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ARTICLE

Hydrophenylation of internal alkynes with boronic acids catalysed by a Ni-Zn hydroxy double salt-intercalated anionic rhodium(III) complex

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$[Rh(OH)_6]^{3-}$ intercalated Ni–Zn mixed basic salts (Rh/NiZn) are efficient catalysts for the hydrophenylation of internal alkynes with arylboronic acids under mild conditions. Turnover numbers per Rh site approached 740 in the reaction between 4-octyne and phenylboronic acid. The catalytic monomeric Rh(III) complex is stabilised within the NiZn interlayers, attributable to a strong electrostatic interaction, promoting its re-use.

Introduction

The region- and stereoselective synthesis of multi-substituted alkenes is an important synthetic approach for constructing complex molecules from relatively simple precursors. Multi-substituted alkenes are commonly derived via Pd(II) catalysed cross coupling reactions between simple arenes and activated olefins in acetic acid (the Fujiwara-Moritani reaction)[1,2] or aryl halides and alkenes (the Mizoroki-Heck reaction).[1,3] Transition metal catalysed hydrophenylation of carbon-carbon triple bonds is also an efficient route to such products.[4] In 2001, Hayashi and co-workers reported the rhodium(I)-catalysed hydrophenylation of internal alkynes with arylboronic acids via a 1,4-shift promoted by rhodium.[5] Thereafter, rhodium-catalysed hydrophenylation has proven challenging for the general synthesis of multi-substituted alkenes.[6] Recently, it was reported that the Zn-Al hydrotalcite docked Rh(I) complex (Rh-*m*-TPPTC/Zn-Al LDH) was able to catalyse this hydrophenylation, however, the reaction was carried out under stoichiometric conditions (S/C ratio was 1).[7]

We have recently developed novel heterogeneous intercalation catalysts based on Ni-Zn hydroxy double salts (NiZn), $Ni^{2+}_{1-x}Zn^{2+}_{2x}(OH)_2A^{n-}_{2x/n}\cdot mH_2O$ (0.15 < x < 0.25), where A^{n-} represents various anions, as heterogeneous base catalysts and/or hosts for catalytically active anions.[8] In particular, a monomeric hexahydroxy rhodate (III) complex, $[Rh(OH)_6]^{3-}$, could be intercalated into NiZn interlayers by simple anion-

exchange to create a Rh/NiZn catalyst[8b] which exhibited extremely high activity for the 1,4-addition reaction between α,β-unsaturated ketones and phenylboronic acids, with Turnover Frequencies (TOFs) reaching 920 h^{-1}. Here, we report the efficient hydrophenylation of internal alkynes with phenylboronic acids to form multi-substituted alkenes. The present catalytic methodology is particularly attractive, featuring facile catalyst synthesis via a simple intercalation procedure and high Turnover Numbers (TONs).

Results and discussion

Acetate anion-intercalated NiZn (CH_3COO^-/NiZn) was synthesised according to a previously reported procedure.[9] The composition and anion-exchange capacity of the parent NiZn were $Ni_{0.63}Zn_{0.37}(OH)_2(CH_3COO)_{0.37}\cdot1.93H_2O$ (i.e. Ni:Zn = 2.2) and 2.44 mmol·g^{-1}, respectively, on the basis of X-ray fluorescence (XRF) and thermogravimetric-differential thermal analysis (TG-DTA). The Rh(III) hydroxyl complex was intercalated into NiZn interlayers via a simple anion-exchange reaction in water at 50 °C for 8 h. The resulting Rh/NiZn catalyst, a green powder, contained 0.034 mmol·g^{-1} of Rh species as determined by atomic absorption spectrometry (AAS). Rh 3d X-ray photoelectron spectroscopy (XPS) and Rh K-edge X-ray absorption fine structure (XAFS) measurements confirmed the presence of Rh(III) as a monomeric hexahydroxy rhodate $[Rh(OH)_6]^{3-}$ anion, which is proposed to reside within the NiZn interlayer accompanied by intercalated OH$^-$.[8b]

