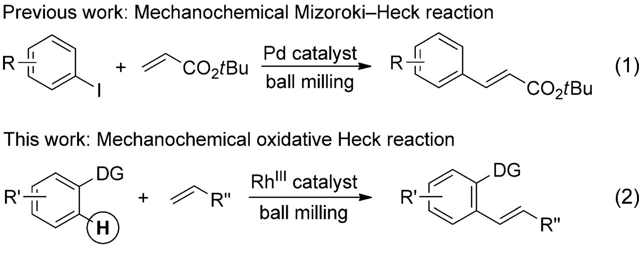
Mechanochemical Rhodium(III)-Catalyzed C–H Bond Functionalization of Acetanilides under Solventless Conditions in a Ball Mill**

*Gary N. Hermann, Peter Becker, and Carsten Bolm**

Abstract: *In a proof-of-principle study, a planetary ball mill was applied to rhodium(III)-catalyzed C–H bond functionalization. Under solventless conditions and in the presence of a minute amount of $Cu(OAc)_2$, the mechanochemical activation led to the formation of an active rhodium species, thus enabling an oxidative Heck-type cross-coupling reaction with dioxygen as the terminal oxidant. The absence of an organic solvent, the avoidance of a high reaction temperature, the possibility of minimizing the amount of the metallic mediator, and the simplicity of the protocol result in a powerful and environmentally benign alternative to the common solution-based standard protocol.*

Transition-metal-catalyzed direct C–H functionalization is a potent tool in organic synthesis that gives access to a wide range of products.[1] Its synthetic versatility has been demonstrated by the construction of complex natural products,[2] wherein rhodium-catalyzed oxidative Heck reactions[3] play a prominent role for the formation of new C–C bonds. Numerous substrates, such as acetanilides,[4] acetophenones,[5] benzamides,[5,6] and others,[7] have been applied to give the corresponding products in high yields. However, with respect to the sustainability of this approach, the use of significant amounts of solvent and, in most cases, the need for a stoichiometric quantity of an oxidant, are still limiting factors.

In recent years, significant progress has been made in organic transformations performed under mechanochemical activation. Such reactions can often be carried out under solventless conditions and tend to yield greater amounts of the product in shorter reaction times as compared to solvent-based systems.[8] This behavior applies to a variety of C–C bond-forming processes, such as Suzuki,[8h,9] Sonogashira,[10] and Heck coupling reactions.[8g,11] Recently, Lamaty and co-workers reported a palladium-catalyzed Mizoroki–Heck reaction performed with mechanochemical activation. Quantitative yields were observed when aryl iodides were treated with *tert*-butyl acrylate and PEG-2000-OH was used as the reducing agent [Scheme 1, Eq. (1)].[11] For many transformations, ball milling offers an environmentally friendly alternative to reactions commonly performed in solvents.[12]



Scheme 1. Mechanochemical functionalization of arenes in ball mills. DG = directing group.

The first mechanochemically induced C–H bond activation was detected by Ćurić and co-workers by solid-state Raman spectroscopy.[13] The approach involved the conversion of azobenzenes with $Pd(OAc)_2$ to give cyclopalladated complexes in good yields. Metal insertion occurred in shorter reaction times as compared to the solution-based reactions, and for asymmetrically substituted substrates, high regioselectivity was observed.

Inspired by these findings, we wondered about the mechanochemical activation of a rhodium(III)-catalyzed oxidative Heck olefination through C–H bond functionalization. Herein, we report a proof-of-principle study demonstrating the realization of this concept [Scheme 1, Eq. (2)].

