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Rhodium-Catalysed Tandem Hydroformylation/Arylation Reaction with Boronic Acids

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Abstract: A new efficient multicatalytic process involving a single catalyst to promote tandem hydroformylation/arylation reactions is disclosed. The effect of the rhodium ligand was evaluated and the rhodium/triphenylphosphine catalytic system was selected to apply the methodology to different olefins and boronic acids. High yields (up to 89%) and good to excellent isomer ratios (up to 98:2) were achieved using aryl olefins as starting materials. This new methodology allows the preparation of secondary alcohols, from simple olefins, and paves the way for the synthesis of high-value products, namely vinylindole and anethole derivatives.

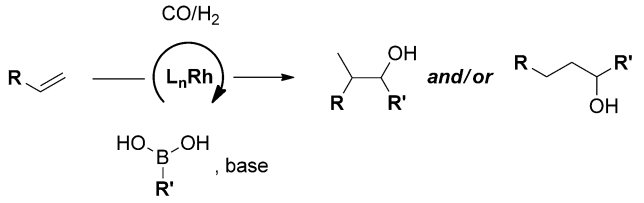
Keywords: arylation; hydroformylation; multicatalytic process; rhodium; tandem reactions

Catalysis remains as one of the most powerful available strategies to prepare new molecules with a broad range of useful properties.[1–5] This rich toolbox is based on a portfolio of transformations that use mostly one molecular entity as catalyst. Over the years, this single catalyst strategy strived to meet a high level of sophistication, due to the fact that, using only one catalyst, the process could be more easily understood and for that reason controlled.[1–5] Although the idea of operating different catalytic steps in a single vial, catalysed by one or more catalysts, recently emerged as a very useful approach to increment the molecular complexity and minimizing intermediate work-ups and purifications.[6–12] Recently, multicatalytic processes using different catalysts have become a very popular approach because they offer the possibility to tune the reaction by exploring the catalyst's distinct mechanisms of action.[7–12] Moreover, the use of a single catalyst to mediate two or more distinct chemical transformations is an even more interesting approach due to its economic advantages.[13]

In this context, hydroformylation is an attractive technology[14] to be incorporated in multicatalytic/tandem processes, since the aldehyde functionality offers great possibilities for subsequent modifications mediated by metals and organocatalysts.[15–17] Its potential is clearly demonstrated by the increasing number of papers published in the last decade, describing this technology in synthetic organic chemistry, namely in tandem hydroformylation/hydrogenation,[18–21] -aldol,[22–24] -cyclization,[25–31] -acetalization,[32–36] -Fisher indole,[37–40] -reductive amination,[41–44] -Mannich,[45] -alkylation,[46] and -Biginelli reactions.[47] Therefore, based on our long-standing interest in hydroformylation[48–51] and in the arylation of aldehydes with boronic acids,[52–54] we envisioned the possibility of coupling both transformations as they may be putatively catalysed by the same metal catalyst (Scheme 1).

It is well established that the arylation reactions catalysed by rhodium metal complexes are extremely dependent on the structure of the aldehydes, boronic acid and also the ligand used. So far, the best results have been obtained with arylaldehydes containing electron -withdrawing groups combined with arylboronic acids bearing electron-donating groups, using basic ligands such as alkylphosphines[55] or N-heterocyclic carbenes.[52–54]

Aiming at the implementation of a tandem hydroformylation/arylation protocol, catalysed by the same rhodium metal complex, we began our study by evaluating the electronic properties of the ligand on the arylation of commercially available aldehydes **1** and **2**,



Scheme 1. Single Rh(I)/L catalyst for tandem hydroformylation/arylation reaction.

which are the aldehydes expected to be obtained from styrene hydroformylation, using phenylboronic acid as model. Despite the fact that alkylphosphines show the best performance in the arylation of arylaldehydes[55] it is known that they give low regio- and chemoselectivity in the hydroformylation reaction.[56] For this reason they were not evaluated in this work.

