Layered double hydroxides supported rhodium(0): An efficient and reusable catalyst for Heck, Suzuki, and Stille reactions of haloarenes[☆]

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Abstract

Layered double hydroxides supported rhodium(0) catalyst was prepared, characterized and effectively used as a catalyst in the Heck, Suzuki and Stille cross-coupling of haloarenes. The catalyst can easily be removed by simple filtration and reused for several cycles with consistent activity.
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1. Introduction

The coupling of haloarenes by Heck, Suzuki, Sonogashira and Stille reactions is a well established methodology in modern organic synthesis as the coupling products find good applications as intermediates in the preparation of materials, natural products and bioactive compounds [1]. Mostly palladium complexes are used to catalyze these couplings reactions as they offer high product yields, high regioselectivity, high stereoselectivity and compatibility with many functional moieties. The activity of other transition metal catalysts such as nickel [2], copper [3], ruthenium [4], rhodium [5], iron [6], platinum [7], and iridium [8] has also been investigated. However the scope and functional group tolerance of the Pd-catalysts are far wider than any other metal species. But the efficiency and selectivity of those Pd-catalyzed systems are often sensitive to the use of ancillary ligands such as phosphanes, *N*-heterocyclic carbenes, etc. among which some are air and moisture sensitive and or expensive. These lead to the development of ligand free catalysts system for the arylation of olefins and related cross-coupling reactions based on supported nanometals [9],

colloidal metal species [10], and polymer entrapped metals [11]. Though rhodium complexes have been widely used in several carbon–carbon bond forming reactions but the examples of Rh-catalyzed Heck-type and related cross-coupling reactions are less in literature [5]. Rh-TPPTS complex [7c] was used in homogeneous catalysis for the vinylation of aryl iodides but it catalyzed only dehalogenation. Recently [RhCl(cod)]$_2$ is reported [5f] to be an efficient catalyst for Suzuki coupling of aryl halides. But the use of heterogeneous rhodium catalyst in such cross-couplings is not well documented. Only recently Fujita et al. reported a rhodium-grafted hydrotalcite as a highly efficient heterogeneous catalyst for 1,4-addition of organoboron reagents to α,β-unsaturated carbonyl compounds [12].

In recent years layered double hydroxides of Mg and Al (LDHs) has been receiving considerable attention due to its cation exchange capacity of the brucite layer, anion exchange by inter layer, adjustable surface basicity and adsorption capacity [13]. Moreover the ability to hold metal particles in the defect sites and provides adequate electron density to stabilize it, make LDHs good support in heterogeneous catalysis and by exploiting these properties of LDHs earlier we reported the effective Heck, Suzuki, Sonogashira and Stille type reactions of chloroarenes using layered double hydroxides supported nanopalladium catalyst [5c]. In continuation of our studies on the scope and limitations of supported transition metals other than palladium in palladium catalyzed organic transformations

[14], we herein wish to report our investigations on the LDHs supported nanorhodium (LDH-Rh^0) catalyzed Heck, Suzuki and Stille cross-coupling reactions.

2. Experimental

2.1. Materials and methods

FTIR spectra were recorded on a Perkin-Elmer spectrophotometer. ^{1}H NMR spectra were recorded on Bruker (300 MHz) and Varian Gemini 200 MHz spectrophotometer using CDCl$_3$ as solvent and TMS as the internal standard. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. X-ray powder diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using Cu Kα radiation. The particle size and external morphology of the samples were observed on a PHILIPS TECNAI F12 FEI transmission electron microscope (TEM). SEM-EDX was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. Diffuse reflectance UV/vis spectra for samples as KBr pellets were recorded on a GBC Cintra 10e UV–VIS spectrometer in the range 200–800 nm with scan speed 400 nm/min. ICP-AES analyses are performed using IRIS Intrepid II XDL ICP-AES (Thermo ELECTRON CORPORATION). The specific surface area of the catalyst samples was estimated using the N$_2$ adsorption isotherm at 77 K by the multipoint BET method using an Autosorb-1 Quantachrom instrument. Temperature programmed reduction (TPR) studies were carried out on an AutoChem 2910 (Micromeritics, USA) instrument. GC analyses were done by using SHIMADZU GC-2010 with Z-B5 capillary column. All known compounds were characterized by comparing their physical data with those in the literature. Solvents used for experiments were dried and distilled according to literature procedures. All the reactants were commercially available and used without purification.