Initially, we used analogous reaction conditions to those reported by Patureau and Glorius[4] for the aerobic coupling of unsubstituted acetanilide (**1a**) with *n*-butyl acrylate (**2a**) in *tert*-amyl alcohol at 120 °C by catalysis with $[\{Cp^*RhCl_2\}_2]$ (0.5 mol %) and AgSbF6 (2 mol %) in the presence of $Cu(OAc)_2$ (10 mol %). Unfortunately, our attempt to perform this reaction without a solvent in a planetary ball mill was unsuccessful, and the expected product **3a** was not detected (Table 1, entry 1). We obtained our first positive result when the amount of the rhodium catalyst was increased from 0.5 to 5 mol %, which resulted in 62 % conversion of **1a** (as determined by NMR spectroscopy) after 15 h of milling [15 × (60 min + 15 min break)]. Under these conditions, a 93:7 mixture of the mono- and disubstituted products **3a** and **4a** was obtained (Table 1, entry 2). Shorter milling times resulted in lower yields (see the Supporting Information).

Pleasingly, with only 2.5 mol % of $[\{Cp^*RhCl_2\}_2]$ in combination with 5 mol % of $Cu(OAc)_2$ both the conversion

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[*] G. N. Hermann, P. Becker, Prof. Dr. C. Bolm
Institute of Organic Chemistry, RWTH Aachen University
Landoltweg 1, 52056 Aachen (Germany)
E-mail: carsten.bolm@oc.rwth-aachen.de
Homepage: http://bolm.oc.rwth-aachen.de/

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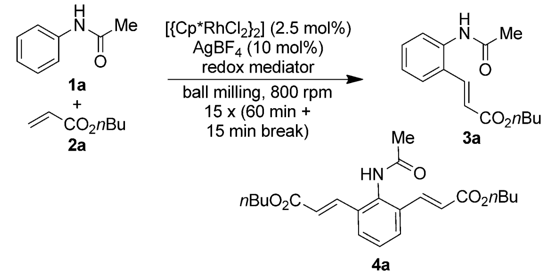
Table 1: Optimization of the mechanochemical oxidative olefination of acetanilides.[a]



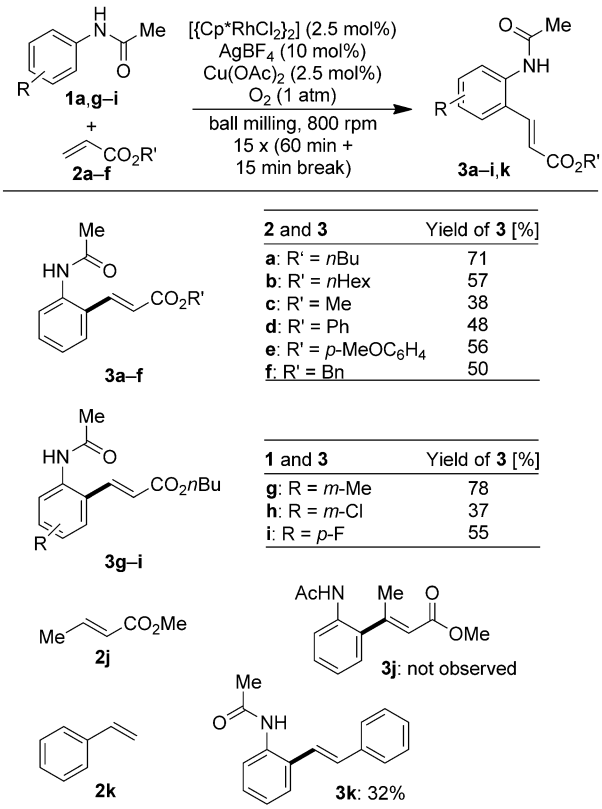
Entry[a]	[{Cp*RhCl$_2$}$_2$] [mol %]	Redox mediator (amount [mol %])	Conv. [%][b]	Product **3a**/**4a**
1[c]	0.5	Cu(OAc)$_2$ (10)	–	–
2[d]	5	Cu(OAc)$_2$ (10)	62	93:7
3	2.5	Cu(OAc)$_2$ (5)	61	95:5
4[e]	1	Cu(OAc)$_2$ (2)	12	**3a** (trace of **4a**)
5	2.5	Fe(OAc)$_2$ (5)	27	93:7
6	2.5	CuCl$_2$ (5)	53	90:10
7	2.5	NaOAc (5)	52[f]	92:8
8	2.5	Cu(OAc)$_2$ (10)	70	93:7
9[g]	2.5	Cu(OAc)$_2$ (5)	95	87:13
10[g]	2.5	Cu(OAc)$_2$ (2.5)	85	**3a** (trace of **4a**)
11[g]	2.5	Cu(OAc)$_2$ (1)	78	**3a** (trace of **4a**)

