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Arylation of alkynes over hydrotalcite docked Rh-*m*-TPPTC complex

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ABSTRACT

Rh-*m*-TPPTC complex was successful immobilized onto a hydrotalcite Zn-Al to convert selectively in aqueous media both the symmetric and nonsymmetric alkynes into functionalized alkenes, with boronic acids. The complex preserved its activity after the ionic exchange, leading to excellent results (~87%) for the symmetric alkynes and also for the non-symmetrical alkynes (up to 99%).

1. Introduction

Since Miyaura has for the first time reported the addition of aryl- and alkenylboronic acids to α,β-unsaturated ketones catalyzed by a rhodium-phosphine complex in an aqueous solvent, organoboron compounds have emerged as reagents of choice in various transition-metal-catalyzed reactions [1]. The interest to this development was further extended for the addition of organoboronic acids to various unsaturated substrates [2,3] including terminal olefins such as styrenes and vinylpyridines [4]. A special attention was focused also onto addition of organoboron acid to alkynes, a reaction that was discovered by Hayashi's group [5] and now catalyzed by various transition metals [6]. The investigation of such reactions in water enlarged the valorisation possibilities but few reports were described so far [7]. Indeed, even though working in water allies economic, environmental and reaction efficiency advantages [8], the use of water requires, however, the presence of cooperative catalysts that should be able to combine the high catalytic efficiency with the metal recycling and the easy product/catalyst separation [9]. The literature reported in the 1980s the use of organometallic systems with water-soluble ligands. TPPTS (trisodium salt of 3,3′,3″-phosphane triylbenzenesulfonic acid) was one of the most popular water soluble ligands and it was widely used in a variety of transition metal-catalyzed reactions [10,11], such as palladium-catalyzed cross-coupling and nucleophilic substitutions [12], nickel-catalyzed cross-couplings [13], palladium, rhodium or nickel-catalyzed ene-reaction [14] and palladium and platinum-catalyzed car-boalkoxycyclization [15]. However, since hydrophilic sulfonated phosphane TPPTS and analogues are ineffective systems [7,11], new ligands [16] such as *m*-TPPTC (trilithium salt of 3,3′,3″-phosphane-triylbenzenecarboxylic acid) were designed to promote the arylation of alkynes in pure water or in a biphasic solvent [7b–d]. Heterogeneization of such water cooperative catalysts may generate even more efficient catalysts [17].

In this approach, and following our endeavor in heterogeneous catalysis [18], we have performed for the first time the addition of arylboronic acids to alkynes in the presence of a heterogeneous catalyst. More specifically, a Rh-*m*-TPPTC complex was successfully immobilized onto a layered double hydroxide Zn-Al (LDH) (Scheme 1) to convert selectively in aqueous media both the symmetric and nonsymmetric alkynes into functionalized alkenes, with boronic acids.

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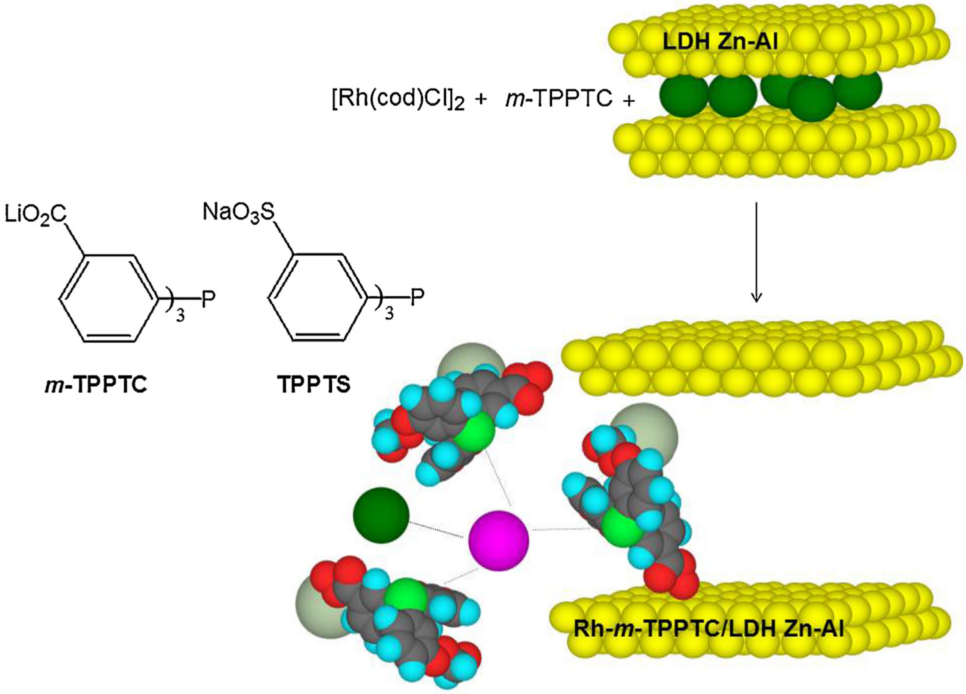

