Layered-Double-Hydroxide-Supported Rhodium(0): An Efficient and Reusable Catalyst for the *Heck*-Type Coupling of Alkenes and Arylboronic Acids

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Layered-double-hydroxide-supported nanorhodium catalyst (LDH–Rh(0)) was employed in the *Heck*-type coupling of alkenes **1** with arylboronic acids **2** to afford the corresponding substituted alkenes **3** in good to high yields (*Table 1*). The catalyst was separated by simple filtration and reused for five cycles with consistent activity.

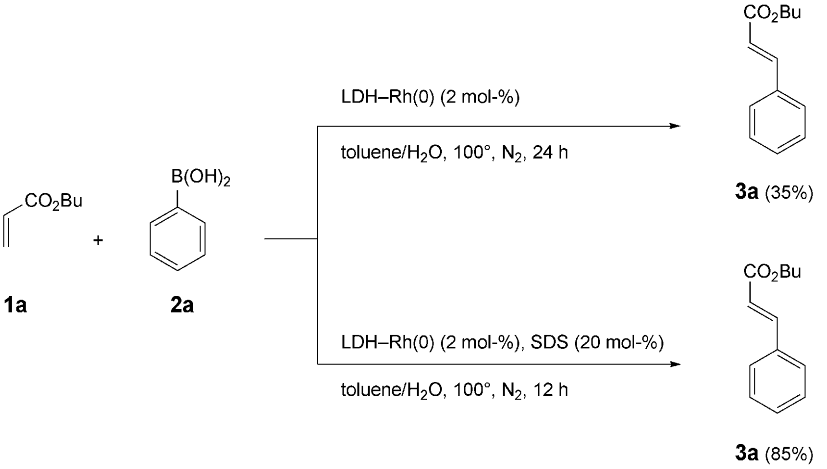
Introduction. – Rhodium-catalyzed addition of arylboronic acids to alkenes is a well established methodology in modern organic synthesis [1–3]. But the efficiency and selectivity of those Rh-catalyzed systems are often sensitive to the use of ancillary ligands such as phosphines, which are air- and moisture-sensitive and/or expensive [1][3]. Moreover, the recovery of the precious rhodium catalyst from the homogeneous reaction mixture is troublesome. From an environmental as well as industrial point of view, it is highly desirable to design a ligand-free and recyclable heterogeneous system for this elegant coupling reaction.

In this context, we recently have reported a silica-supported nanorhodium-catalyzed *Heck*-type reaction of alkenes with arylboronic acids [4]. In recent years, Mg and Al layered double hydroxides (LDHs) have been receiving considerable attention due to the cation-exchange capacity of the brucite ($Mg(OH)_2$) layer, anion exchange by interlayers, adjustable surface basicity, and adsorption capacity [5]. Moreover, the LDHs have the ability to hold the nanometal particles in the defect sites and provide adequate electron density to stabilize it, which make LDHs good supports in heterogeneous catalysis. Earlier we have reported the synthesis, characterization, and catalytic activity of layered-double-hydroxides-supported rhodium(0) (LDH–Rh(0)) in the *Heck*, *Suzuki*, and *Stille* coupling of aryl halides [6]. Herein, we wish to report the coupling of alkenes and arylboronic acids in the presence of layered-double-hydroxides-supported rhodium (LDH–Rh(0)) catalyst. The reusability of the catalyst is also discussed.

Results and Discussion. – To check the catalytic activity of LDH–Rh(0) catalyst in the *Heck*-type reaction of alkene and arylboronic acid, LDH–Rh(0) was subjected to arylation of butyl acrylate (=butyl prop-2-enoate; **1a**) with phenylboronic acid (**2a**) under the optimized conditions of our earlier report on silica-supported nanorhodium catalyst (*Scheme*) [4]. But we got the butyl cinnamate (=butyl (2*E*)-3-phenylprop-2-

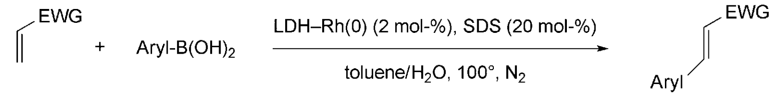
enoate; **3a**) in only low yields (35%). However, addition of a catalytic amount of surfactant (sodium dodecyl sulfate (SDS)) gave butyl cinnamate (**3a**) in 85% yield within 12 h. Addition of a base like K_2CO_3 only increased the deborylation of boronic acid, and eventually yields were diminished (60%).