Catalytic investigations first optimised the reaction solvent for the hydrophenylation of internal alkynes with phenylboronic acid (**2a**) over Rh/NiZn in the presence of a catalytic amount of 1,5-cyclooctadiene (1,5-COD). 4-Octyne (**1a**) and **2a** were chosen as model substrates for this optimization process (Table 1). Initial reaction conditions utilised 0.1 g of Rh/NiZn catalyst

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Table 1 Solvent effect on hydrophenylation between **1a** and **2a** with Rh/NiZn catalyst[a]
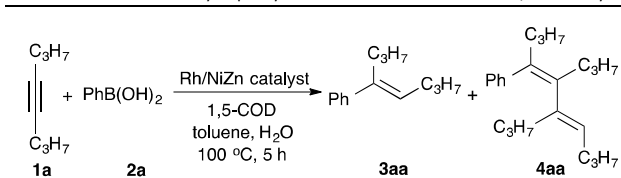
Entry	Solvent	Conv. (%)[b]	Yield (%)[b] 3aa	Yield (%)[b] 4aa
1	toluene	>99	71	8
2[c]	1,2-dichloroethane	45	27	3
3[c]	ethanol	8	trace	trace
4[c]	tetrahydrofuran	trace	trace	trace
5	1,4-dioxane	trace	trace	trace
6	N,N-dimethylformamide	n.d.	n.d.	n.d.

[a] Rh/NiZn catalyst (Rh: 0.34 mol%), **1a** (1 mmol), **2a** (3 mmol), 1,5-COD (3 eq. relative to Rh), solvent (4 mL), H_2O (0.9 mL), 100 ^{o}C, 5 h. [b] Determined by GC using an internal standard technique. [c] Reaction was carried out in sealed tube.

(i.e. 3.4 μmol Rh), 1 mmol of **1a**, 3 mmol of **2a**, and three equivalents of 1,5-COD relative to Rh in a solvent mixture comprising 4 mL toluene and 0.9 mL water at 100 °C under air for 5 h. Solvent screening revealed toluene as the most effective, affording the highest 71 % yield of hydrophenylation product, (E)-4-phenyl-4-octene (**3aa**), accompanied by a small amount of (4Z,6E)-4-phenyl-5,6-dipropyl-4,6-decadiene (**4aa**) (entry 1). Although 1,2-dichloroethane also afforded **3aa** the resulting yield was low (entry 2). Solvents such as ethanol, tetrahydrofuran, 1,4-dioxane and N,N-dimethylformamide did not yield any products (entries 3-6).

Water addition proved essential to obtain high yields of hydrophenylation product (Table 2), with neither **3aa** nor **4aa** obtained in its absence (entry 1). When the reaction was conducted in toluene-water biphasic solvents, catalysis proceeded efficiently (entries 2-6), with the optimum solvent mixture comprising 4 mL toluene and 0.45 mL water, resulting in 89 % yield of **3aa** (entry 3). It should be noted that catalytic reaction did not proceed in water alone (entry 7).

Table 2 Effect of water on hydrophenylation between **1a** and **2a** with Rh/NiZn catalyst[a]

Entry	Toluene (mL)	H_2O (mL)	Conv. (%)[b]	Yield (%)[b] 3aa	Yield (%)[b] 4aa
1	4	-	n.d.	n.d.	n.d.
2	4	0.09	14	6	trace
3	4	0.45	>99	89	5
4	4	0.90	>99	87	7
5	2	0.45	>99	82	7
6	1	0.45	>99	82	5
7	-	4.45	n.d.	n.d.	n.d.

[a] Rh/NiZn catalyst (Rh: 0.68 mol%), **1a** (0.5 mmol), **2a** (1.5 mmol), 1,5-COD (3 eq. relative to Rh), 100 ^{o}C, 5 h. [b] Determined by GC using an internal standard technique.