[a] Reaction conditions: **1a** (81.00 mg, 0.6 mmol), **2a** (85.00 mg, 0.66 mmol, 1.1 equiv), [{Cp*RhCl$_2$}$_2$] (9.27 mg, 0.015 mmol, 2.5 mol %), AgBF$_4$ (12.00 mg, 0.06 mmol, 10 mol %), 800 rpm, Pulverisette 7 premium line, both the vessel (20 mL) and the balls (5 mm diameter) are made of ZrO$_2$. [b] Conversion of **1a** as determined by ^{1}H NMR spectroscopy with benzene-1,3,5-triol as an internal standard. [c] The reaction was performed with **1a** (135.00 mg, 1 mmol), **2a** (192.00 mg, 1.5 mmol), and AgSbF$_6$ (6.87 mg, 0.02 mmol, 2 mol %). [d] The reaction was performed with AgBF$_4$ (23.0 mg, 0.12 mmol, 20 mol %). [e] The reaction was performed with AgBF$_4$ (4.67 mg, 0.024 mmol, 4 mol %). [f] See Ref. [14] for details. [g] The reaction was performed under an atmosphere of O$_2$. Cp* = pentamethylcyclopentadienyl.

of **1a** (61 %) and the **3a**/**4a** selectivity (95:5) remained essentially unchanged (Table 1, entry 3). A further decrease in the loading of the two metals (to 1 mol % of [{Cp*RhCl$_2$}$_2$] and 2 mol % of Cu(OAc)$_2$) resulted in a lower conversion of **1a** (Table 1, entry 4). A negative effect was also observed when Cu(OAc)$_2$ was replaced with Fe(OAc)$_2$ (Table 1, entry 5). With CuCl$_2$ or NaOAc instead of Cu(OAc)$_2$, the conversion of **1a** was good (53 and 52 %, with a **3a**/**4a** selectivity level of 90:10 and 92:8, respectively; Table 1, entries 6 and 7).[14] When the rhodium loading was kept the same (2.5 mol %) but the Cu(OAc)$_2$ amount was doubled from 5 to 10 mol %, the conversion of **1a** increased to 70 %, whereas the **3a**/**4a** selectivity (93:7) remained unchanged (Table 1, entry 8). On the basis of our previous studies,[7l,m] we anticipated a positive effect when the reactions were performed under an atmosphere of dioxygen instead of air. This assumption was confirmed, and with a combination of 2.5 mol % of [{Cp*RhCl$_2$}$_2$] and 5 mol % of Cu(OAc)$_2$, 95 % conversion of **1a** was observed (Table 1, entry 9). Because the ratio of **3a** to **4a** was now 87:13, the metal quantities were varied. The best overall result was finally observed with 2.5 mol % of both [{Cp*RhCl$_2$}$_2$] and Cu(OAc)$_2$ in a reaction carried out under an atmosphere of dioxygen. Under these conditions, the conversion of **1a** was 85 %, and **3a** was formed almost exclusively (with a trace amount of **4a** in the product mixture; Table 1, entry 10). With the same amount of the rhodium catalyst (2.5 mol %), lowering of the Cu(OAc)$_2$ quantity to 1 mol % had a slightly negative effect on the conversion of **1a** (78 %), whereas the selectivity for **3a** remained unchanged (Table 1, entry 11).

Two aspects of this transformation are significant: First, under solventless conditions, we observed high substrate conversion in a directed aerobic C–H functionalization with catalytic amounts of both rhodium and copper and obtained the monosubstituted product with high selectivity. Second, the presence of dioxygen had a positive effect on the catalysis, thus allowing the cross-coupling to proceed without additional heating.