Scheme 1. *m*-TPPTC and TPPTS ligand structure and immobilized of Rh-*m*-TPPTC complex onto layered double hydroxide Zn-Al (LDH); (color code: black = C, blue = H, red = O, grey = Li, green = Cl, pink = Rh).

2. Experimental

2.1. Catalyst preparation

Two types of catalysts were prepared. Rh-*m*-TPPTC and Rh-TPPTS complexes were immobilized onto layered double hydroxides (LDH) containing Zn and Al. The heterogeneization of Rh-*m*-TPPTC complex on LDH followed the same procedure as for the Rh-TPPTS complex, as described elsewhere [18a]. The Zn_3AlCl LDH was prepared following methods described in the literature [19]. The ionic exchange capacity of $[Zn_{0.76}Al_{0.24}(OH)_2]Cl_{0.24}\cdot 0.8H_2O]$ (Zn_3AlCl) was 1.1 meq g^{-1}.

2.1.1. Rh-ligand complex synthesis:
The complex Rh-*m*-TPPTC and Rh-TPPTS were prepared under inert atmosphere starting from $[Rh(cod)Cl]_2$ precursor (0.25 mmol of metal) and (1 mmol) *m*-TPPTC and TPPTS ligand, respectively in 50 mL deionizated water (the solution was stirred for 12 h).

2.1.2. Heterogeneization of Rh-ligand complex:
The preparation of catalysts Rh-*m*-TPPTC and Rh-TPPTS supported on LDH were synthesized by ionic exchange method. To the mixture containing the Rh-ligand complex described above, under inert atmosphere, 1 g of Zn_3AlCl LDH was added. After 24 h of stirring, the solution was filtered and the solid was washed with deionized water, and dried under vacuum at room temperature for 16 h.

2.2. Catalysts characterization

The characterization of the catalysts was carried out using several techniques. N_2 adsorption–desorption isotherms of the LDH support and the Rh-catalysts were measured at −196 °C with a Micromeritics ASAP 2020. Prior to measurements, the samples were degassed at 150 °C under vacuum for more than 6 h. The specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) method in the p/p^0 (low case, according to IUPAC) range of 0.05–0.35. Pore size distribution curves were calculated from the adsorption branch of the isotherms with the Barrett–Joyner–Halenda (BJH) method, and pore sizes were obtained from the peak positions of the distribution curves. Both Rh-catalysts and LDH support were characterized by powder X-ray diffraction (XRD) using a Siemens D5000 X-ray diffractometer with nickel filtered Cu Kα radiation ($\lambda = 1.5418$ Å) at a scanning rate of $0.1° \cdot min^{-1}$ in the 2θ range of 10–80°. X-ray photoelectron spectroscopy (XPS) was performed in an analysis chamber (Specs) by using a monochromatized Al $K_{\alpha 1}$ X-ray source (photon energy 1486.74 eV) on powders pressed on carbon tapes by using ultrasonically cleaned tools. Electrons are collected in normal emission and analyzed by a 150 mm radius Phoibos electron analyzer operating in large area mode with pass energy of 30 eV. The estimated experimental resolution in these conditions is in the range of 0.90 eV Gaussian width (FWHM), with a total width (including the core hole width) of 1.15 eV obtained on Au $4f_{7/2}$ core levels [20]. A flood gun with acceleration voltage of 1 eV and electron current of 0.1 mA was employed to ensure the sample neutralization. It has been demonstrated that this flood gun parameters and experimental arrangements is effective in neutralizing charging effects on highly insulating thin films [21] and also on insulating powders pressed on carbon tapes, as in the actual case [22]. The XPS data are analyzed with normalized Voigt profiles, which are convolutions of lorentzian and gaussian lineshapes [22]. The inelastic background is simulated with integrals of Voigt lineshapes, derived also from Ref. [23]. For a doublet, when the spin-orbit splitting approaches the range of ionization energy or workfunction of the material, the lorentzian core level widths are allowed to vary (e.g. from Rh $3d_{5/2}$ to Rh $3d_{3/2}$) to account for the opening of Coster–Kronig decay channels yielding to a lower core hole lifetime of the state with higher binding energy [24]. The gaussian width was kept the same for all components. Chemical composition of the catalysts was determined by Atomic Emission Spectroscopy (ICP-AES) using a Plasma 40, Perkin-Elmer equipment after appropriate dissolution

