

A simple procedure for the polymer-supported N-heterocyclic carbene rhodium complex via Click chemistry: A recyclable catalyst for the addition of arylboronic acids to aldehydes

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1 Experimental

All chemicals were reagent grade and used as purchased. Chloromethylated polystyrene resin (1% divinylbenzene, 1.0 mmol/g of Cl, grain size range: 100-200 mesh) was obtained from GL Biochem (Shanghai) Ltd. (Shanghai, China). IR spectra were recorded in KBr disks with a SHIMADZU IRPrestige-21 FT-IR spectrometer. Elemental analyses were performed on a Vario ELIII recorder. Scanning electron microscopy (SEM) analyses were performed with JEOL JSM-6380LV instrument. ¹H NMR spectra were measured with a Bruker Avance III 500 analyzer. Rhodium content of the catalyst was measured by inductively coupled plasma (ICP) on Varian AA240FS analyzer. Thermogravimetric analysis was carried out under nitrogen with a flow rate of 30 ml/min using a TGA/SDTA851e instrument. Differential scanning calorimetry was performed with DSC823° analyzers under nitrogen with a flow rate of 30 ml/min.

1.1 Synthesis of 3-methyl-1-propargylimidazolium bromide

Methylimidazole (1.46 g, 17.8 mmol) was added dropwise to an 80% solution of propargyl bromide (2.33 mL, 21.4 mmol, 1.2 equiv, 80% in toluene) in toluene (5 ml) at 0 °C. The reaction was allowed to warm to room temperature, and toluene (15 ml) was added, and then the mixture was reacted overnight.

The solvent was removed *in vacuo* to yield a pale brown product.

^1H NMR (500MHz, D_2O): δ = 3.06-3.07 (m, 1H, $\text{C}\equiv\text{CH}$), 3.88 (s, 3H, CH_3), 5.06 (d, 2H, CH_2), 7.45 (m, 1H, ImH), 7.56 (m, 1H, ImH), 8.87 (m, 1H, ImH) ppm.

^{13}C NMR (75MHz, D_2O): δ = 36.17, 39.23, 74.76, 77.76, 122.13, 124.0, 136.23 ppm.

1.2 Preparation of azidomethyl polystyrene

Merrifield resin (1.0 g, 1.0 mmol/g) was reacted in a round-bottom flask with NaN_3 (5 eq) in DMSO (10 ml) at 70 °C for 48 h. After being cooled to room temperature, the suspension was filtrated and the resin was washed alternatingly with MeOH (5×6 ml) and CH_2Cl_2 (5×6 ml) to give azidomethyl polystyrene **2**. Found (%): C, 82.41; H, 7.328; N, 3.319.

1.3 Procedure for the preparation of imidazolium-loaded polymeric support

Addition of azidomethyl polystyrene (0.5 g), 3-methyl-1-propargylimidazolium bromide (0.40 g, 2.0 mmol), CuI (0.017g, 0.09 mmol), DMSO/THF (1:1) (10ml) and DIPEA (2 ml) was followed by agitation at 35 °C. Reaction was stopped when the IR-signal of the azido group had completely disappeared. The resin was collected by filtration and washed alternatingly with pyridine (5×6 ml), MeOH (5×6 ml) and CH_2Cl_2 (5×6 ml). Drying of the residue in vacuum gave **3**. Found (%): C, 77.65; H, 6.962; N, 4.912.

1.4 Preparation of the polymer-supported NHC-Rh complex

$[\text{Rh}(\text{COD})\text{Cl}]_2$ (17.26 mg 0.035 mmol) and KO^tBu (23.5 mg, 0.21 mmol) were added to a Schlenk tube. The vessel was evacuated and flushed with N_2 three times. Anhydrous THF (20 ml) was syringed in and stirred at room temperature for 2 h. Then, imidazolium-loaded polymeric support **3** (100 mg) was added. The mixture was stirred at room temperature for another 24 h. After filtration, the

polymeric support was washed vigorously with THF (10 ml×5) and CH₂Cl₂ (10 ml×5) to give **4**. The content of rhodium was 2.02 % as determined by ICP.

1.5 Rhodium-catalyzed addition of arylboronic acids to aldehydes

Aldehyde (0.5 mmol), arylboronic acid (1 mmol), KO^tBu (0.056 g, 0.5 mmol), catalyst (Rh 2.0 mol %) and 1, 4-dioxane (3 ml) were introduced into a single round-bottom flask and then water (0.5 ml) was added. The resulting mixture was heated at 80 °C for a certain time. After cooling to room temperature, the reaction mixture was filtered, the catalyst was washed with ether (10 ml×3), and then, the filtrate and the washing solution were combined. The solvents were evaporated and the residue was purified by flash chromatography to give the corresponding products. All the products were known compounds, and were identified by comparison with their physical and spectroscopic data with those of authentic samples. Select data for benzhydrol (compound 1).