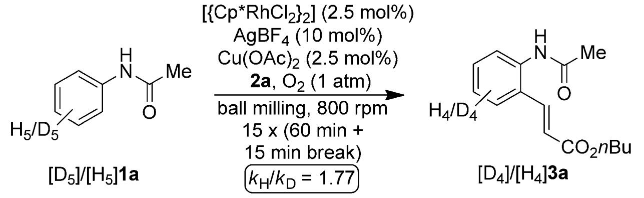
Next, the scope and limitations of the mechanochemically induced rhodium-catalyzed *ortho*-olefination were investigated (Scheme 2). First, the acrylate was varied in reactions with **1a** as the coupling partner (Scheme 2). The use of *n*-butyl acrylate (**2a**) led to the formation of **3a** in 71 % yield after column chromatography. *n*-Hexyl acrylate (**2b**) and methyl acrylate (**2c**) afforded the corresponding substituted products **3b** and **3c** in 57 and 38 % yield, respectively. Aryl esters **3d** and **3e** were obtained from coupling reactions of **1a** with **2d** and **2e** in 48 and 56 % yield, respectively. Benzyl ester **3f** was isolated in 50 % yield. Products **3g–i** were formed by treating **2a** with substituted acetamides **1g–i**. The highest



Scheme 2. Mechanochemical rhodium-catalyzed *ortho*-olefination of acetanilides. Bn = benzyl.

yield of 78 % was observed for the reaction of the *m*-methyl-substituted derivative **1g**. Methyl crotonate (**2j**) did not react to give **3j**. Finally, styrene (**2k**) was applied as a representative example of an unactivated olefin. Pleasingly, it also reacted with **1a** to afford **3k** in 32 % yield.

To gain insight into the reaction mechanism of the process, we determined kinetic isotope effects (KIEs) by investigating intermolecular competition reactions between [D_5]**1a** and [H_5]**1a** with **2a** as the coupling partner.[15] Under solventless conditions in a ball mill, a KIE value of 1.77 was found (Scheme 3). An analogous experiment performed under the previously reported reaction conditions[4,16] with *tert*-amyl alcohol as the solvent at 120 °C led to a KIE value of 1.48. As these two numbers are close, we assume that both processes follow a similar reaction path, in which the metal insertion into the C–H bond of the acetanilide is not turnover-limiting.



Scheme 3. KIE experiment for the mechanochemical *ortho*-olefination of acetanilide **1a**.

In summary, in a proof-of-principle study we have demonstrated the first mechanochemically induced directed C–H functionalization by rhodium catalysis in a ball mill. The process occurs in the absence of a solvent and does not require any additional heating. $Cu(OAc)_2$ was needed in only small quantities as a redox modulator, thus enabling the use of dioxygen as the terminal oxidant. Monoolefinated acetanilides were formed as products in moderate to good yields.

Experimental Section

An acetanilide **1** (0.6 mmol), an alkene **2** (0.66 mmol, 1.1 equiv), [$\{Cp^*RhCl_2\}_2$] (9.27 mg, 0.015 mmol, 2.5 mol %), $AgBF_4$ (12.00 mg, 0.06 mmol, 10 mol %), and $Cu(OAc)_2$ (2.72 mg, 0.015 mmol, 2.5 mol %) were transferred to a ball-milling vessel (ZrO_2, 20 mL) loaded with 16 grinding balls (ZrO_2, diameter: 0.5 cm). The ball-milling vessel was flushed with O_2 and placed in the ball mill (milling cycle: 60 min followed by a 15 min break, 15 repetitions). The crude product was isolated by washing the vessel and the balls with CH_2Cl_2 (3 × 20 mL) and EtOAc (3 × 20 mL). The mixture was then filtered through a thin layer of SiO_2 and concentrated in vacuo, and the product was purified by flash chromatography (SiO_2, *n*-pentane/EtOAc 3:1). To decrease the amount of solvent used for the vessel extraction, the crude product can alternatively be taken up by adding SiO_2 (2 × 1 g) to the ball-mill vessel and stirring the resulting mixture for 1 min.

Keywords: ball milling · C–H functionalization · mechanochemistry · oxidative Heck reaction · rhodium catalysis

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