

Supporting Information

## Mesoporous Silica-Supported Rhodium Complexes Alongside Organic Functional Groups for Catalysing 1,4-Addition Reaction of Arylboronic Acid in Water

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### Contents

NMR measurements	S2
XAFS data acquisition	S2
FT-IR measurements	S2
Materials	S2
Preparation of Catalyst	S3
Elemental Analysis	S4
Curve-Fitting Analysis	S5
Rh K-edge XANES and FT-EXAFS	S5
Catalytic reaction procedures	S7
Hammett plot	S8
Water contact angle analysis	S9
Time-course analysis	S10
References	S10

## Materials

Unless otherwise noted, all other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and Aldrich Inc. and used without further purification. In the catalytic reactions, 1,3,5-triisopropylbenzene was used as an internal standard.

## NMR measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  with an AVANCE 400 spectrometer (Bruker) operating at 400.0, 100.6, and 161.9 MHz, respectively. An AVANCE 500 spectrometer (Bruker) was also used, operating at 500.1 and 125.8 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively.

## XAFS data acquisition

XAFS was measured in transmission mode at the NW10 of PF-AR (proposal No. 2020G033, KEK-IMSS-PF, Tsukuba, Japan) at room temperature. The electron storage ring was operated at 6.5 GeV and 60 mA. Synchrotron radiation from the storage ring was monochromatized with Si (311) channel-cut crystals. Ionization chambers filled with Ar gas and Kr were used as detectors for monitoring incident ( $I_0$ ) and transmitted X-rays ( $I$ ), respectively. The angle of the monochromator was calibrated using Rh foil, with the inflection point at the edge set to 23220.0 eV.

XAFS spectra were analyzed using Athena<sup>[1]</sup> and REX2000 (for curve-fitting analysis, Rigaku Co. Japan). The empirical backscattering amplitude and phase shift of Rh-C/O were extracted from the  $[\text{Rh}(\text{OH})\text{cod}]_2$  complex.

A goodness of curve fit was estimated using the following equation.

$$R_{factor} = \sqrt{\frac{\sum_i [k^n (\chi_i^{obs}(k) - \chi_i^{fit}(k))]^2}{\sum_i [k^n \chi_i^{obs}(k)]^2}}$$

Where,  $\chi_i^{obs}(k)$  and  $\chi_i^{fit}(k)$  are the experimental data and theoretical curve-fitted data, respectively.

## FT-IR measurements

FT-IR spectra were recorded from 4000–400  $\text{cm}^{-1}$ , using a Shimadzu IR Tracer-100 spectrometer with TGS detector. Each spectrum was the average of 45 scans using a spectral resolution of 2  $\text{cm}^{-1}$ . FT-IR pellets were prepared as follows: *ca.*  $2.0 \times 10^{-3}$  g of sample and 0.4 g of KBr were mixed. Then, the mixture was pressed. The pellet diameter

was 4 mm.

### Water adsorption measurement

Water adsorption was measured using Micromeritics 3Flex at 25 °C. All the samples were evacuated at 110 °C for 12 h prior to the measurements.

### Preparation of Catalyst

#### *Preparation of Mesoporous Silica (MS)*

MS(C8, C10, C12, C18) supports with different pore diameters were prepared by modified reported method using primary amine with C8 to C18 alkyl chain as a template molecule.<sup>[2]</sup> Typical preparation procedure is as follows. Dodecylamine (C12, 53.8 mmol) was dissolved in deionized water (100 g) and ethanol (82 g) solvent at room temperature. Then, tetraethoxysilane (TEOS, 200 mmol) was added to the solution and vigorously stirred for 30 min at room temperature. The reaction mixture was aged at room temperature for 30 h. The obtained solid was filtrated, washed with deionized water, and air-dried. The template amine was removed by mixing in 200 mL of ethanol solution containing 0.1N HCl for 2 h at 60 °C, then the slurry was filtrated. This extraction procedure was reported three times, and the obtained solid was finally mixed in pure ethanol (200 mL) for 2 h at 60 °C, filtrated, and dried at 80 °C for 12 h, generating MS(C12). SBA-15 was also prepared according to the previously reported methods.<sup>[3]</sup>

The physicochemical properties of prepared MS are summarized in Table S1.