2.2. Preparation of LDH-Rh(III)

LDH-CO$_3$ (Mg:Al = 3:1, 1 g) [12] was treated with RhCl$_3$, H$_2$O (294 mg, 1.5 mmol) dissolved in 100 mL doubly deionized water with stirring for 24 h at ambient condition to afford brownish-yellow colored LDH-Rh(III). Then the catalyst was filtered, and washed with deionized water followed by acetone, and air-dried.

2.3. Preparation of LDH-Rh^0

LDH-Rh(III) (1 g) was reduced with molecular hydrogen (flow rate: 60 mL/min) at 250 °C for 3 h to get black colored air stable LDH-Rh^0 (Rh: 0.91 mmol/g).

2.4. Heck coupling reaction catalyzed by LDH-Rh^0

Aryl halide (1 mmol), olefin (3 mol), KOAc (3 mmol), DMF (3 mL) and LDH-Rh^0 (5 mol%) were taken in a 10 mL reaction vessel and stirred under N$_2$ atmosphere at 140 °C. After the completion of the reaction as judged by GC, the catalyst was separated by filtration and washed with water followed by acetone and dried in air and then used in the next run. The filtrate was diluted with ether and washed with water. The organic layer was concentrated to get the crude product, which was purified by column chromatography using a mixture of hexane–ethyl acetate to get pure product. All the products are known and characterized by ^{1}H NMR and mass spectrometry.

2.5. Suzuki coupling reaction catalyzed by LDH-Rh^0

In an oven dried 10 mL round bottom flask haloarene (1 mmol), phenylboronic acid (1.5 mmol), NaOAc (3 mmol), LDH-Rh^0 (3 mol%), and dimethoxyethane (DME)–water = 1:1 (3 mL) were taken and stirred at 100 °C under N$_2$ atmosphere. After the completion of the reaction as judged by GC, the catalyst was filtered and washed with water followed by acetone and dried in air and then used in the next run. The filtrate was diluted with ethyl acetate and washed with 10% aqueous NaOH solution and finally with saturated aqueous NaCl solution. The organic layer was dried with Na$_2$SO$_4$ and concentrated under reduced pressure. The crude reaction mixture was chromatographed on silica gel using hexane/ethyl acetate (10:1) as an eluent to afford the pure product. NMR and mass spectrometry were used to identify the purity of the products.

2.6. Stille coupling reaction catalyzed by LDH-Rh^0

In an oven dried 10 mL round bottom flask, haloarene (1 mmol), and phenyltributyltin (1.5 mmol), NaOAc (2 mmol), LDH-Rh^0 (3 mol%), and NMP (3 mL) were taken and stirred at 80–100 °C under N$_2$ atmosphere. After the completion of the reaction as judged by GC, the catalyst was filtered, washed with water followed by acetone and dried in air and then used in the next run. The filtrate was diluted with ethyl acetate and washed with saturated aqueous NaCl solution. The organic layers were combined and dried with Na$_2$SO$_4$ and concentrated to get the crude product. The crude reaction mixture was chromatographed on silica gel using hexane/ethyl acetate (10:1) as an eluent to afford the pure product.