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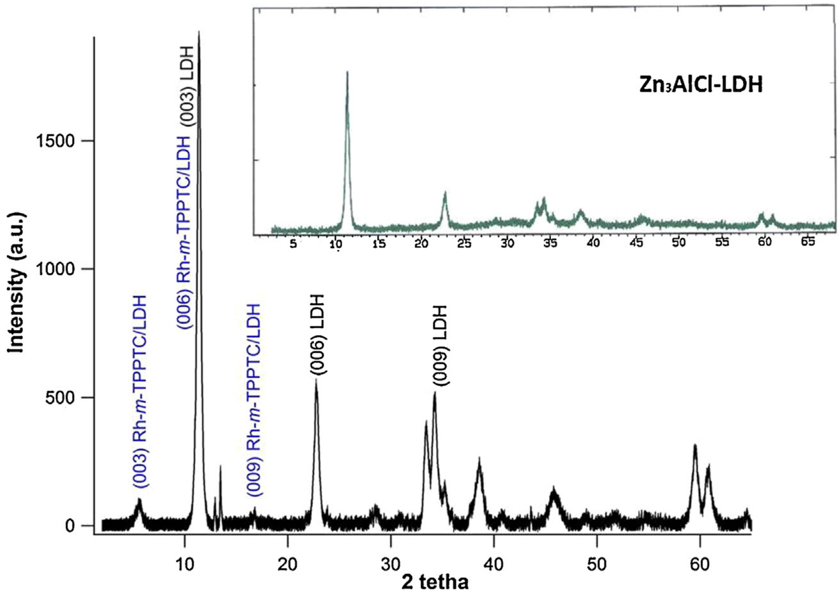

Fig. 1. PXRD pattern of Zn_3Al-LDH ionic exchanged with Rh-*m*-TPPTC complex.

of the solid samples. ^{31}P NMR analyses were performed on a Bruker 500 MHz NMR spectrometer. DRIFTs investigation of the materials were realized with a Nicolet 4700 spectrometer (400 scans, 500–4000 cm^{-1} scan range, 4 cm^{-1} resolution).

2.3. Catalytic test

Typical experiments were carried out by adding, at room temperature, to a reaction mixture of arylboronic acid (2.5 equiv) and 30 mg heterogeneous Rh-*m*-TPPTC/LDH catalyst 1 equivalent alkyne and the solvent (water or water/toluene (1/1), 2.5 M). The mixture was heated at 100 °C under stirring, for 3 h. After cooling the reaction mixture, the catalyst was centrifuged and separated from the mixture, and the resulted product was extracted with toluene (two times) and dichloromethane (two times). The resulted light yellow oil did not require any further purification. The ^{1}H NMR and ^{13}C NMR analyses (performed on a Bruker AV 300 instrument) and GS–MS analyses (Varian Trace GC Ultra – DSQ instrument) of the products **3a–f** and **4a–h** were identical at those published in the literature [7c,d].

