Construction of an organoruthenium complex $(-[biphRuCp]PF_{6}-)$ within a biphenylene-bridged inorganic-organic hybrid mesoporous material, and its catalytic activity in the selective hydrosilylation of 1-hexyne

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Abstract An organoruthenium complex (–[biphRuCp]PF₆–; biph = –(C₆H₄)₂–, Cp = C₅H₅), constructed within a biphenylene-bridged inorganic–organic hybrid mesoporous material (HMM–biph) by use of a simple ligand-exchange reaction, has been used as a heterogeneous catalyst. UV–visible and X-ray absorption fine structure (XAFS) studies furnished evidence that the structure of the complex is closely similar to that of [(C₆H₆)RuCp]PF₆, suggesting that the biphenylene moiety within HMM–biph directly coordinates the metal center of the organoruthenium complex. The –[biphRuCp]PF₆– complex constructed within the HMM–biph (HMM–biphRuCp) catalyzes hydrosilylation of 1-hexyne with triethylsilane in a solid–gas heterogeneous system and gives α-vinylsilane as a main product. Moreover, HMM–biphRuCp has higher catalytic activity than the –[phRuCp]PF₆– (ph = –C₆H₄–) complex constructed within phenylene-bridged HMM (HMM–phRuCp). The high catalytic performance of HMM–biphRuCp can be attributed to the high loading of the HMM–biph with the Ru complex, because of the electron-donating ability of the biphenylene moieties.

Keywords Inorganic–organic hybrid mesoporous materials \cdot Periodic mesoporous organosilicas \cdot –[biphRuCp]PF₆– \cdot Hydrosilylation \cdot Biphenylene moieties

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Introduction

Inorganic–organic hybrid mesoporous materials (HMMs), also known as periodic mesoporous organosilicas, have attracted attention as adsorbents, sensors, and light-harvesting or emitting optical devices [1–13]. A variety of organic moieties ($-C_2H_4-$, $-C_6H_4-$, $-(C_6H_4)_2-$, etc.) covalently embedded within HMM structures are readily available for post-synthetic introduction of unique functional sites [11–19]. For example, Inagaki and coworkers [16–19] developed solid acid and base catalysts by introduction of sulfuric acid and amino groups, respectively, into the organic moieties of HMMs. Moreover, the organic moieties, particularly phenylene moieties, of HMMs can be used as "framework ligands" that directly coordinate the metal centers of organometallic complexes [20, 21].

In our previous work, an organoruthenium complex (–[phRuCp]PF₆–; ph = $-C_6H_4$ –, Cp = cyclopentadienyl) was successfully constructed within phenylene-bridged HMM (HMM–ph) by use of a simple ligand-exchange reaction between [(CH₃CN)₃RuCp]PF₆ and the phenylene moiety of HMM–ph [22]. In this complex, the metal center directly coordinated a phenylene moiety of HMM–ph that behaved as a "framework ligand", enabling high dispersion of the complex on the HMM–ph [18, 19]. As a consequence, the constructed organoruthenium complex had excellent catalytic activity in the selective hydrosilylation of 1-hexyne. Because the chemical properties of organic moieties within HMMs that can behave as framework ligands are expected to affect the catalytic performance of the constructed organometallic complexes, there is much interest in the effect of the type of framework ligand on the catalytic performance of such organoruthenium complexes.

In the work discussed in this paper we focused on biphenylene-bridged HMM (HMM– biph; biph = $-(C_6H_4)_2-)$ and attempted to construct an organoruthenium complex (-[biphRuCp]PF₆-) on the biphenylene moiety by means of a simple ligand-exchange reaction (Scheme 1). The thus-synthesized HMM–biphRuCp was characterized in detail by X-ray diffraction (XRD), UV–visible, and X-ray absorption fine structure (XAFS) spectroscopy. To investigate the effect of the type of framework ligand on catalytic performance, HMM–biphRuCp and HMM–phRuCp were used as catalysts for selective hydrosilylation of 1-hexyne with triethylsilane in a solid–gas heterogeneous system.