3. Results and discussion

3.1. Preparation of LDH-Rh^0 catalyst

The LDHs consist of alternative cationic M(II)$_{1-x}$M(III)$_x$ (OH)$_2$$^{x+}$ and anionic A^{n-}·zH$_2$O layers [12]. The positively charged layers contain edge-shared metal M(II) and M(III) hydroxide octahedral with charges neutralized by A^{n-} anions located in the interlayer spacing or at the edges of the lamellae. Small hexagonal LDH-CO$_3$ crystals with Mg:Al = 3:1 and CO$_3$$^{2-}$ anion were synthesized following the existing procedures [12]. Rh^{3+} was grafted onto the LDH from the aqueous solution of RhCl$_3$ to obtain yellow colored LDH-Rh(III) [12], which was subsequently reduced with molecular hydrogen to get black powder of LDH-Rh^0.
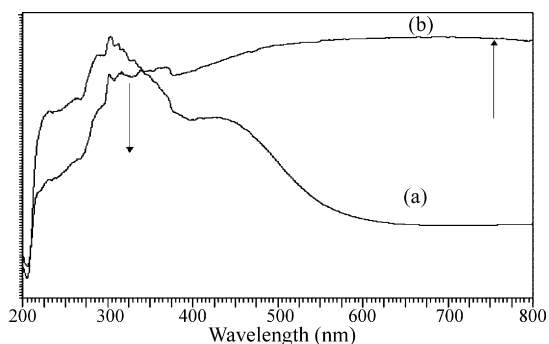
Fig. 1. UV–vis/DRS of (a) LDH-Rh(III) and (b) LDH-Rh(0).

3.2. Characterization of LDH-Rh^0

The LDH-Rh^0 catalyst developed was well characterized by UV–vis/diffuse reflectance spectroscopy, XRD, TPR, XPS, SEM-EDX, and TEM. The partial reduction of rhodium in LDH-Rh^0 was confirmed by UV–vis/DRS, in which the peak at 300 nm corresponding to Rh^{3+} diminished upon reduction and the absorbance in the visible region increased indicating the formation of the Rh^0 particles (Fig. 1).

X-ray powder diffraction patterns of LDH, LDH-Rh(III), and LDH-Rh^0 hardly differ in the range $2\theta = 3$–$65°$. The observed d_{003} basal spacing of the support that appeared at 7.8 Å remained unchanged after the cation grafting and reduction which indicates that the Rh^{3+} ions and Rh^0 particles located on the surface in the respective samples (Fig. 2).

Temperature programmed reduction (TPR) studies on the LDH-Rh(III) show multiple reduction peaks (Fig. 3). The peaks at temperatures lower than 150 °C indicate the reduction of the metal (Rh) whereas the peak at higher temperature (>290 °C) shows the reduction of the support [15]. An X-ray photo-electron spectroscopic investigation of LDH-Rh(III) showed binding energy peak for Rh $3d_{5/2}$ at 309.56 eV, whereas two binding energy peaks are observed in LDH-Rh^0 at 308.39 and 309.63 eV which are attributed to Rh(0) and Rh(III) oxidation states, respectively (Fig. 4) [16] and the ratio of Rh(0)/Rh(III) is found to be 61:39. The average size of the rhodium particles in the LDH-Rh^0 were measured from transmission electron microscope images (Fig. 5) and found to be in the range of 50–60 nm. The BET surface areas of LDH, LDH-Rh(III) and LDH-Rh^0 were found to be 65, 75.4 and 81.6 m^2/g, respec-
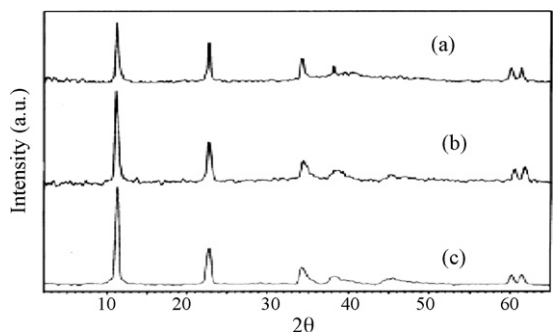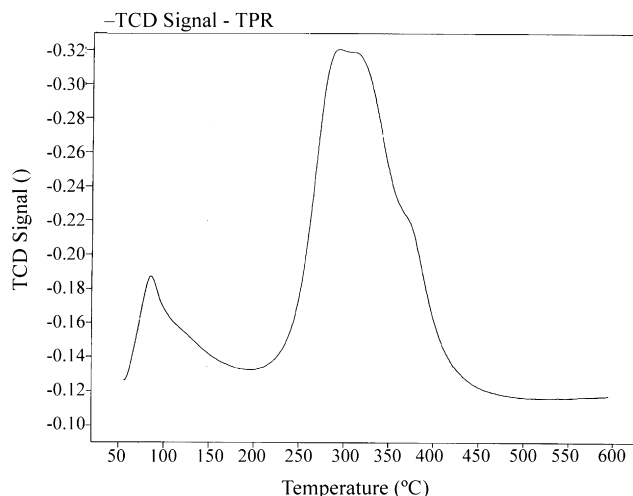

Fig. 3. TPR profile of LDH-Rh(III).

tively. The ICP-AES analysis of LDH-Rh^0 shows the presence of rhodium (0.91 mmol/g) in the sample.