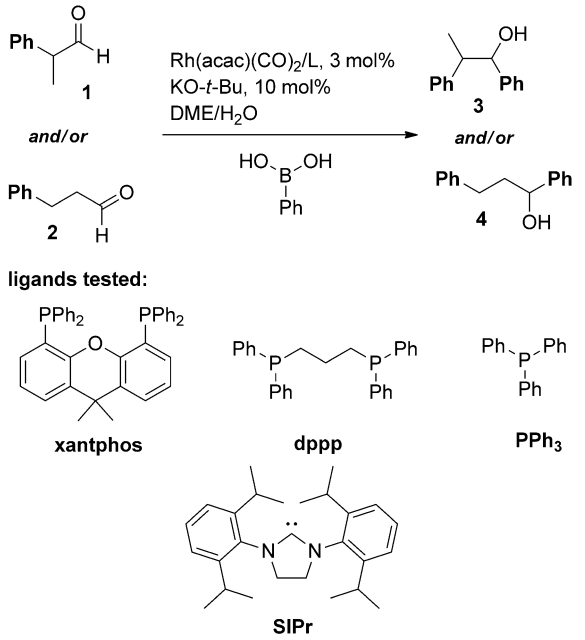
As shown in Table 1, the arylation step was individually studied using DME/H_2O (2:1) since the use of DME is compatible with the hydroformylation step. Under these conditions, using monodentate PPh_3 and SIPr ligands and KO-*t*-Bu as base, the alcohols **3** and **4** were isolated in yields up to 87% (Table 1, entries 5, 6, 9 and 10). Furthermore, the bidentate phosphines dppp and xantphos were also evaluated and the catalytic systems were considerably less efficient (Table 1, entries 2–4, 7 and 8). In all cases the branched aldehyde **1** led to higher yields when compared with aldehyde **2**, under the same conditions (Table 1, entries 1–5).

Encouraged by these results, then we studied the sequential styrene hydroformylation/arylation reaction. First, the hydroformylation catalyst was prepared *in situ* by reacting [Rh(acac)$(CO)_2$] with the appropriate ligand (Rh:P = 1:2) using DME as solvent. Then, styrene was added *via* cannula and the autoclave was pressurized with 35 bar of CO/H_2 (1:1) and heated to 65 °C.[57] After checking an almost quantitative conversion in the hydroformylation step, the autoclave was opened in a glove-box and phenylboronic acid, KO-*t*-Bu and degassed water were added. The autoclave was closed under an argon atmosphere and placed under stirring at 90 °C for 24 h.

As shown in Table 2, excellent conversions (up to 98%), chemoselectivity (up to 99%) and regioselectivity (up to 98%) in favour of the branched aldehyde **1** were obtained in the hydroformylation step (Table 2). Very gratifyingly, the catalytic systems remained active towards the arylation of aldehydes, and similarly to the aforementioned study, bidentate ligands like dppp and xantphos were only moderately active, while PPh_3 and SIPr afforded the alcohols in 83% and 77% isolated yields, respectively (Table 2, entries 3 and 4).

Triphenylphosphine and SIPr ligands gave similar isolated yields of the alcohol, although triphenylphosphine afforded a better regioselectivity in hydroformylation step and consequently a better **3**:**4** ratio (98:2).

Table 1. Ligand effect on the rhodium-catalysed arylation of **1** and **2** with phenylboronic acid.[a]



Entry	Aldehyde	Ligand	Time [h]	Yield [%][b]
1	1	–	48	n.r.
2	1	dppp	72	traces[c]
3	1	dppp	24	42
4	1	xantphos	24	33
5	1	PPh_3	24	85
6	1	SIPr	24	87
7	2	dppp	24	22
8	2	xantphos	48	traces
9	2	PPh_3	24	48
10	2	SIPr	24	80

[a] [Rh(acac)$(CO)_2$] = 0.03 mmol; Rh/P/aldehyde = 1:2:30; 2 mmol $PhB(OH)_2$; 1 mmol KO-*t*-Bu; 0.5 mL H_2O and 1 mL of DME; T = 90 °C.

[b] Isolated yield after purification by column chromatography (hexane:AcOEt = 5:1).