3. Results and discussions

3.1. Catalysts characterization

The XRD patterns of Rh-TPPTS/LDH were already reported in other work [17a,18a]. As in the case of Rh-TPPTS/LDH, the XRD analysis of Rh-*m*-TPPTC-LDH shows patterns indicating the partial insertion of the ligand between the layers of the double hydroxide. Patterns shown in Fig. 1 indicate both the well-ordered layered structure of the initial LDH and of the LDH ionic exchanged with the Rh-*m*-TPPTC complex. After ionic exchange can be observed a main phase of the initial Zn_3Al-LDH, which contain Cl^- between the layers, but also another phase with the three harmonics located at 2θ 5.5° (0 0 3), ~11° (0 0 6) and 16.7° (0 0 9). This new phase corresponds to a higher ***c*** parameter of the lattice (Table 1) representing an evidence of the enlargement of the distance between layers, caused by the docked complex. In their work, Chen et al. [17b] are demonstrating that the insertion of one molecule of TPPTS ligand between the layers of a hydrotalcite will increase the d_{003} basal spacing to a value ~16 Å. Based on these observations and on our previous reports [17a,18g], we can conclude that the basal spacing 16.03 Å of the (0 0 3) refection plan, observed in the new formed phase, is enough to accommodate only one molecule of ligand (*m*-TPPTC) and not the whole Rh-complex. Probably, due to the high dimension of the complex, the ionic exchange had place on the external surface or better at the edge of the LDH (Scheme 1). However, the low intensity of the peaks assigned to the new phase formed containing Rh-*m*-TPPTC complex indicates a relatively small contribution of this phase and a low extent of ion-exchange of Rh-complex for the inorganic anions. The chemical composition and the textural characterization of the investigated catalysts revealed an important decrease of the surface area. The surface area of the docked complexes represented ca. 50% of that of the initial LDH (Table 2). This decrease provides additional evidences on the ionic exchange of Rh-*m*-TPPTC and Rh-TPPTS complexes inside the LDH.

Table 3 compiles the XPS binding energies of the constitutive elements (Al 2p, Zn 2p, P2p, Rh3d [5]) and the atomic XPS Rh:Zn ratios. No change of the binding energies of Al 2p and Zn 2p after the ionic exchange with Rh-*m*-TPPTC or Rh-TPPTS complexes was observed, meaning that the oxidation state of the constitutive elements was not altered by ionic exchange.

Fig. 2 presents XPS spectra of the Rh precursor ($[Rh(cod)Cl]_2$) and of Rh-*m*-TPPTC/LDH. According to previous findings, the binding energy of Rh 3d in ($[Rh(cod)Cl]_2$) corresponds to the oxidation state of Rh(I) [25]. After the complexation of the ($[Rh(cod)Cl]_2$) complex with phosphine, the XPS spectrum shows a shift of the binding energy of the Rh 3d level to lower binding energies and an asymmetry assigned to two components. The band at 306.0 eV may be assigned to the new Rh–P bond in the Rh-*m*-TPPTC complex, while

Table 1
Lattice parameters ***a*** and ***c*** resulted from the PXRD pattern of the Zn_3Al-LDH fresh and after ionic exchange.

	LDH initial (Å)	Rh-*m*-TPPTC/LDH (Å)
d_{003}	7.79	16.03
d_{006}	3.91	8.04
d_{009}	2.62	5.31
c (lattice parameter)	23.48	48.04
d_{110}	1.55	1.55
a (lattice parameter)	3.11	3.11

Table 2
The chemical composition and the surface areas of the investigated catalysts.

Catalyst	Chemical composition				Specific surface area, $m^2\ g^{-1}$
	Zn:Al ratio	Rh:Al ratio	Rh, wt%	TPPTS or *m*-TPPTC wt%	
LDH	3	–	–	–	94
Rh/TPPTS LDH	3	0.43	2.51	41.9	51
Rh/*m*-TPPTC LDH	3	0.42	2.45	29.5	55

Table 3
XPS binding energies and atomic XPS Rh:Zn ratios.

Catalyst	XPS binding energies, eV					XPS composition
	Al2p	Zn2p^3	P2p	Rh3d		Rh:Zn ratio
				Rh3d$_{3/2}$	Rh3d$_{5/2}$	
LDH	74.1	1021.7	–	–	–	–
$[Rh(COD)Cl]_2$	–	–	–	313.1	308.4	–
Rh-*m*-TPPTC/LDH	74.2	1021.6	132.5	310.8	306.0	0.055
				312.8	308.0	

Table 4
^{31}P NMR of the *m*-TPPTC the Rh-*m*-TPPTC complex in D_2O, and ^{31}P MAS NMR the ionic-exchange Rh-*m*-TPPTC/LDH.

No	Sample	Chemical shift
1	*m*-TPPTC	–5.6
2	RhCl(*m*-TPPTC)$_3$	30.2
3	Rh-*m*-TPPTC/LDH	29.9

that at 308.0 eV to the remanent Rh–Cl bond. The immobilization of the complex on LDH caused no change in the XPS spectrum. The binding energy of P 2p level at 132.5 eV confirms the preservation of the phosphorous oxidation state during the immobilization procedure of the complex (Fig. 2b). Similar spectra were recorded for the Rh-TPPTS/LDH complex [17a].