3.3. Synthetic applications of LDH-Rh^0 catalyst

3.3.1. Heck coupling of haloarenes with olefins using LDH-Rh^0 catalyst

After trying several combination of base, solvent and temperature we found that when iodobenzene (1 mmol) was treated with ethyl acrylate (3 mmol) in the presence of KOAc (3 mmol) as a base and LDH-Rh^0 (5 mol%) in DMF at 140 °C for 16 h under nitrogen, *trans*-ethyl cinnamate being formed in 92% yield (Table 1, entry 1) along with a small amount of dehalo-genated product (less than 2%). Then several other olefins and

Table 1

Heck reaction of olefins and aryl halides catalyzed by LDH-Rh^{0a}

$$\text{EWG} + \text{Aryl-X} \xrightarrow[\text{KOAc, DMF, 140 }^0\text{C}]{\text{LDH-Rh}^0 (5 \text{ mol\%})} \text{Aryl} \diagdown \text{EWG}$$

Entry	EWG	Aryl-X	Yield (%)
1	CO$_2$Et	PhI	92(88), 85^b, 0^c, 67^d, 98^e
2	CO$_2$Bu	PhI	85
3	Ph	PhI	88
4	CO$_2$Me	PhI	92
5	CO$_2{}^t$Bu	PhI	70
6	4-Me-C$_6$H$_4$	PhI	83
7	Ph	4-MeO-C$_6$H$_4$I	84 (80)
8	Ph	4-NO$_2$-C$_6$H$_4$I	95 (91)
9	Ph	4-Me-C$_6$H$_4$I	86
10	Ph	4-CH$_3$CO-C$_6$H$_4$I	90 (88)
11	Ph	4-NO$_2$-C$_6$H$_4$Br	68
12	Ph	4-CH$_3$CO-C$_6$H$_4$Br	45
13	Ph	PhBr	Trace

^{a} Reaction conditions: olefin (3 mmol), aryl halide (1 mmol), LDH-Rh^0 (5 mol%), KOAc (3 mmol), DMF (5 mL), 140 °C, 14–30 h, yields based on GC. Isolated yields in parenthesis.
^{b} Yield after 5th cycle.
^{c} 5 mol% RhCl$_3$ used as catalyst.
^{d} 5 mol% LDH-Rh(III) used.
^{e} 5 mol% 10%-Pd/C used as catalyst, reaction time: 2 h.

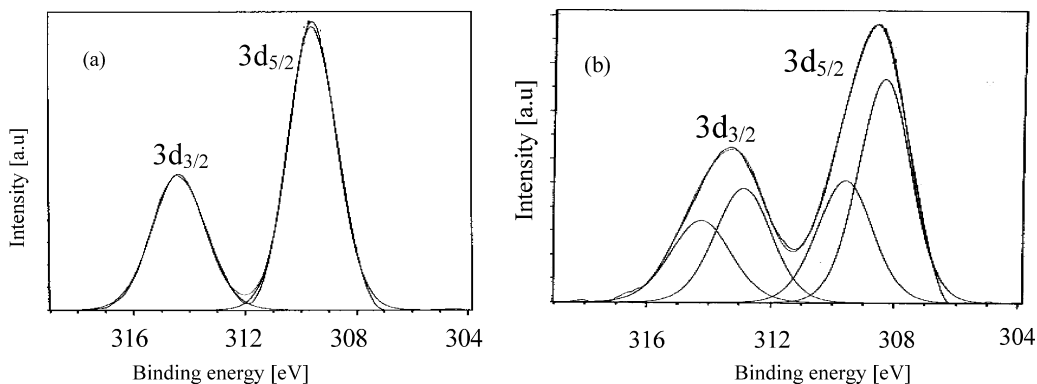Fig. 2. XRD of (a) LDH-Rh^0, (b) LDH-Rh(III) and (c) LDH-CO$_3$.