Catalytic activity was strongly dependent upon the use of olefins as ligands (Table 3), with no hydrophenylation without such ligands (entry 1). While hydrophenylation only occurred in the presence of 1,5-COD and 2,5-norbornadiene (entries 3 and 4), 2,5-norbornadiene was less effective. Other dienes such as 1,3-cyclopentadiene and 1,4-cyclohexadiene did not promote hydrophenylation (entries 2 and 5), and neither did trienes such as 1,5,9-cyclododecatriene or monoenes such as cyclooctene, 2-norbornene and cyclohexene (entries 6-9). This

Table 3 Ligand effect on hydrophenylation between **1a** and **2a** with Rh/NiZn catalyst[a]

Entry	Ligand (eq. relative to Rh)	Time (h)	Conv. (%)[b]	Yield of 3aa (%)[b]
1	none (-)	5	trace	trace
2	1,3-cyclopentadiene (3)	5	trace	trace
3	1,5-cyclooctadiene (3)	5	99	89
4	2,5-norbornadiene (3)	5	23	17
5	1,4-cyclohexadiene (3)	5	trace	trace
6	cyclooctene (3)	5	trace	trace
7	2-norbornene (3)	5	trace	trace
8	cyclohexene (3)	5	trace	trace
9	1,5,9-cyclododecatriene (3)	5	trace	n.d.
10	1,5-cyclooctadiene (1)	1.5	24	17
11	1,5-cyclooctadiene (2)	1.5	19	16
12	1,5-cyclooctadiene (3)	1.5	44	40
13	1,5-cyclooctadiene (4)	1.5	84	71
14	1,5-cyclooctadiene (6)	1.5	74	63
15	1,5-cyclooctadiene (7)	1.5	74	62

[a] Rh/NiZn catalyst (0.1 g, Rh: 0.68 mol%), **1a** (0.5 mmol), **2a** (1.5 mmol), ligand, toluene (4 mL), H_2O (0.45 mL), 100 ^{o}C. [b] Determined by GC using an internal standard technique.

observation suggests that 1,5-COD may coordinate to Rh under reaction conditions to form an activated catalytic complex in situ. We speculate that 1,5-COD acts as a weak electron-donating ligand upon the Rh catalytic centre. Variation of the 1,5-COD amount up to seven equivalents relative to the amount of Rh (entries 10-15) revealed that the optimum 1,5-COD level was four equivalents, which yielded 71 % of **3aa** over 1.5 h reaction (entry 13).

The catalytic activity for hydrophenylation over Rh/NiZn was subsequently compared with over Rh catalysts under identical conditions (Table 4). Rh/NiZn exhibited the highest catalytic activity (entry 1), achieving 71 % yield over 1.5 h versus 45 % for $Na_3RhCl_6 \cdot 12H_2O$[10] over 5 h (entry 7). The Rh/NiZn catalyst showed almost identical activity under air, O_2 or N_2 atmospheres (entries 2-4). Control reactions in the absence of any catalyst, or in the presence of CH_3COO^-/NiZn or OH^-/NiZn unfucntionalised by Rh, were completely inactive (entries 5, 6, and 11). $Rh(OH)_3$, Rh_2O_3, and Rh^0/carbon were also ineffective catalysts (entries 8-10). We conclude that anionic $[Rh(OH)_6]^{3-}$ intercalated into NiZn interlayers is a highly efficient catalyst for hydrophenylation under mild conditions.

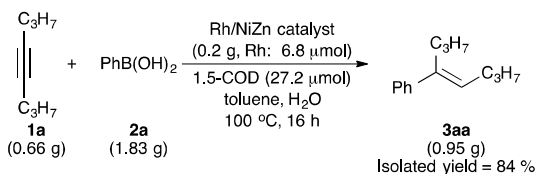**Table 4** Effects of catalyst on hydrophenylation between **1a** and **2a**[a]

Entry	Catalyst	Time (h)	Conv. (%)[b]	Yield (%)[b]
1	Rh/NiZn	1.5	84	71
2	Rh/NiZn	1	62	52
3[c]	Rh/NiZn	1	63	50
4[d]	Rh/NiZn	1	60	48
5[e]	CH_3COO^-/NiZn	5	n.d.	n.d.
6[e]	OH^-/NiZn	5	n.d.	n.d.
7	$Na_3RhCl_6 \cdot nH_2O$	5	54	45
8	$Rh(OH)_3$	5	trace	trace
9	Rh_2O_3	5	trace	trace
10[f]	Rh(0)/carbon	5	trace	trace
11	-	5	n.d.	n.d.