Scheme. *LDH–Rh(0)-Catalyzed* Heck-*Type Coupling of Butyl Acrylate* (**1a**) *and Phenylboronic Acid* (**2a**)



To extend the scope of the reaction, we examined the *Heck*-type arylation of various alkenes **1a**–**1g** and arylboronic acids **2a**–**2f** under the optimized conditions, and the results are summarized in *Table 1*. Although the unsubstituted acrylates **1a**–**1e** and the styrenes **1e** and **1f** reacted smoothly to give good yields and >99% (*E*)-selectivity (*Table 1*, *Entries 1* and *7–11*), the sterically hindered methacrylate (=2-methylprop-2-enoate) **1g** (*Table 1*, *Entry 12*) reacted very sluggishly which indicates that steric factors played a crucial role in the reaction which is in accordance with the observations noticed in homogeneous reactions [3]. The presence of electron-donating or -withdrawing groups in the boronic acids **2** did not significantly influence the reaction. Napthalen-1-ylboronic acid (**2f**) also afforded a high yield of the corresponding product (*Table 1*, *Entry 6*). When we employed 4-ethenylpyridine with phenylboronic acid (**2a**), neither a *Heck*-type nor a conjugate adduct was formed (not shown in *Table 1*), but *Lautens* and co-workers [1] observed the formation of a conjugate adduct only, in a similar Rh-catalyzed coupling. Most probably the 4-vinylpyridine covered all the rhodium particles and subsequently hindered the reaction in our case. So we conducted another experiment by employing butyl acrylate (**1a**), phenylboronic acid (**2a**), and the rhodium catalyst in presence of 2 equiv. of pyridine under identical conditions, and only 3% of product **3a** were formed after 24 h (*Table 1*, *Entry 14*). When LDH–Rh(III) was employed as catalyst, low yields of **3a** (15%) were obtained (*Table 1*, *Entry 13*). It is noteworthy that LDH–Rh(III) is reported to be an excellent catalyst for the 1,4-conjugate addition of arylboronic acid to activated alkenes [7]. The parent LDH–CO_3 did not yield any product when applied as catalyst (*Table 1*,

Table 1. *LDH–Rh(0) Catalyzed Arylation of Alkenes* **1** *with Arylboronic Acids* **2**[a])



1a – 1g **2a – 2f** **3a – 3l**

Entry	Alkene	EWG	Boronic acid	Aryl	Product[b])	Yield [%][c])
1	**1a**	CO_2Bu	**2a**	Ph	**3a**	85
2	**1a**	CO_2Bu	**2b**	4-MeO–C_6H_4	**3b**	83
3	**1a**	CO_2Bu	**2c**	3-NO_2–C_6H_4	**3c**	76
4	**1a**	CO_2Bu	**2d**	4-Me–C_6H_4	**3d**	78
5	**1a**	CO_2Bu	**2e**	4-Cl–C_6H_4	**3e**	80
6	**1a**	CO_2Bu	**2f**	napthalen-1-yl	**3f**	78
7	**1b**	$CO_2{}^tBu$	**2a**	Ph	**3g**	80
8	**1c**	CO_2Me	**2a**	Ph	**3h**	88
9	**1d**	CO_2Et	**2a**	Ph	**3i**	85
10	**1e**	Ph	**2a**	Ph	**3j**	82
11	**1f**	4-Me–C_6H_4	**2a**	Ph	**3k**	80
12	**1g**[d])	(Me)CO_2Me[d])	**2a**	Ph	**3l**	12[e])
13	**1a**	CO_2Bu	**2a**	Ph	**3a**	15[f])
14	**1a**	CO_2Bu	**2a**	Ph	**3a**	3[g])
15	**1a**	CO_2Bu	**2a**	Ph	**3a**	0[h])
16	**1a**	CO_2Bu	**2a**	Ph	**3a**	0[i])

[a]) Reaction conditions: alkene **1** (2 mmol), arylboronic acid **2** (1 mmol), LDH–Rh(0) (2 mol-%), SDS (20 mol-%), toluene/H_2O 5 : 1 (4 ml), 100°, 12–16 h, N_2. [b]) Products were characterized by their ^1H-NMR spectra with $^3J_{trans} = 15.5-16.0$ Hz and their $M^{+\bullet}$ peak in the MS. [c]) Yield of isolated product. [d]) Methyl methacrylate ($CH_2=C(Me)CO_2Me$; **1g**). [e]) GC Yield and confirmed by GC/MS. [f]) LDH–Rh(III) (2 mol-%) was used as catalyst. [g]) In the presence of pyridine (2 mmol) after 24 h. [h]) LDH–CO_3 (22 mg) was used as catalyst. [i]) Without catalyst.