Fig. 4. XPS narrow scan for Rh 3d in (a) LDH-Rh(III) and (b) LDH-Rh(0).

aryl iodides were reacted under this optimized condition and the results are summarized in Table 1. Reaction of aryl iodide with electron-donating group required longer duration than the aryl iodide with electron-withdrawing group but yields are almost comparable. Aryl bromides with electron-withdrawing functionalities are also found to be reactive under this condition (Table 1, entries 11 and 12). To compare our catalytic system with the classical Pd system, 10%-Pd/C (5 mol%) was employed in the Heck coupling of ethyl acrylate and iodobenzene and the reaction was complete within 2 h affording ethyl *trans*-cinnamate in 98% yield (Table 1, entry 1). When a control experiment was done with LDH-CO$_3$ instead of LDH-Rh^0, no product formation was observed. LDH-Rh^0 exhibited higher catalytic activity in the reaction compared to LDH-Rh(III) (Table 1, entry1) which is in agreement with the considerations described by Djakovitch and Koehler [17,9c] that metal in zero oxidation state was the active species in heterogeneous systems.

Moreover the supported catalyst was quantitatively recovered at the end of the reaction by a simple filtration and reused for four cycles with consistent activity (1st cycle 92%, 2nd cycle 90%, 3rd cycle 90%, 4th cycle 88%, 5th cycle 85%). The difference of rhodium content between the fresh and used catalyst was 2.7%. The reaction between iodobenzene and ethyl acrylate was discontinued after 1 h (conversion 17%) and the catalyst was removed from the reaction mixture by hot filtration. With the filtrate, we continued the reaction for an additional 24 h and the conversion remained same. According to Lipshutz et al. [18]

significant amount of supported metal can be dissolved during the reaction and would redeposit quickly on the solid during the filtration as a result of unavoidable minor temperature difference during the filtration. It may be assumed in this case also during filtration the solid matrix can trap rhodium species dissolved from the catalyst during the reaction [18]. Then we studied the catalyst after the third catalytic run by XRD and TEM. XRD pattern of the used catalyst was almost similar to fresh catalyst. TEM images of the fresh and used catalysts were also found to be similar (Fig. 6). These studies suggest that the reaction occurs at the surface. To get insight into the mechanism, we heated LDH-Rh^0 with PhI in DMF for 10 h under argon atmosphere. After cooling, the catalyst was filtered and analyzed by XPS. In XPS we have observed the Rh 3d$_{5/2}$ line at 309.9 eV (in LDH-Rh^0, Rh 3d$_{5/2}$ at 308.3 eV) and I 3d$_{5/2}$ line at 620.56 eV, which confirms the oxidative addition of PhI to rhodium. Based on these primary results we postulate that the same mechanism as in palladium catalysis is operating, i.e. oxidative addition of haloarene to Rh followed by insertion of olefin then reductive elimination of product [19]. A detailed mechanistic study is under progress.