**Table S1.** Physicochemical properties of silica supports

Silica Support	Template Amine Carbon Number	Surface area [m <sup>2</sup> g <sup>-1</sup> ] <sup>a</sup>	Pore size [Å]	Pore volume [ml/g] <sup>b</sup>
MS(C8)	C8	1865	16	1.46
MS(C10)	C10	1707	19	0.67
MS(C12)	C12	1175	23	1.01
MS(C18)	C18	876	31	1.01
SBA-15	-	930	72	1.05
Nonporous Silica (Aerosil300)	-	300±30	-	-

<sup>a</sup> Determined by N<sub>2</sub> adsorption-desorption measurement.

<sup>b</sup> Determined by BJH method.

### Preparation of MS/diamine/Rh/octyl

MS was pretreated at 120 °C for 3 h under vacuum. Typical procedure using MS as a support is as follows: MS (0.27 g) was placed in a round-bottom flask and treated with 12 mL of a toluene solution containing 3-(2-aminoethylamino)propyltrimethoxysilane (0.10 mmol,  $2.3 \times 10^{-2}$  g) and trimethoxyoctylsilane (1.5 mmol, 0.35 g) at 40 °C for 1 h. Toluene was removed by vacuum evaporation, affording MS/diamine/octyl. Then, the MS/diamine/octyl was treated with 5 mL of a dioxane solution containing [Rh(cod)OH]<sub>2</sub> ( $5.0 \times 10^{-2}$  mmol, Rh: 0.10 mmol) at 90 °C for 4 h. The resulting mixture was evaporated and dried under vacuum, affording MS/diamine/Rh/octyl.

The elemental analysis data for the prepared samples are summarized in Table 1 and Table S2.

**Table S2.** Elemental analysis results of MS-supported Rh catalysts with different organic group.

catalyst	Pore size (nm)	Element (mmol / g) <sup>a</sup>		
		C	N	Rh
MS(C10)/diamine/Rh/octyl	1.9	25.6	0.5	0.153
MS(C12)/diamine/Rh/octyl	2.3	23.3	0.4	0.157
MS(C18)/diamine/Rh/octyl	3.1	23.4	0.4	0.148
SBA-15/diamine/Rh/octyl	9.6	21.6	0.5	0.163