[a] Rh catalyst (Rh: 0.68 mol%), **1a** (0.5 mmol), **2a** (1.5 mmol), 1,5-COD (4 eq. relative to Rh), toluene (4 mL), H_2O (0.45 mL), 100 ^{o}C. [b] Determined by GC analysis using an internal standard technique. [c] Reaction was carried out under O_2 atmosphere. [d] Under N_2. [e] CH_3COO^-/NiZn (0.1 g) or OH^-/NiZn (0.1 g) was used as a catalyst. [f] 5 wt% of Rh, purchased from Aldrich.

The hydrophenylation between **1a** and **2a** catalysed by Rh/NiZn was also successfully undertaken on a preparative scale. For example, **1a** (0.66 g; 6 mmol) and **2a** (1.83 g; 15 mmol) successfully gave **3aa** (0.95 g; 84% of isolated yield) in the presence of the Rh/NiZn catalyst (0.2 g, Rh: 6.8 μmol) for 16 h

(Scheme 1). The TON per Rh atom approached 740, an order of magnitude higher than previous reports for homogeneous Rh complexes: (Rh(acac)(CO)$_2$ = 18;[6a] Rh(acac)(CO)$_2$/Janaphos = 46;[6b] [Rh(1,5-COD)(OH)]$_2$/m-TPPTC = 59;[6c,6d] [Rh(1,5-COD)Cl]$_2$/TPPDS = 43;[6e] Rh(acac)(C$_2$H$_4$)$_2$/dppb = 32.[5]

Scheme 1 Large-scale reaction with Rh/NiZn catalyst

Reaction conditions: Rh/NiZn catalyst (0.2 g, Rh: 6.8 μmol), **1a** (0.66 g; 6 mmol), **2a** (1.83 g; 15 mmol), 1,5-COD (27.2 μmol), toluene (20 mL), H$_2$O (2.25 mL), 100 °C, 16 h. 0.13 g of (4Z, 6E)-4-phenyl-5,6-dipropyl-4,6-decadiene (**4aa**) was also isolated.

Deactivation, whether arising from structural changes in the active metal species or support architecture, or leaching of the active metal species into the reaction mixture, profoundly influences the prospects of catalyst commercialization. In order to establish whether deactivation occurred under our reaction conditions, additional reactants **1a** and **2a** were added to a reaction mixture after 1.5 h of an initial reaction (without additional 1,5-COD). Figure 1 shows that hydrophenylation immediately re-commenced at the same rate as during the first reaction cycle, evidencing no loss in catalytic activity.[11]
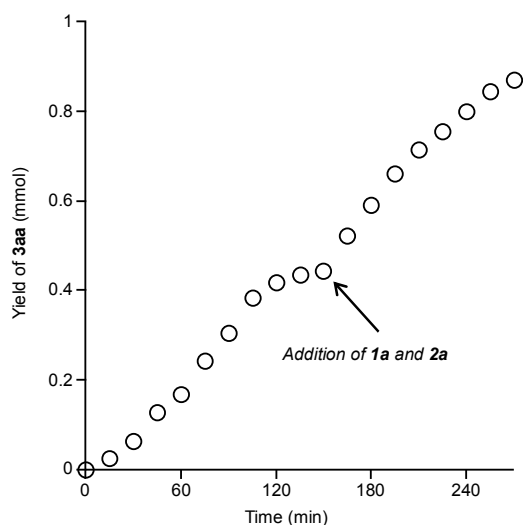

Fig. 1 Time profile of hydrophenylation of **1a** and **2a** with the Rh/NiZn catalyst. Reaction conditions: Rh/NiZn catalyst (Rh: 0.68 mol %) **1a** (0.5 mmol), **2a** (1.5 mmol), 1,5-COD (4 equiv relative to Rh), toluene (4 mL), H$_2$O (0.45 mL), 100 °C.