3.3.2. Suzuki coupling of haloarenes with arylboronic acids using LDH-Rh^0 catalyst

Buoyed with the impressive results obtained in the Heck coupling reaction the LDH-Rh^0 catalyst was next employed in the Suzuki cross-coupling of aryl halides with aryl boronic acids to obtain unsymmetrical biaryls. Using 3 mol% LDH-Rh^0 in
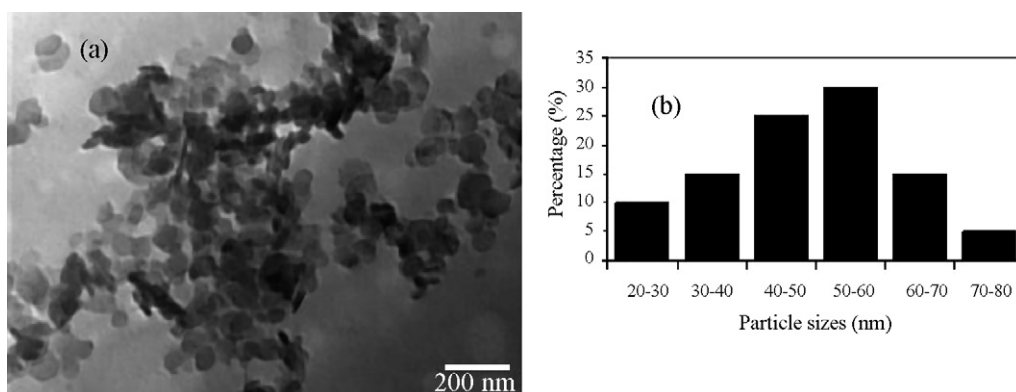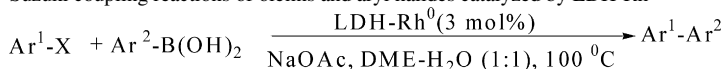

Fig. 5. (a) TEM images of LDH-Rh^0 and (b) histogram of particle size distribution.

Table 2

Suzuki coupling reactions of olefins and aryl halides catalyzed by LDH-Rh[0a]

$$Ar^1\text{-}X \; + \; Ar^2\text{-}B(OH)_2 \quad \xrightarrow[\text{NaOAc, DME-H}_2\text{O (1:1), 100 }^0\text{C}]{\text{LDH-Rh}^0 (3 \text{ mol\%})} \quad Ar^1\text{-}Ar^2$$

Entry	Ar^1-X	Ar^2-B(OH)$_2$	Yield (%)
1	PhI	PhB(OH)$_2$	91 (87), 88[b]
2	PhI	4-MeO-C$_6$H$_4$B(OH)$_2$	96 (90)
3	PhI	4-Me-C$_6$H$_4$B(OH)$_2$	90 (86)
4	4-MeO-C$_6$H$_4$I	PhB(OH)$_2$	90
5	4-Me-C$_6$H$_4$I	PhB(OH)$_2$	90
6	4-CH$_3$CO-C$_6$H$_4$I	PhB(OH)$_2$	92 (90)
7	4-NO$_2$-C$_6$H$_4$I	PhB(OH)$_2$	92 (88)
8	4-NO$_2$-C$_6$H$_4$Br	PhB(OH)$_2$	83
9	4-CH$_3$CO-C$_6$H$_4$Br	PhB(OH)$_2$	78
10	PhBr	4-MeO-C$_6$H$_4$B(OH)$_2$	60
11	4-MeO-C$_6$H$_4$Br	PhB(OH)$_2$	30

[a] Reaction conditions: haloarene (1 mmol), arylboronic acid (1.5 mmol), LDH-Rh[0] (3 mol%), NaOAc (3 mmol), DME–H$_2$O (1:1) (3 mL), 100 °C, N$_2$, 12–18 h, yields based on GC. Isolated yields in parenthesis.
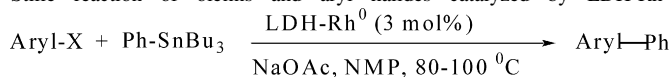
[b] Yield after 5th cycle.

DME–water mixed solvent in presence of NaOAc base several aryl iodides were reacted with a variety of arylboronic acids at 100 °C (Table 2). From Table 2, it is evident that electronic variations on the aryl halides as well as on the aryl boronic acids influence the efficiency of the reaction. Moreover LDH-Rh[0] can also activate electron rich bromoarenes (Table 2, entry 11) albeit with moderate yields. Here also the catalyst was recycled for four cycles with consistent activity (Table 2, entry 1).