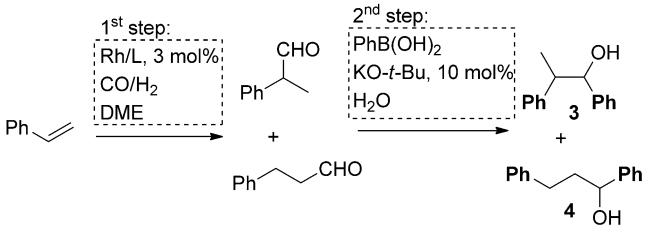
[c] No base used.

After performing the optimization of the tandem hydroformylation/arylation protocol, this methodology was extended, using Rh/PPh_3, to other aromatic and aliphatic olefins and boronic acids (Scheme 2). The results are collected in Table 3.

The sequential methodology proceeded, in most of the cases, with remarkable efficiency for aromatic olefins and aromatic boronic acids with isolated yields up to 89% (Table 3, entry 4) and good to excellent **6**:**7** ratio (up to 98:2) (Table 3, entry 1). As expected, an attempt to perform the reaction with an aliphatic boronic acid was unsuccessful (Table 3, entry 6).[58]

Using vinylindole as starting olefin, significantly lower yields were obtained despite the excellent **6**:**7**

Table 2. Sequential hydroformylation/arylation of styrene: ligand effect.[a]



Entry	Ligand	Hydroformylation[b] Conv.	Chemo.	Regio.[c]	Alcohol Yield [%][d] (**3**:**4**)
1	dppp	98	>99	98	42
2	xantphos	98	>99	95	37
3	PPh_3	98	>99	95	83 (98:2)
4	SIPr	96	>99	80	77 (84:16)

[a] *Hydroformylation step:* [Rh(acac)(CO)$_2$] = 0.03 mmol; Rh/P/olefin = 1:2:30; 1 mL of DME; $P(CO) = P(H_2) =$ 35 bar; $T = 65$ °C. *Arylation step:* 2 mmol $PhB(OH)_2$; 1 mmol KO-*t*-Bu; 0.5 mL H_2O; $T = 90$ °C.
[b] Determined by GC.
[c] Regioselectivity for branched aldehyde.
[d] Isolated yield after purification by column chromatography (hexane:AcOEt = 5:1).

ratio (Table 3, entries 7 and 8). When anethole was used as substrate, two branched aldehyde regioisomers were obtained, which were subsequently converted into the respective secondary alcohols with isolated yields up to 64% and **6**:**7** ratio of 89:11 (Table 3, entries 9 and 10).

This tandem procedure is not limited to aryl olefins and was also extended to the alkyl olefins 1-dodecene and the natural product β-pinene (Table 3, entries 11–13). Despite the excellent conversions in the hydroformylation step (up to 98%) the arylation process gave lower yields (Table 3, entries 11–13) as previously observed for the arylation of aliphatic aldehydes with rhodium/phosphine catalysts.[55]

In general, the presence of electron-donating groups at the *para* position of the aryl olefin as well as of the arylboronic acid did not induce a critical change in the overall alcohol yields. However, the presence of a chlorine atom at the *para* position of the aryl olefin produced a significantly lower yield (Table 3, entry 3).

Remarkably, secondary alcohols of the type **6**, with two stereogenic centers, resulting from the hydroformylation/arylation multicatalytic process were obtained with *syn*:*anti* ratios (determined by ^{1}H NMR) ranging from 70:30 to 80:20. When vinylindole was used the *syn*:*anti* ratio increased up to 87:13.

In summary, we have developed a new efficient multicatalytic process using a single catalyst to promote sequential hydroformylation/arylation reactions of aryl and alkyl olefins with arylboronic acids.

Considering the biological importance of vinylindole and anethole derivatives[59,60] this sequential methodology proved to be a novel and versatile tool for the transformation of simple olefins into particularly relevant secondary alcohols.