AAS analysis of the reaction filtrate confirmed that negligible Rh was leached under our conditions (below 0.4 μmol). In order to further demonstrate the requirement of the heterogeneous Rh/NiZn catalyst, the catalyst was removed by hot filtration when hydrophenylation between **1a** and **2a** had reached almost 35 % conversion (Fig. S1).[12] After removal of the catalyst, the reaction was monitored for an additional hour, however almost no formation of **3aa** was observed. Rh K-edge

XANES, and k^3-weighted Rh K-edge EXAFS spectra of fresh and spent Rh/NiZn catalysts (Fig. 2) confirmed no change in either Rh oxidation or coordination environment, suggesting that Rh species in the NiZn matrix remained in a trivalent monomeric state throughout the reaction, likely due to strong electrostatic interactions between the anionic [Rh(OH)$_6$]$^{3-}$ species and NiZn lamellar host, which appears to inhibit the aggregation of

Catalyst	Shell	C.N.[b]	r (nm)[c]	σ (nm)[d]
fresh Rh/NiZn	Rh-O	6.2	0.205	0.0057
recovered Rh/NiZn	Rh-O	6.4	0.205	0.0071

[a] Inverse Fourier transformations were performed for the regions of 0.112 - 0.199 nm. [b] Coordination number. [c] Bond distance. [d] Debye-Waller factors.
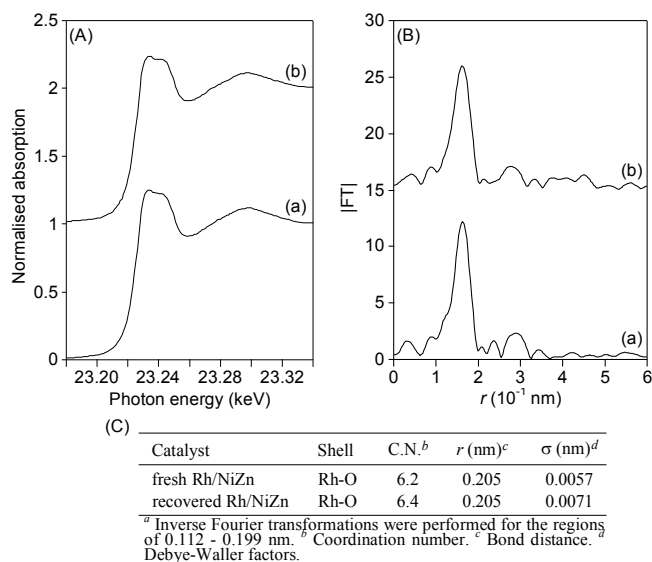
Fig. 2 XAFS analysis for (a) fresh Rh/NiZn and (b) recovered Rh/NiZn: (A) Rh K-edge XANES spectra, (B) FT of k^3-weighted Rh K-edge EXAFS spectra, and (C) results of curve fitting.
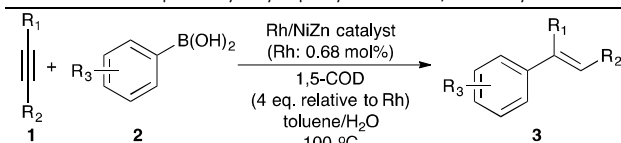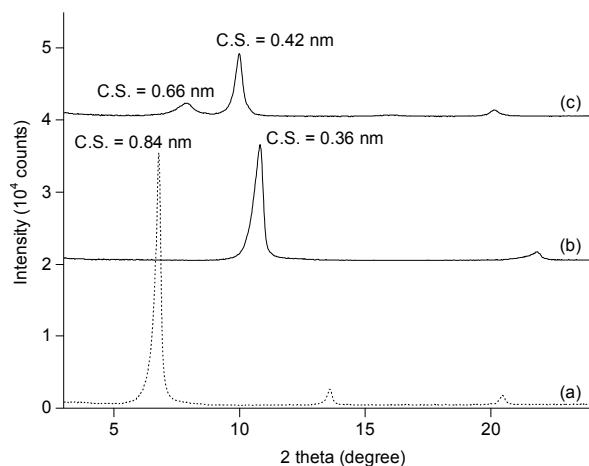

Fig. 3 XRD profiles for (a) CH$_3$COO$^-$/NiZn, (b) fresh Rh/NiZn, and (c) recovered Rh/NiZn

hydrated rhodium oxide species such as Rh(OH)$_3$. However, powder XRD revealed expansion of the interlayer spacing of the recovered Rh/NiZn catalyst from 0.42 to 0.66 nm (Fig. 3), which may reflect the incorporation of water and/or reactively-formed product alongside [Rh(OH)$_6$]$^{3-}$ and OH$^-$ anions during reaction.[13]