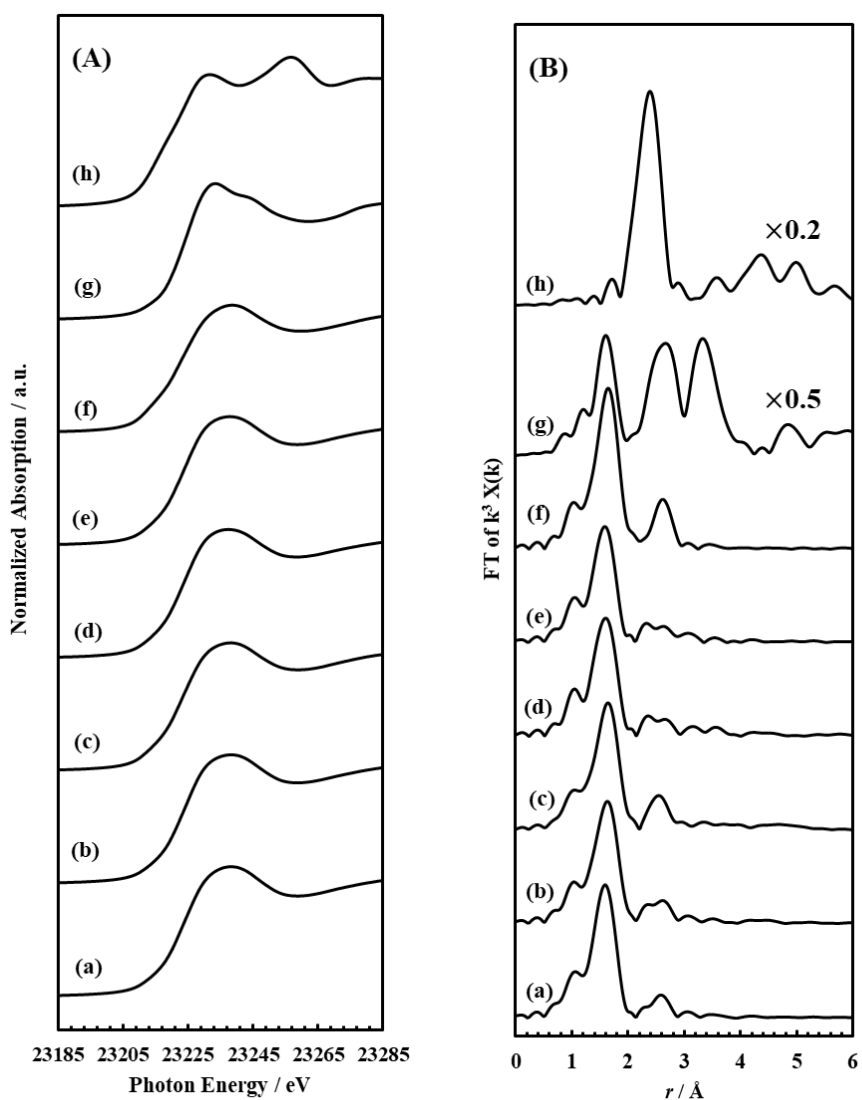
<sup>a</sup> The amount of C and N were measured by elemental analysis and Rh was determined by inductively coupled plasma-atomic emission spectroscopy. (ICP-AES).

**Table S3.** Curve-fitting analysis for the prepared MS-supported Rh catalysts<sup>a</sup>

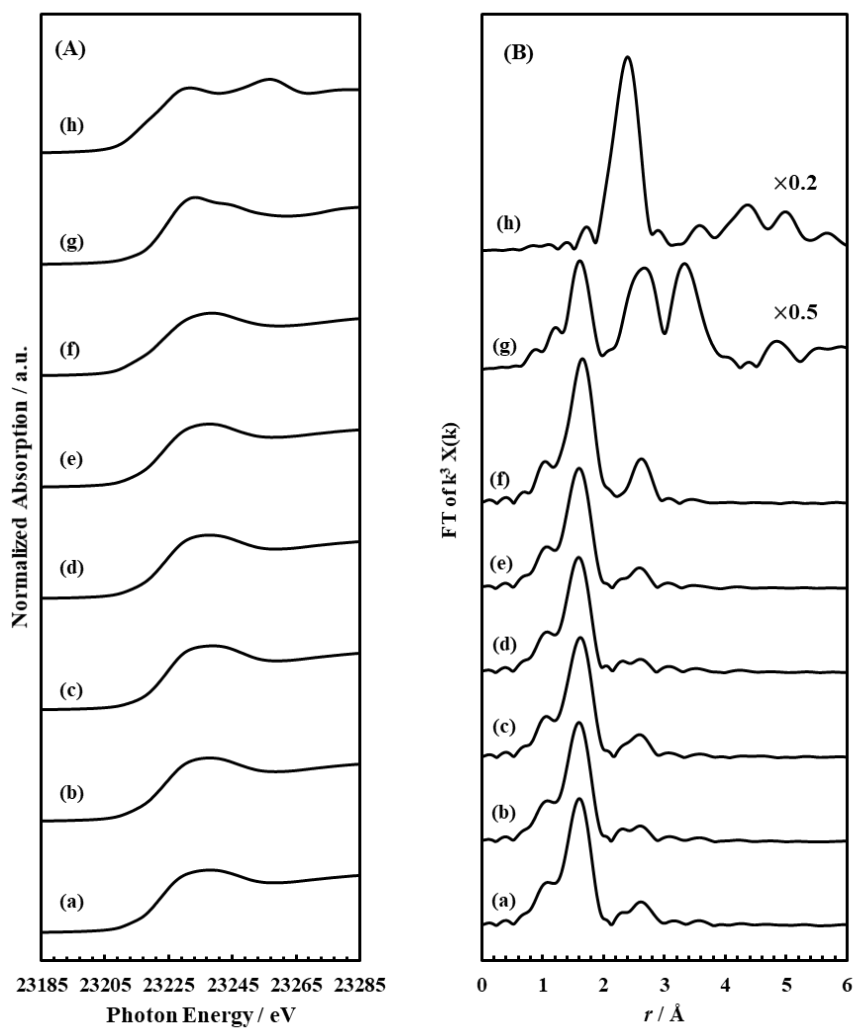
Sample	<i>N</i> <sup>b</sup>	<i>R</i> (Å) <sup>c</sup>	$\Delta\sigma^2$	$\Delta E_0$ <sup>e</sup>	Rf <sup>f</sup>
			(Å $\times 10^{-3}$ ) <sup>d</sup>	(eV)	(%)
MS(C8)/diamine/Rh/octyl (1:1)	5.9 ( $\pm 1.3$ )	2.08 ( $\pm 0.01$ )	2.64 ( $\pm 0.63$ )	-2.6 ( $\pm 2.8$ )	0.856
MS(C8)/diamine/Rh/octyl (1:5)	6.4 ( $\pm 1.4$ )	2.09 ( $\pm 0.01$ )	2.64 ( $\pm 0.58$ )	-1.6 ( $\pm 2.8$ )	0.875
MS(C8)/diamine/Rh/octyl (1:10)	6.9 ( $\pm 1.4$ )	2.10 ( $\pm 0.01$ )	4.68 ( $\pm 0.48$ )	-1.2 ( $\pm 2.7$ )	1.650