^{31}P NMR was used to investigate the complexation of the phosphine ligand with ($[Rh(cod)Cl]_2$). Table 4 compiles the ^{31}P chemical shift for the *m*-TPPTC ligand, the Rh-*m*-TPPTC complex and the ionic-exchanged Rh-*m*-TPPTC/LDH. The spectra were recorded considering H_3PO_4 as standard. The spectrum of *m*-TPPTC shows resonance at −5.6 ppm [16a], while that of the Rh-*m*-TPPTC complex at 30.2 ppm. These results are in agreement with the reported literature data [26]. The ionic exchange led to no significant chemical shift of the ^{31}P nuclei, proving once more that the Rh-complex is not affected by the immobilization procedure.

DRIFT analyses were recorded for both LDH and Rh-*m*-TPPTC/LDH materials (Fig. 3). No significant difference could be observed between the two spectra, except an increase in the range 1400–1470 cm^{-1}, which could be assigned to the phenyl group of the *m*-TPPTC ligand.

ICP-AES analysis of the Rh-*m*-TPPTC or Rh-TPPTS supported on LDH indicated a similar Rh content. The TPPTS:Rh (wt%) ratio was found of 2.87 that is in agreement with the structure of the expected complex [27].

3.2. Catalytic tests

Both catalysts Rh-*m*-TPPTC/LDH and Rh-TPPTS/LDH were tested in the addition of boronic acids to different alkynes (symmetric or non-symmetric). As it was anticipated [7c,d], the Rh-TPPTS/LDH catalyst shows no activity for this addition. We had indeed observed a lower activity (and selectivity) of the Rh/TPPTS catalyst compared to the Rh-*m*-TPPTC complex under homogeneous conditions. The heterogeneization of such systems enhances this phenomenon. Table 5 presents the results of the addition of different boronic acids to the symmetric alkyne (4-octyne) in the presence of Rh-*m*-TPPTC/LDH. Following our previous findings on the use of *m*-TPPTC ligand for such transformation under homogeneous conditions [7c,d], we chose a biphasic system (toluene/water) as the reaction medium. Pleasingly the supported catalyst was found to be effective

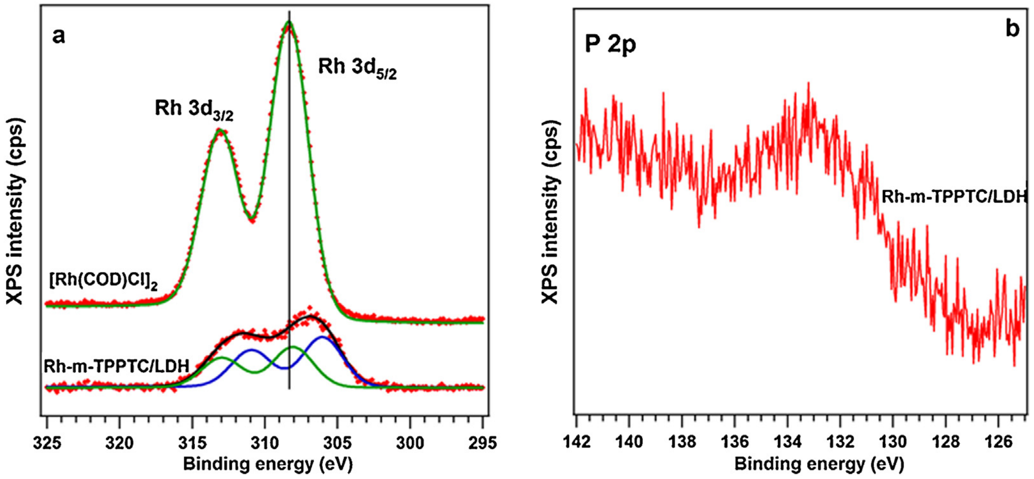

Fig. 2. Rh 3d (a) and P2p (b) XPS spectra of Rh-m-TPPTC/LDH catalyst.