Experimental

Synthesis of HMM-biphRuCp

HMM–biph was prepared by the procedure reported by Inagaki et al. [9, 11, 23]. 4,4'-bis(triethoxysilyl)biphenyl ((C₂H₅O)₃Si–(C₆H₄)₂–Si(OC₂H₅)₃) (2.5 mmol) was



Scheme 1 Ligand-exchange reaction for construction of -[biphRuCp]PF₆- complex within HMM-biph

added into a mixture of octadecyltrimethylammonium chloride (C₁₈TMACl) surfactant, 30.4 mmol 6 M sodium hydroxide, and 3.3 mmol distilled water, with vigorous stirring, at ambient temperature. The suspension was stirred for another 20 h and then heated at ca. 368 K for 22 h under static conditions. The resulting precipitate was recovered by filtration and washed with deionized water. Finally, the surfactant was removed from the powder by extraction with a mixture of 150 mL ethanol and 3.1 g 2 M aqueous HCl solution at ambient temperature for 8 h. Subsequently, the -[biphRuCp]PF6- complex was constructed within the HMMbiph by means of a ligand-exchange reaction, using [(CH₃CN)₃RuCp]PF₆ in CHCl₃. Typically, 58 mg [(CH₃CN)₃RuCp]PF₆, which was synthesized in two steps from readily available bis-benzeneruthenium(II) chloride [24, 25], was dissolved in 20 mL dry-CHCl₃. HMM-biph (400 mg) pretreated at 473 K for 2 h under vacuum was then added to this solution. After heating under reflux for 24 h under an Ar atmosphere, a white powder was recovered by filtration, repeatedly washed with CHCl₃, and then dried under vacuum, yielding HMM-biphRuCp. For comparison purposes, HMM-phRuCp was also prepared by the same method except for using 1,4-bis(triethoxysilyl)benzene ((C_2H_5O)₃Si- C_6H_4 -Si(OC_2H_5)₃).

Characterization of HMM-biphRuCp

X-ray diffraction (XRD) patterns were collected by means of a Shimadzu XRD-6100 using Cu K α radiation ($\lambda = 1.5406$ Å). Diffuse reflectance UV–visible spectra were obtained by use of a Shimadzu UV-2200A spectrophotometer. Ru K-edge X-ray absorption fine structure (XAFS) spectra were also recorded, at the BL-01B1 facility of SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI). All spectra were recorded in fluorescence mode with an Si(111) two-crystal monochromator at 298 K. The extended X-ray absorption fine structure (EXAFS) data were examined by use of Rigaku REX2000 software. To obtain the radial structure function, Fourier transformations of k³-weighted EXAFS oscillations in the range of 3–12 Å⁻¹ were performed.

Selective hydrosilylation of 1-hexyne with triethylsilane

Selective hydrosilylation of 1-hexyne with triethylsilane was performed in a closed solid–gas heterogeneous system at 523 K for 15 h (cell volume 80 mL). Typically, 30 mg catalyst was placed in the reaction cell and pre-treated at 473 K for 3 h in vacuo. 1-Hexyne and triethylsilane (527 μ mol of each) were then added to the reaction cell by use of a vacuum line. Reactions were conducted at 523 K for 15 h. The resulting substances were collected by condensation in liquid N₂, diluted with 2.0 mL CHCl₃, then analyzed by gas chromatography with a Shimadzu GC-14B equipped with a flame ionization detector and an InertCap 1 capillary column. The turnover number (TON) was defined as follows:

TON = [moles of reaction products]/[mole of Ru in the catalyst].