<sup>a</sup> Fourier transform and Fourier-filtering regions were limited, for which  $\Delta k=3.0-11 \text{ \AA}^{-1}$  and  $\Delta r=1.2-2.2 \text{ \AA}$ , respectively. <sup>b</sup> Coordination number. <sup>c</sup> Bond distance between absorber and backscatter atoms. <sup>d</sup> The Debye-Waller (DW) factor, which is relative to the

DW factor of the reference. <sup>e</sup> Inner potential correction accounting for the difference in the inner potentials of the sample and reference. <sup>f</sup> Goodness of curve fit.



**Figure S1.** (A) Rh K-edge XANES and (B)  $k^3$ -weighted FT-EXAFS spectra of (a) MS(C8)/diamine/Rh/octyl (1:15), (b) MS(C8)/diamine/Rh/octyl (1:10), (c) MS(C8)/diamine/Rh/octyl (1:5), (d) MS(C8)/diamine/Rh/octyl (1:1), (e) MS(C8)/diamine/Rh, (f)  $[Rh(cod)OH]_2$ , (g)  $Rh_2O_3$ , and (h) Rh foil

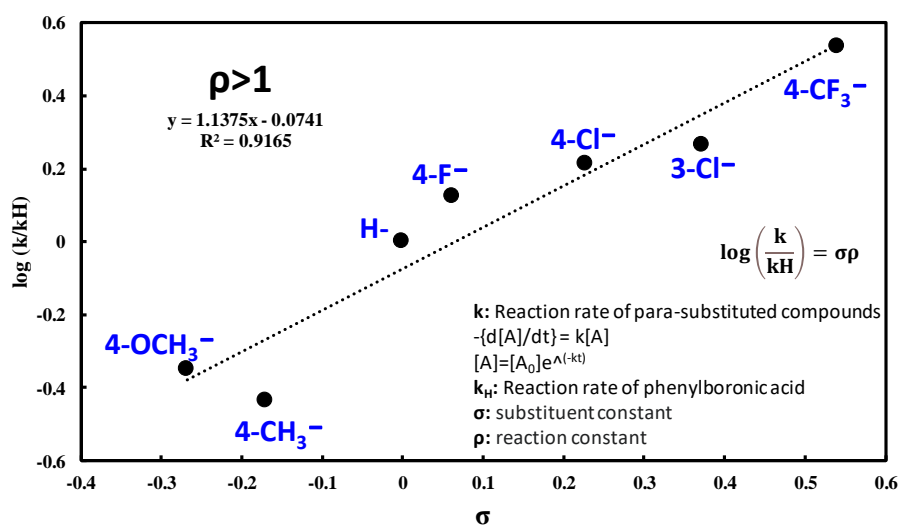
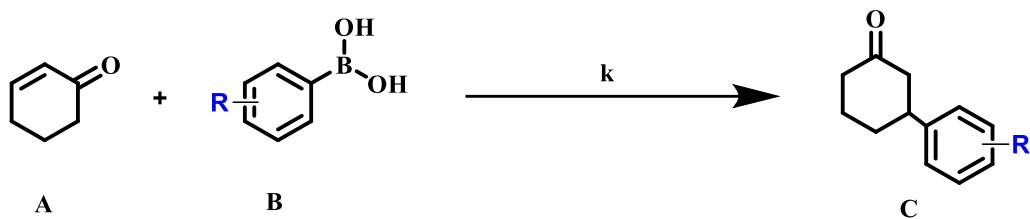


**Figure S2.** (A) Rh K-edge XANES and (B)  $k^3$ -weighted FT-EXAFS spectra of (a) SBA-15/diamine/Rh/octyl, (b) MS(C18)/diamine/Rh/octyl (c) MS(C12)/diamine/Rh/octyl, (d) MS(C10)/diamine/Rh/octyl, (e) MS(C8)/diamine/Rh/octyl, (f)  $[\text{Rh}(\text{cod})\text{OH}]_2$ , (g)  $\text{Rh}_2\text{O}_3$ , and (h) Rh foil

## **Catalytic reaction procedures**

### ***1,4-Addition reaction using silica-supported Rh catalyst***

The silica-supported Rh catalyst (1.5  $\mu\text{mol}$ ),  $\text{H}_2\text{O}$  (2.0 mL), cyclohexenone (1.0 mmol), and phenylboronic acid (1.5 mmol) were placed in a Pyrex glass reactor. The resulting mixture was stirred vigorously for 1 h at 60  $^\circ\text{C}$  under Ar. After the reaction, the organic phase was extracted by using  $\text{CHCl}_3$ . The water phase was washed by saturated aqueous NaCl solution. The product was confirmed by GC-MS and NMR. Yield and conversion were determined by  $^1\text{H}$  NMR using a  $\text{CDCl}_3$  solution of the reaction mixture. The  $^1\text{H}$  NMR chemical shift of the products (Table 5 and 6) corresponded with the literature values.[4]