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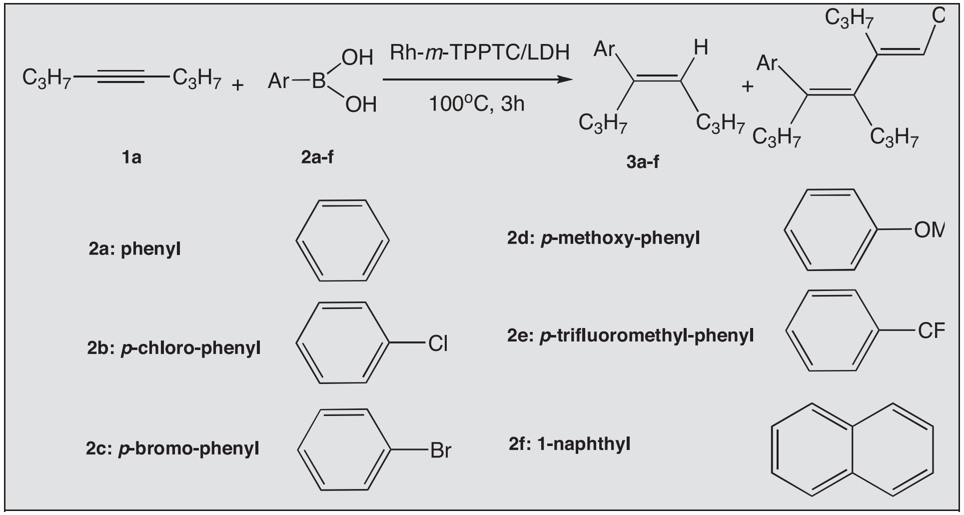
Table 5
Addition of arylboronic acids to 4-octyne (in the presence of Rh-*m*-TPPTC/LDH catalyst).



Entry[a]	ArB(OH)$_2$	Solvent	Alkene/ dimer ratio	Yield[a] (Conv.) [%]
1	**2a**	H_2O/toluene	96/4	87 (100)
2	**2b**	H_2O/toluene	96/4	85 (100)
3	**2c**	H_2O/toluene	96/4	87 (100)
4	**2d**	H_2O/toluene	96/4	84 (100)
5	**2e**	H_2O/toluene	96/4	86 (100)
6	**2f**	H_2O/toluene	96/4	86 (100)
7	**2d**	H_2O	88/12	85 (100)

[a] Isolated yield.

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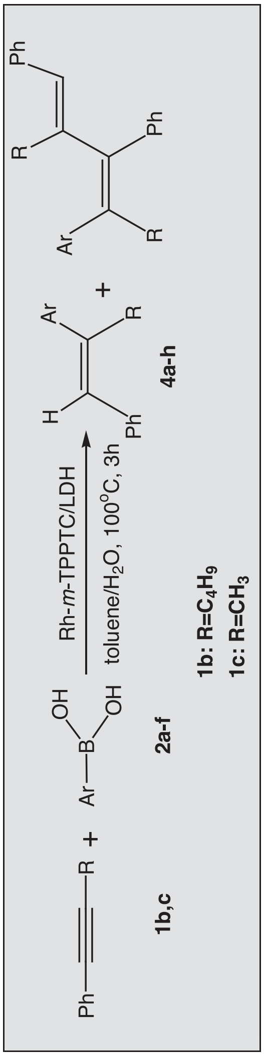
Table 6
Arylboronic acids addition to non-symmetric alkynes.



Entry[a]	Alkyne	ArB(OH)$_2$	Alkene/dimer ratio	Yield[a] (Conv.) [%]
1	**1b**	**2a**	95/5	30 (100)
2	**1c**	**2a**	52/48	59 (100)
3	**1b**	**2d**	100/0	13 (100)
4	**1c**	**2d**	6/94	56 (100)
5	**1b**	**2e**	100/0[b]	83 (100)
6	**1c**	**2e**	58/42	99 (100)
7	**1b**	**2f**	100/0	99 (100)
8	**1c**	**2f**	100/0	88 (100)

[a] Isolated yield (alkene or alkene–diene mixture for entries 2, 4, 6).
[b] 20% of trimer detected by GC–MS.