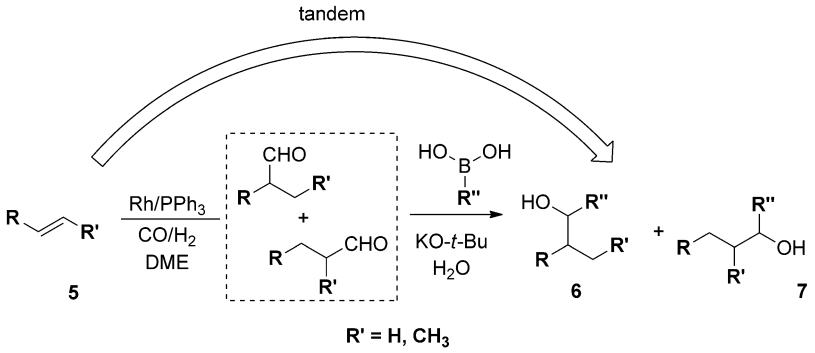
The rhodium/triphenylphosphine catalytic system was able to induce high conversions in the hydroformylation step (up to 99%) and regioselectivities for the branched aldehyde (up to 98%) combined with high yields (up to 89%) and **6**:**7** ratios (up to 98:2) for the final alcohols.

The scope of this multicatalytic synthetic methodology is demonstrated by the possibility of using different olefins and/or arylboronic acids containing electron-donating and electron-withdrawing groups, even at a gram scale. Thus, this new protocol opens a broad potential for the preparation of pharmacologically important targets.

Experimental Section

General Procedure

The rhodium precursor Rh(acac)(CO)$_2$ (0.03 mmol) with the desired ligand (0.03 mmol for bidentate ligands or 0.06 mmol monodentate ligands) were placed in a glass-lined stainless steel autoclave, which was closed and purged



Scheme 2. Transformation of olefins into secondary alcohols using Rh(I)/PPh_3 a multicatalytic tandem hydroformylation/arylation reaction.

Table 3. Sequential hydroformylation/arylation of different olefins and boronic acids using Rh/PPh_3 as unique ligand for both steps.[a]

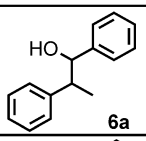
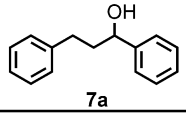
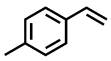
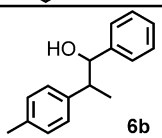
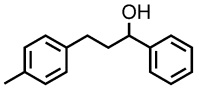
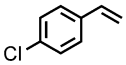
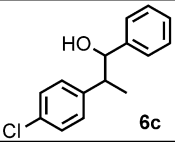
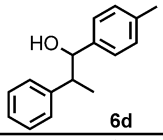
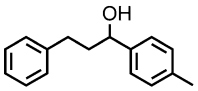
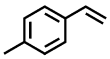
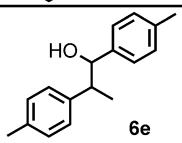
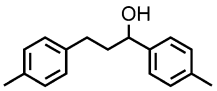
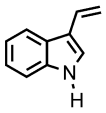
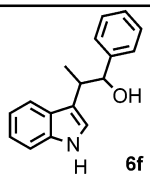
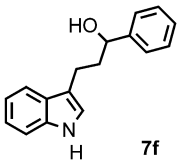
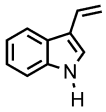
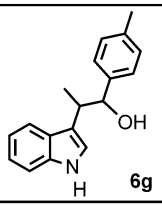
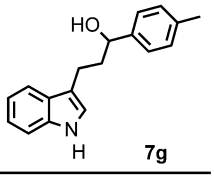
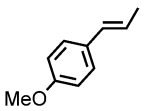
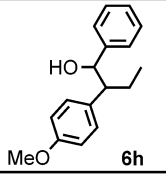
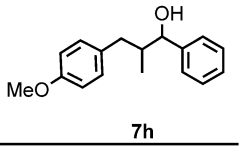
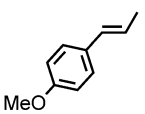
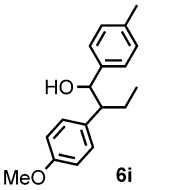
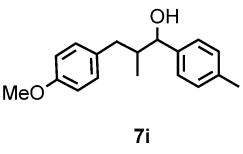
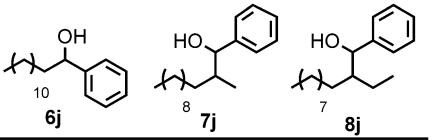
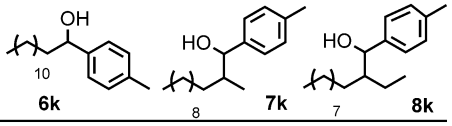
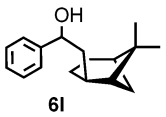
Entry	Olefin (**5**)	R''	Hydroformylation[b]			Alcohol Yield [%][d] (**6**:**7**)	Products	
			Conv.	Chemo.	Regio.[c]			
1		C_6H_5	98	>99	98	83 (98:2)	 **6a**	 **7a**
2		C_6H_5	99	>99	95	87 (97:3)	 **6b**	 **7b**
3		C_6H_5	99	>99	98	56	 **6c**	—
4		4-MeC_6H_4	98	>99	98	89 (96:4)	 **6d**	 **7d**
5		4-MeC_6H_4	99	>99	95	88 (95:5)	 **6e**	 **7e**
6		C_6H_{11}	98	>99	98	0	—	—
7		C_6H_5	>99	>99	87	58 (93:7)	 **6f**	 **7f**
8		4-MeC_6H_4	>99	>99	87	57 (90:10)	 **6g**	 **7g**
9[e]		C_6H_5	>99	>99	78[f]	64 (89:11)	 **6h**	 **7h**
10[e]		4-MeC_6H_4	>99	>99	78[f]	58 (89:11)	 **6i**	 **7i**