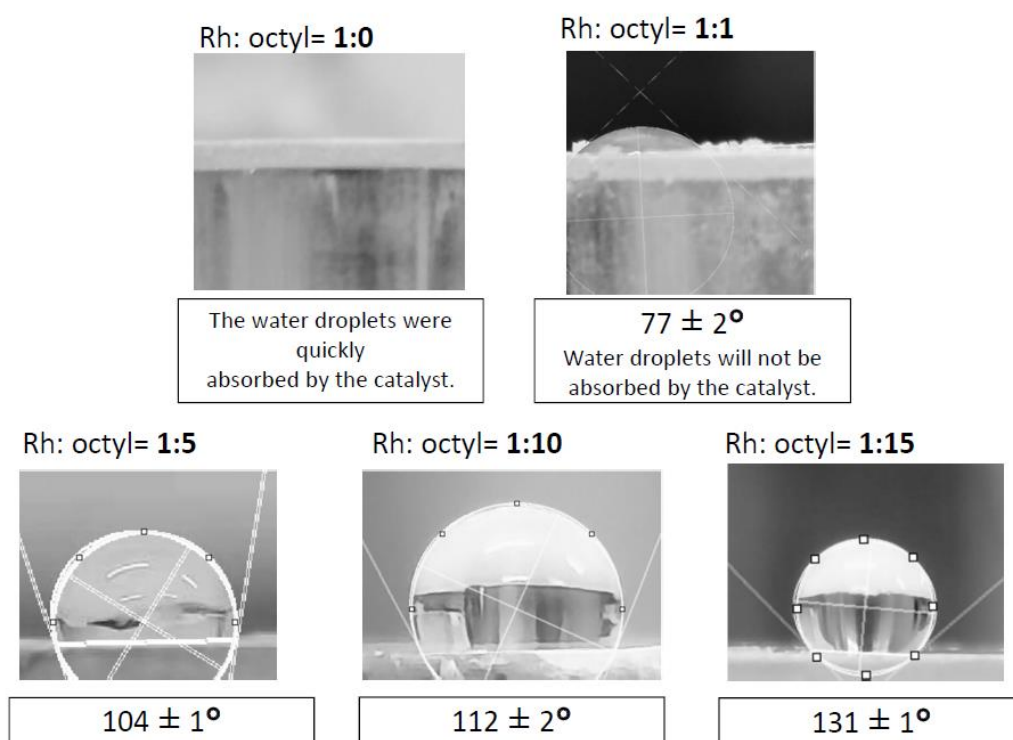


**Figure S3.** Hammett plot for the 1,4-addition of arylboronic acid catalyzed by MS(C8)/diamine/Rh/octyl

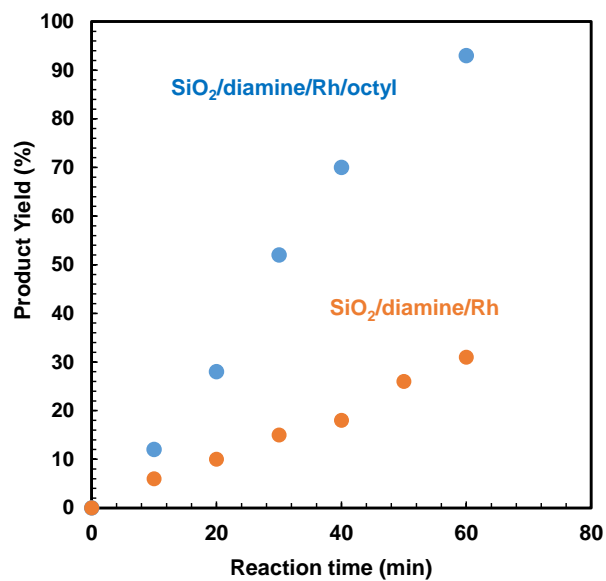


### Water contact angle analysis

Samples were prepared from powdered catalysts by tableting press at 20 MPa. After preparation of tablets with different ratio of Rh and octyl group (1:0, 1:1, 1:5, 1:10, 1:15), using 25 $\mu$ L syringe to slowly drop water (5~7  $\mu$ L) on the sample at the distance of 1~1.5 cm from the sample, and take a picture within 10 s after contact of water and sample. The water contact angle of the sample is calculated by Image-J software, and the results are summarized in the table.



**Figure S4.** Photos of water droplet on SiO<sub>2</sub>/diamine/Rh/octyl catalyst



**Fig. S5** Time-course analysis of 1,4-addition reaction in water. Reaction conditions: cyclohexenone (1.0 mmol), phenylboronic acid (1.5 mmol), Rh catalyst (Rh: 1.5  $\mu$ mol), solvent (2 mL: H<sub>2</sub>O), 60 °C.

### References

- [1] (a) B. Ravel, M. Newville, *J. Synchrotron Rad.* **2005**, *12*, 537-541. (b) M. Newville, *J. Synchrotron Rad.* **2001**, *8*, 322-324.
- [2] P. T. Tanev, T. J. Pinnavaia, *Science* **1995**, *267*, 865-867.
- [3] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science* **1998**, *279*, 548-552.