3.3.3. Stille coupling of haloarenes using LDH-Rh[0] catalyst

Stille coupling is another important reaction to make unsymmetrical and symmetrical biaryls using aryl halides. LDH-Rh[0] (3 mol%) in presence of NaOAc can smoothly catalyze the reaction between iodobenzene and phenyltributyltin to afford 90% of the biphenyl in NMP solvent at 80 °C. Then several other aryl halides are also employed in the same reaction and the results are shown in Table 3. Aryl bromides (100 °C) require higher temperature than aryl iodides (80 °C). In some cases biphenyl (from the self-coupling of phenyltributyltin and from Ullmann coupling of haloarenes) as side products was obtained. Moreover

Fig. 6. TEM images of LDH-Rh[0] after third catalytic run.

Table 3

Stille reaction of olefins and aryl halides catalyzed by LDH-Rh[0a]

$$Aryl\text{-}X \; + \; Ph\text{-}SnBu_3 \quad \xrightarrow[\text{NaOAc, NMP, 80-100 }^0\text{C}]{\text{LDH-Rh}^0 (3 \text{ mol\%})} \quad Aryl\text{—}Ph$$

Entry	Aryl-X	Yield (%)
1	PhI	95
2	4-MeO-C$_6$H$_4$I	90 (85)
3	4-NO$_2$-C$_6$H$_4$I	92 (89)
4	4-Me-C$_6$H$_4$I	90
5	4-CH$_3$CO-C$_6$H$_4$I	95 (92), 90[b]
6	4-NO$_2$-C$_6$H$_4$Br	86
7	4-CH$_3$CO-C$_6$H$_4$Br	83
8	PhBr	60
9	4-MeO-C$_6$H$_4$Br	45

[a] Reaction conditions: haloarene (1 mmol), phenyltributyltin (1.5 mmol), LDH-Rh[0] (3 mol%), NaOAc (3 mmol), NMP (3 mL), 80 °C (iodoarene) or 100 °C (bromoarene), 12–16 h, yields based on GC. Isolated yields in parenthesis.

[b] Yield after 5th cycle.

in the coupling of 4-acetyl iodobenzene with phenyltributyltin the LDH-Rh[0] was reused for four cycles with consistent activity (Table 3, entry 5). Chloroarenes were found to be unreactive under the present reaction condition.

4. Conclusion

In conclusion, the recyclable LDH-Rh[0] catalyst was used in Heck, Suzuki and Stille cross-coupling reactions to afford good to excellent yields of coupling products. The catalyst was quantitatively recovered from the reaction by simple filtration and reused for a number of runs with consistent activity in all the reactions.

References

[1] (a) I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009;
(b) A. Zapf, M. Beller, Chem. Commun. (2005) 431;
(c) N. Miyaura, Cross-coupling Reactions, Springer, Berlin, 2002;
(d) F. Diederich, P.J. Stang, Metal-catalyzed Cross-coupling Reactions, Wiely/VCH, Weinheim, 1998;
(e) K. Sonogashira, J. Organomet. Chem. 653 (2002) 46.

[2] (a) V. Percec, J.-Y. Bae, D.H. Hill, J. Org. Chem. 60 (1995) 1060;
(b) S. Saito, S. Oh-Tani, N. Miyaura, J. Org. Chem. 62 (1997) 8024;
(c) B.H. Lipshutz, J.A. Sclafani, P.A. Blomgren, Tetrahedron 56 (2000) 2139;
(d) D. Zim, V.R. Lando, J. Dupont, A.L. Monteiro, Org. Lett. 3 (2001) 3049.

[3] S. Iyer, C. Ramesh, A. Sarkar, P.P. Wadgaonkar, Tetrahedron Lett. 38 (1997) 8113.

[4] (a) T.-A. Mitsudo, M. Takagi, S.-W. Zhang, Y. Watanabe, J. Organomet. Chem. 423 (1992) 405;
(b) E.J. Farrington, J.M. Brown, C.F.J. Barnard, E. Rowsell, Angew. Chem. Int. Ed. 41 (2002) 169;
(c) Y. Na, S. Park, S.B. Han, H. Han, S. Ko, S. Chang, J. Am. Chem. Soc. 126 (2004) 250.