The scope of the hydrophenylation reaction was examined using a variety of alkynes and phenylboronic acids (Table 5) using the optimised amount of 1,5-COD and toluene/H_2O mixed solvent. *p*-Substituted phenylboronic acids such as the electron-donating 4-methylphenylboronic acid (**2d**), 4-methoxyphenylboronic acid (**2e**), and electron-withdrawing 4-chlorophenylboronic acid (**2f**) gave the corresponding hydrophenylation products (**3ad**, **3ae**, and **3af**) in high yield (entries 7-12). For short reaction times, electron-donating

Table 5 Substrate scope on alkyne hydrophenylation with Rh/NiZn catalyst[a]

Entry	Alkyne	Boronic acid	Time (h)	Product	Conv. (%)[b]	Yield (%)[b]
1	**1a**: $R_1 = R_2 = C_3H_7$	**2a**: $R_3 = H$	1.5	**3aa**	84	71
2	**1a**	**2a**	3	**3aa**	>99	90
3	**1a**	**2b**: $R_3 = $2-Me	1.5	**3ab**	trace	trace
4	**1a**	**2b**	24	**3ab**	53	52
5	**1a**	**2c**: $R_3 = $3-Me	1.5	**3ac**	60	55
6	**1a**	**2c**	3	**3ac**	92	88
7	**1a**	**2d**: $R_3 = $4-Me	1.5	**3ad**	12	10
8	**1a**	**2d**	24	**3ad**	>99	95
9	**1a**	**2e**: $R_3 = $4-MeO	1.5	**3ae**	55	52
10	**1a**	**2e**	6	**3ae**	96	94
11	**1a**	**2f**: $R_3 = $4-Cl	1.5	**3af**	40	38
12	**1a**	**2f**	9	**3af**	92	89
13	**1b**: $R_1 = $Me, $R_2 = $Ph	**2a**	12	**3ba**	20	20
14	**1c**: $R_1 = $Ph, $R_2 = $H	**2a**	24	**3ca**	n.d.	n.d.
15	**1d**: $R_1 = R_2 = $Ph	**2a**	12	**3da**	>99	98
16	**1e**: $R_1 = R_2 = CO_2Me$	**2a**	24	**3ea**	n.d.	n.d.

[a] Rh/NiZn catalyst (Rh: 0.68 mol%), **1** (0.5 mmol), **2** (1.5 mmol), 1,5-COD (4 eq. relative to Rh), toluene (4 mL), H_2O (0.45 mL), 100 °C. [b] Determined by GC using an internal standard technique.

phenylboronic acids generally reacted with alkynes more readily, while the electron-withdrawing analogue provided a relatively lower yield. Steric hindrance in the boronic acid aromatic ring strongly influenced hydrophenylation. For example, reaction between **1a** and 2-methylphenylboronic acid (**2b**) did not proceed effectively, with only a 52 % yield of **3ab** obtained after 24 h (entries 3 and 4), possibly due to strong inhibition of transmetalation by *o*-substituents. In comparison, 3-methylphenylboronic acid (**2c**) and *p*-substituted **2d**, reacted more readily with **1a** (entries 5-8). However, a low product yield was obtained over our Rh/NiZn catalyst for the reaction between 1-phenyl-1-propyne (**1b**) and **2a** (entry 13), in which phenyl addition occurred exclusively at the β position of the phenyl group in **1b** with no other isomer detectable by GC. Terminal alkynes such as 1-phenylethyne (**1c**) did not react at all (entry 14). Our Rh/NiZn catalyst was also able to promote the hydrophenylation of 1,2-diphenylethyne (**1d**) with **2a** (entry 15), however, no hydrophenylation product was formed with electron deficient alkynes such as 1,2-bis(methoxylcarbonyl) ethyne (**1e**), a well-known acceptor (entry 16). It therefore seems that the diester group in **1e** may strongly coordinate to, and hence deactivate, the catalytic rhodium species.