Entry 15). Moreover, a control reaction conducted under identical conditions but without LDH–Rh(0) catalyst gave no coupled product (*Table 1*, *Entry 16*).

To develop any heterogeneous catalyst, it is always necessary to know whether the reaction occurs on the solid surface or is catalyzed by the dissolved metal in the liquid phase. To evaluate the heterogeneity of LDH–Rh(0), we conducted different experiments. First, we checked the amount of leached Rh in the filtrate after the completion of the reaction, and Rh was not detected in the filtrate by inductively coupled plasma (ICP) atomic emission. Next, in the *Heck*-type reaction of **1a** with **2a**, the catalyst was removed after 5 h (yield of **3a** 57%) by hot filtration, and the reaction was continued with the filtrate for an additional 20 h. No increase in the yield was observed after the removal of the catalyst. Further, the resultant filtrate was tested for rhodium by ICP atomic emission. There was no leaching of Rh into the solution. Next, we checked the reusability of the LDH–Rh(0) catalyst. After the completion of the reaction between **1a** and **2a**, LDH–Rh(0) was separated by filtration, washed sequentially with 10% aqueous NaOH solution, water, and acetone, and dried in air. The recovered LDH–Rh(0) was used in the next run. Almost consistent activity was observed for five cycles (*Table 2*). The rhodium content in the fresh and used catalyst after the 5th cycle was almost the same (0.91 mmol/g of Rh in the fresh catalyst and 0.89 mmol/g in the used catalyst). These studies showed that the reaction was catalyzed by supported rhodium only.

Table 2. *Yields of the Reaction of* **1a** *and* **2a** *with Reused LDH–Rh(0) in* Cycles 1–5

Cycle	*1*	*2*	*3*	*4*	*5*
Yield [%]	85	84	84	82	82

In conclusion, the LDH-supported rhodium(0) catalyst was used in *Heck*-type cross-coupling reactions of alkenes **1** with arylboronic acids **2** without using any external ligand to afford good to high yields of the coupling products **3**. The catalyst was quantitatively recovered from the reaction by simple filtration and reused for a number of runs with consistent activity.

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Experimental Part

General. All the alkenes **1**, arylboronic acids **2**, and $RhCl_3 \cdot xH_2O$ were purchased from *Aldrich*. Solvents were from commercial sources. GC: *Shimadzu GC 2010*, *ZB-5* capillary column. NMR Spectra: *Bruker-Avance-300* and *Varian-Gemini-200* spectrometers.

Layered-Double-Hydroxide-Supported Rhodium(0) (LDH–Rh(0)). LDH–CO_3 (Mg/Al 3:1, $Mg_3Al(OH)_2(CO_3) \cdot x\,H_2O$; 1 g) [8] and $RhCl_3 \cdot x\,H_2O$ (294 mg, 1.5 mmol) in doubly deionized H_2O (100 ml) were stirred for 24 h at r.t. to afford brownish-yellow LDH–Rh(III). This catalyst was filtered, washed with deionized H_2O followed by acetone, and air-dried. LDH–Rh(III) (1 g) was reduced with H_2 (flow rate 60 ml/min) at 250° for 3 h to give black air-stable LDH–Rh(0) (Rh: 0.91 mmol/g).

Heck-*Type Coupling of Alkenes* **1** *with Arylboronic Acids* **2** *in the Presence of LDH–Rh(0).* In an oven-dried flask, alkene **1** (2 mmol), arylboronic acid **2** (1.0 mmol), SDS (20 mol-%), LDH–Rh(0) (22 mg, 2 mol-%), and toluene/H_2O 5:1 (4 ml) were stirred at 100° under N_2. After the completion of the reaction (TLC monitoring), the catalyst was filtered and reused. The filtrate was diluted with AcOEt and washed with 10% aq. NaOH soln. and finally with sat. aq. NaCl soln. The org. layer was dried (Na_2SO_4) and concentrated and the crude mixture subjected to column chromatography: pure product **3**, checked for purity by NMR and MS.

Reusability of the Catalyst. After completion of the reaction between **1a** and **2a**, LDH–Rh(0) was filtered off, washed sequentially with copious amounts of AcOEt, H_2O, and acetone, and dried in air. Then, the recovered catalyst was charged in the next cycle. The reaction of **1a** (2 mmol) and **2a** (1 mmol) in the presence of reused LDH–Rh(0) (2 mol-%) and SDS (20 mol-%) in toluene/H_2O 5:1 (4 ml) under N_2 at 110° for 12 h gave **3a** in the yields given in *Table 2*.

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