¹H NMR (500MHz, CDCl₃): δ = 2.30-2.31 (d, 1H, OH), 5.87 (s, 1H, CH), 7.28-7.31 (m, 2H), 7.35-7.38 (m, 4H), 7.40-7.42 (m, 4H) ppm.

¹³C NMR (75MHz, CDCl₃): δ = 76.28, 77.04, 77.29, 126.56, 127.58, 128.51, 143.82 ppm.

1.6 Recycling of polymer-supported NHC-Rh complex

The addition reaction of *p*-methoxybenzeneboronic acid to *p*-chlorobenzaldehyde was chosen as a model reaction. The mixture was stirred for 6 h at 80 °C. After cooling to room-temperature, the mixture was filtered. The solid catalyst was filtered off, washed with ether, dried under vacuum, and then reused for the next cycle.

2 Infrared Spectra

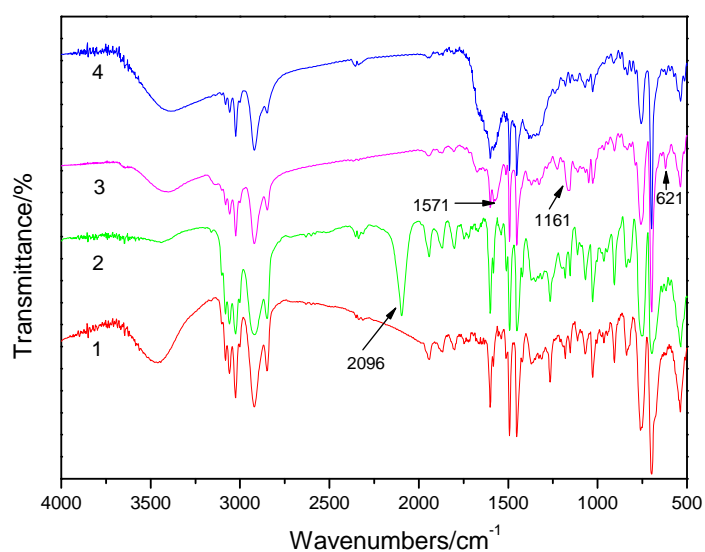


Fig. 1 IR spectra of Merrifield resin **1**, azidomethyl polystyrene **2**, imidazolium-loaded polymeric support **3**, and polymer-supported NHC-Rh complex **4**.

3 TGA and DSC curves

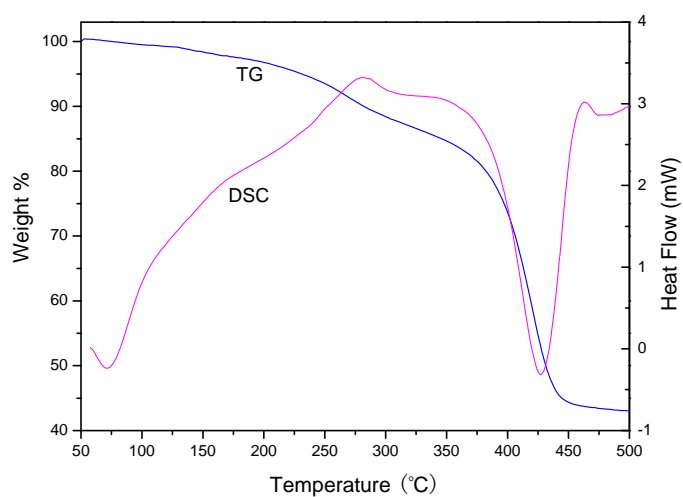


Fig. 2 TGA and DSC curves of the polymer-supported NHC-Rh complex **4**.