Rh leaching was not observed by AAS, nor any changes in the Rh chemical environment by XAS (Fig. 2). Since neither the parent CH_3COO^-/NiZn or OH^-/NiZn materials were able to catalyse reaction (Table 4, entries 5 and 6), we speculate the following reaction pathway for hydrophenylation over Rh/NiZn (Scheme S1), which is in agreement with previous proposals for homogeneous Rh catalysts:[15] initial transmetallation between the interlayer Rh species and the arylboronic acid16 to generate a Rh-Ar species. The internal alkyne triple bond then inserts into the Rh-Ar bond, yielding a 2-(alkynyl)phenylrhodium species which is subsequently readily hydrolysed by water. Finally, the desired addition product is obtained, accompanied by the regeneration of the initial Rh species. At present, the precise nature of the active Rh species is unclear. Although it is possible that a low valent Rh(I) species could form in situ via reduction of Rh(III) species we observe by XAS, our catalytic system proved inactive towards the well-known Rh(I)-catalysed 1,2-addition of **2a** to benzaldehyde[17] under our reaction conditions. Moreover, biphenyl was not observed as a by-product of our Rh/NiZn catalyst in hydrophenylation process.[18] Together these observations demonstrate that neither reductive elimination from Ar-Rh(III)-Ar to Rh(I), nor indicative Rh(I)-catalysed homocoupling of **2a**, occured. Furthermore, hydrophenylation under an O_2 proceeded at almost the same rate as under N_2 (Table 4, entries 3 and 4), suggesting that the re-oxidation of Rh(I) formed in situ to Rh(III) by molecular oxygen cannot occur.

Conclusions

In conclusion, Rh/NiZn is an effective heterogeneous catalyst for the hydrophenylation of internal alkynes with phenylboronic acids in the presence of 1,5-COD. X-ray spectroscopies confirm the catalytically active species as a hydroxo-rhodium(III) complex stabilised within the NiZn interlayers by strong electrostatic interaction. Re-use experiments evidence no loss in hydrophenylation catalytic activity over Rh/NiZn.

Acknowledgements

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10 Rh/NiZn pretreated with 1,5-COD showed no catalytic activity for the hydrophenylation of **1a** with **2a**.

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15 To further clarify the catalytically active species, FTIR and Rh K-edge XAS experiments were conducted using the Rh/NiZn catalyst with 1,5-COD in toluene/water solvent, however, no significant spectral changes were observed.

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Graphical abstract
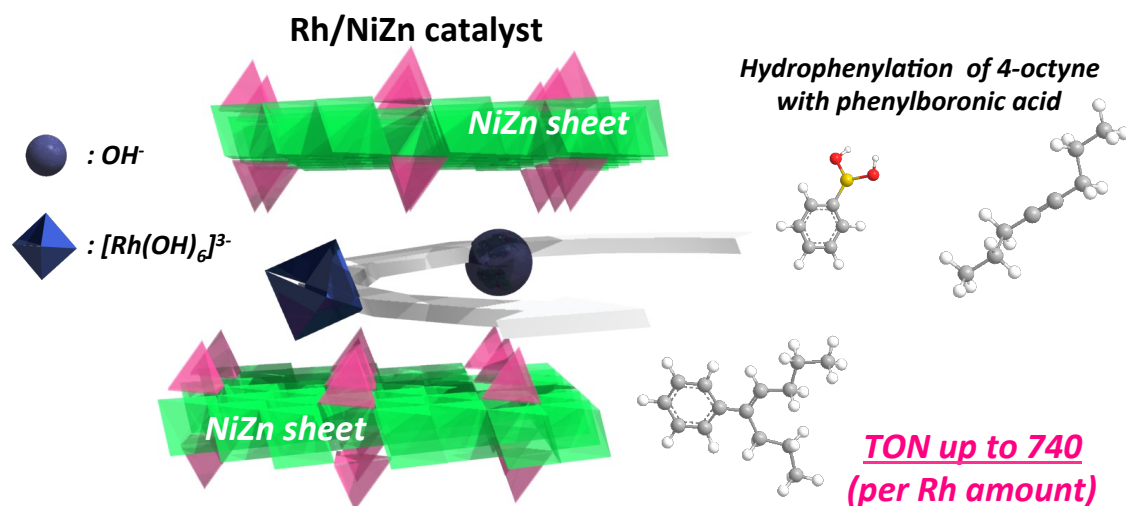
Hydrophenylation of internal alkynes with boronic acids

catalysed by a Ni-Zn hydroxy double salt-intercalated

anionic rhodium(III) complex

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