[5] (a) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai, N. Miyaura, J. Am. Chem. Soc. 120 (1998) 5579;
(b) C.-J. Li, Y. Meng, J. Am. Chem. Soc. 122 (2000) 9538;
(c) M. Lautens, A. Roy, K. Fukuoka, K. Fagnou, B. Martin-Matute, J. Am. Chem. Soc. 123 (2001) 5358;
(d) A. Mori, Y. Danda, T. Fujii, K. Hirabayashi, K. Osakada, J. Am. Chem. Soc. 123 (2001) 10774;
(e) S. Oi, Y. Honma, Y. Inoue, Org. Lett. 4 (2002) 667;
(f) K. Ueura, T. Satoh, M. Miura, Org. Lett. 7 (2005) 2229.

[6] A. Furstner, A. Leitner, M. Méndez, H. Krause, J. Am. Chem. Soc. 124 (2002) 13856.

[7] (a) A.A. Kelkar, Tetrahedron Lett. 37 (1996) 8917;
(b) C. Mateo, C. Fernandez-Rivas, D.U.J. Cardenas, A.M. Echavarren, Organometallics 17 (1998) 3661;
(c) B.M. Bhanage, F.G. Zhao, M. Shirai, M. Arai, Tetrahedron Lett. 39 (1998) 9509;
(d) R.B. Bedford, S.L. Hazelwood, Organometallics 21 (2002) 4009;

(e) C.H. Oh, Y.M. Lim, C.H. You, Tetrahedron Lett. 43 (2002) 4645;
(f) J. Horniakova, H. Nakamura, R. Kawase, K. Komura, Y. Kubota, Y. Sugi, J. Mol. Catal. A: Chem. 233 (2005) 49.

[8] (a) S. Iyer, J. Organomet. Chem. 490 (1995) C27;
(b) T. Koike, X. Du, T. Sanada, Y. Danda, A. Mori, Angew. Chem. Int. Ed. 42 (2003) 89.

[9] (a) B.M. Choudary, S. Madhi, N.S. Chowdari, M.L. Kantam, B. Sreedhar, J. Am. Chem. Soc. 124 (2002) 14127;
(b) M.L. Kantam, S. Roy, M. Roy, B. Sreedhar, B.M. Choudary, Adv. Synth. Catal. 347 (2005) 2002;
(c) A. Cwik, Z. Hell, F. Figueras, Adv. Synth. Catal. 348 (2006) 523.

[10] (a) R.L. Augustine, S.T. O'Leary, J. Mol. Catal. A: Chem. 95 (1995) 277;
(b) C.R. LeBlond, A.T. Andrews, Y. Sun, J.R. Sowar, Org. Lett. 3 (2001) 1555;
(c) J. Le Bars, U. Specht, J.S. Bradley, D.G. Blackmond, Langmuir 15 (1999) 7621;
(d) E.B. Mobufu, J.H. Clark, D.J. Macquarrie, Green Chem. 3 (2001) 23.

[11] R. Akiyama, S. Kobayashi, J. Am. Chem. Soc. 125 (2003) 3412.

[12] N. Fujita, K. Motokura, K. Mori, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, Tetrahedron Lett. 47 (2006) 5083.

[13] B.F. Sels, D.E. De Vos, P.A. Jacobs, Catal. Rev. 43 (2001) 443.

[14] (a) B.M. Choudary, M. Roy, S. Roy, M.L. Kantam, J. Mol. Catal. A: Chem. 241 (2005) 215;
(b) B.M. Choudary, M. Roy, S. Roy, M.L. Kantam, K. Jyothi, B. Sreedhar, Adv. Synth. Catal. 347 (2005) 2009.

[15] G. Fagherazzi, A. Beneditti, S. Polizzi, A. Di Mario, F. Pinna, M. Signoretto, N. Pernicone, Catal. Lett. 32 (1995) 293.

[16] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomden, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp., 1992.

[17] L. Djakovitch, K. Koehler, J. Mol. Catal. A: Chem. 142 (1999) 275.

[18] B.H. Lipshutz, S. Tasler, W. Chrisman, B. Spliethoff, B. Tesche, J. Org. Chem. 68 (2003) 1177.

[19] B.M. Choudary, S. Madhi, M.L. Kantam, B. Sreedhar, Y. Iwasawa, J. Am. Chem. Soc. 126 (2004) 2292.