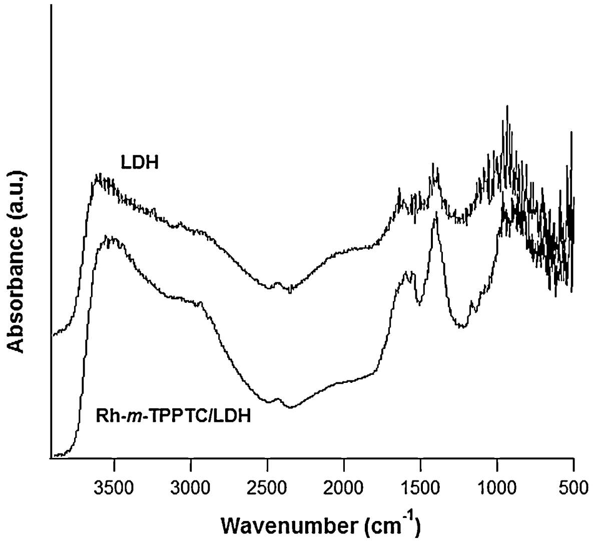


Fig. 3. DRIFTs spectra of the LDH and Rh-*m*-TPPTC/LDH.

and isolated yields in the range 84–87% were obtained irrespective of the boronic acids substituent (Table 5, entries 1–6). The reaction conditions were compatible with electron-withdrawing, electron-donating or sterically hindered groups on the boronic acid. As anticipated [7c,d], working in pure water led to an increased yield of dimer, which should be associated to the hydrophobicity of the resulted alkene (Table 5, entry 7). The formed alkenes (hydrophobic molecules) often generate emulsion clusters in water, favoring the reaction between two alkenes or more thus leading to secondary products, like dimers. Carrying the reactions out in a biphasic mixture (toluene:water 1:1) therefore diminished the formation of side products. Under these conditions the alkene/dimer ratio was increased from 88/12 to 96/4 irrespective of the investigated boronic acid partner (Table 5, entries 4, 7).

We then turned our attention to the arylation of other alkynes such as non-symmetrical ones (Table 6). The reaction of phenylboronic **2a** and 2-methoxy-phenyl boronic acids **2d** with the non-symmetric alkynes hex-1-ynylbenzene **1b** and prop-1-ynylbenzene **1c** performed only with moderate yields (Table 5, entries 1–4). Moreover, the dimer formation became a highly competitive process in the case of **1c** (Table 6, entries 2, 4 and 6). The lower steric hindrance of the alkyne **1c** compared to **1b** may account for this observation. When the steric hindrance of the boronic acid was increased, such as for **2f**, the high selectivity of the reaction towards the formation of the desired alkene 4h was recovered (Table 6, entry 8). In the case of alkyne **1b**, the naphthylboronic acid **2f** and trifluoromethyl phenyl acid **2e** were good partners (Table 6, entries 5 and 7). The naphthylboronic acid **2f** afforded only the formation of the alkene (Table 6, entries 7, 8) most presumably due to its steric hindrance, while the trifluoromethyl phenyl boronic acid **2e** allowed the formation of the corresponding dimer (Table 6, entry 6).

Table 7 presents the results for the first four runs using substrate **1a** with the arylboronic **2a** and **2f** acids in the presence of Rh-*m*-

Table 7
Recycling tests for the substrate **1a** with **2a** and **2f** arylboronic acid in the presence of the Rh-*m*-TPPTC/LDH catalyst (3 h reaction time).

Alkyne (**1**) and boronic acid (**2**)	Run 1	Run 2	Run 3	Run 4
1a with **2a**	87[a] (100)[b]	87 (100)	85 (99)	84 (97)
1a with **2f**	86 (100)	86 (100)	85 (98)	85 (98)

[a] Isolated yield [%].
[b] Conversion [%].

TPPTC/LDH catalyst after 3 h. The supported catalytic system can easily be separated by centrifugation under ambient conditions. The recovered catalyst (by simple decantation) was simply added to the next reaction mixture without any additional treatment. The supported catalysts were recycled with a slightly loss of conversion and yield after the second run (Table 7). The absence of any leaching was also confirmed by the ICP-AES analysis of the reaction products.

4. Conclusions

The heterogeneization of Rh-*m*-TPPTC complex used in homogeneous catalysis for the 1,4-addition of arylboronic acids to alkynes was successfully achieved. The complex preserved its activity after the ionic exchange, leading to excellent results (~87%) for the symmetric alkynes. As in the case of homogeneous conditions, the biphasic system (water/toluene) was found to be highly important for the selectivity of the reaction. Good to excellent activity of the Rh-*m*-TPPTC/LDH was also observed for the non-symmetrical alkynes (up to 99%), with a high dependence of the steric hindrance regarding the selectivity of the reaction. Recycling of the catalyst was successfully performed (up to four runs) without evidence of leaching.

Acknowledgments

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