4 Recycling experiment

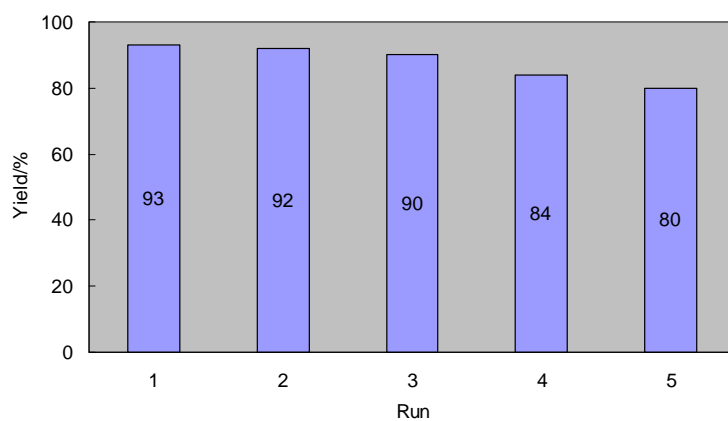
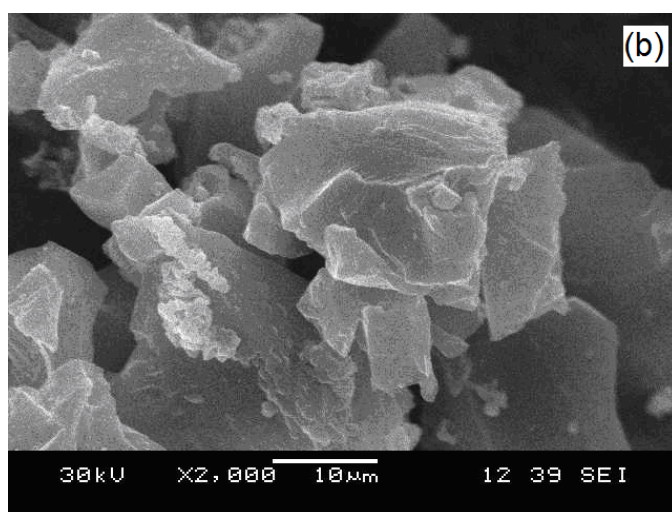
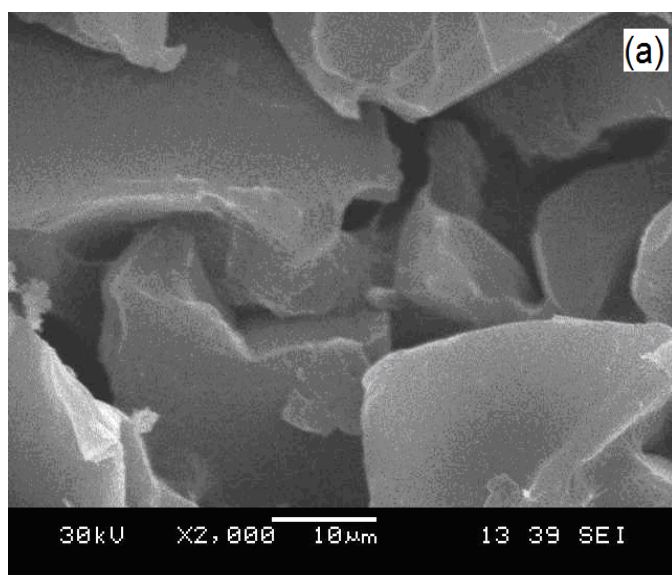


Fig. 3 Recycling experiment.

5 SEM images



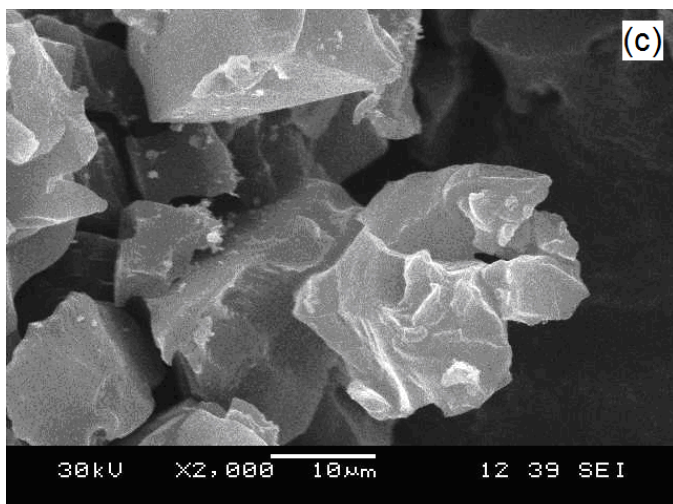


Fig. 4 Scanning electron micrographs (SEM) images of imidazolium-loaded polymeric support **3** (a), polymer-supported NHC-Rh complex **4** (b) and four-times reused catalyst (c).

Notes and references

- [1] (a) C. H. Xing, T. P. Liu, J. R. Zheng, J. Ng, M. Esposito and Q. S. Hu, *Tetrahedron. Lett.*, 2009, 50, 4953; (b) T. Yamamoto, M. Iizuka, H. Takenaka, T. Ohta and Y. Ito, *J. Organomet. Chem.*, 2009, 694, 1325; (c) C. Yan, X. M. Zeng, W. F. Zhang and M. M. Luo, *J. Organomet. Chem.*, 2006, 691, 3391.