Table 3. (Continued)

Entry	Olefin (**5**)	R''	Hydroformylation[b]			Alcohol	Products
			Conv.	Chemo.	Regio.[c]	Yield [%][d] (**6**:**7**)	
11	 9	C_6H_5	98	>99	68[g]	35 (66:17:17)	 **6j** **7j** **8j**
12	 9	4-MeC_6H_4	98	>99	68[g]	40 (70:18:12)	 **6k** **7k** **8k**
13[h]		C_6H_5	80	99	78[i]	20	 **6l** —

[a] *Hydroformylation step:* [Rh(acac)(CO)$_2$] = 0.03 mmol; Rh/P/olefin = 1:2:30; 1 mL of DME; P(CO) = P(H$_2$) = 35 bar; T = 65 °C. *Arylation step:* 2 mmol PhB(OH)$_2$; 1 mmol KO-*t*-Bu; 0.5 mL H$_2$O; T = 90 °C.
[b] Determined by GC.
[c] Regioselectivity for branched aldehyde.
[d] Isolated yield after purification by column chromatography (hexane:AcOEt = 5:1).
[e] Hydroformylation at 80 °C.
[f] Regioselectivity for α-aldehyde.
[g] Regioselectivity for linear aldehyde.
[h] Hydroformylation at 100 °C.
[i] Selectivity *cis*-10-formylpinane according to dos Santos.[61]

with three cycles of vacuum and an equimolar CO/H$_2$ mixture. [For the 1,3-bis(2,6-diisopropylphenyl)dihydroimidazol-2-ylidene ligand a solution in DME was introduced through the inlet cannula and the reactor was pressurized with *syngas* at 35 bar at the working temperature during 45 min.] After this incubation period, the reactor was cooled and pressure was released. Then, the desired substrate (1 mmol) and DME (1 mL) was cannuled under vacuum and the autoclave was pressurized to 35 bar with an equimolar CO/H$_2$ mixture and heated at the desired temperature. The conversion and selectivity for the hydroformylation reaction were determined by gas chromatography analysis of aliquots taken from the reaction.

After cooling, the autoclave was slowly depressurized, opened in a glove-box and the appropriate boronic acid (2 mmol), KO-*t*-Bu (1 mmol) and degassed/distilled water (0.5 mL) were added. The autoclave was closed and the reaction mixture stirred under an argon atmosphere at 90 °C for 24 h. Finally, the mixture was extracted with CH_2Cl_2 and the organic layer washed with H_2O and dried over $MgSO_4$.

The product was further purified by preparative thin-layer chromatography. Furthermore, a ten-times tandem scale-up procedure was implemented using styrene/phenylboronic acid as starting materials and similar isolated yields (75%) of **6a** and **7a** (97:3) were obtained.

Characterization data are available in the Supporting Information.

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