Results and discussion

Figure 1 shows XRD patterns of the synthesized HMM-ph and HMM-biph. In both XRD patterns, a sharp diffraction peak was observed at $2\theta = 2.0^{\circ}$ (d = 44 Å), corresponding to the (100) reflection of the hexagonal structure of mesopores [9, 23]. The pattern of HMM-ph also contained three other peaks in the range $2\theta = 10-40^{\circ}$ (d = 7.6, 3.8, and 2.5 Å) derived from the periodicity of the phenylene and silica layers (i.e., O_{1.5}-Si-C₆H₄-Si-O_{1.5} units) with a spacing of 7.6 Å in the pore wall [11]. The pattern of HMM–biph, on the other hand, contained five peaks in the range $2\theta = 6-40^{\circ}$ (d = 11.6, 5.9, 3.9, 2.9, and 2.4 Å) derived from the periodicity of biphenylene and silica layers (i.e., O₁₅-Si-C₆H₄-C₆H₄-Si-O₁₅ units) with a spacing of 11.6 Å in the pore wall [9, 23]. This different periodicity is because of the different lengths of the organic moieties, that is, longer biphenylene moieties than phenylene moieties lead to the increase in the interval of the periodicity. These results reveal that phenylene or biphenylene units were successfully embedded in the periodic mesoporous structures. Moreover, the diffraction patterns of both HMMs were almost maintained even after ligandexchange reactions. In addition, the BET surface area of HMM-biphRuCp $(878 \text{ m}^2 \text{ g}^{-1})$ was larger than that of HMM–phRuCp (789 m² g⁻¹).

Subsequently, UV–visible measurements were performed to verify the construction of the –[biphRuCp]PF₆– complex within the HMM–biph framework [22]. Figure 2 shows diffuse reflectance UV–visible spectra of HMM–biph before and after the ligand-exchange reaction. The UV–visible absorption spectra of $[(C_6H_6)RuCp]PF_6$ and $[(CH_3CN)_3RuCp]PF_6$ complexes dissolved in CH₃CN, as reference compounds, are also shown in the inset of Fig. 2. The spectrum of $[(C_4_3CN)_3RuCp]PF_6$ in CH₃CN contained an absorption band at 370 nm with a tail extending into the visible region, whereas that of $[(C_6H_6)RuCp]PF_6$ in CH₃CN contained to a *d*–*d* transition in the UV-wavelength region only. It was found that the synthesized HMM–biph furnished no absorption bands above 330 nm, although a new absorption band was observed in the range 300–400 nm after the ligand-exchange reaction. The position of the new band was identical with that of *d*–*d* transition band of the $[(C_6H_6)RuCp]PF_6$ complex $(\lambda = ~325 \text{ nm})$, indicating that a similar complex to $[(C_6H_6)RuCp]PF_6$ was







Fig. 2 Diffuse reflectance UV-visible spectra of HMM-biph (*dotted line*) and HMM-biphRuCp (*solid line*). *Inset* shows UV-visible absorption spectra of a $[(C_6H_6)RuCp]PF_6$ and b $[(CH_3CN)_3RuCp]PF_6$ in CH₃CN

formed by the ligand-exchange reaction between $[(CH_3CN)_3RuCp]PF_6$ and the biphenylene moiety of HMM–biph [26, 27]. Similarly, the spectrum of HMM–phRuCp contained an absorption band at approximately 325 nm, indicative of construction of the –[phRuCp]PF_6– complex within HMM–ph [22]. These findings revealed that this ligand-exchange reaction is an effective method for construction of –[biphRuCp]PF_6– and –[phRuCp]PF_6– complexes within HMMs containing arene moieties.

To gain insight into the local structures of the $-[phRuCp]PF_6-$ and $-[biphRuCp]PF_6-$ complexes constructed within HMM–phRuCp and HMM– biphRuCp, respectively, Ru K-edge XAFS measurements were performed. Figure 3 shows the X-ray absorption near-edge structure (XANES) and Fourier transform of EXAFS (FT-EXAFS) spectra of HMM–phRuCp and HMM–biphRuCp, with those of $[(C_6H_6)RuCp]PF_6$ and $[(CH_3CN)_3RuCp]PF_6$. The edge positions and spectral shapes, particularly in the region of the white line, in the XANES spectra of HMM– phRuCp and HMM–biphRuCp corresponded well to those in the $[(C_6H_6)RuCp]PF_6$ spectrum. This result strongly suggests that $-[phRuCp]PF_6-$ and $-[biphRuCp]PF_6$ complexes were constructed within the respective frameworks of HMM–ph and HMM–biph by direct coordination of ruthenium centers with the phenylene moieties in their frameworks.

All the the FT-EXAFS spectra contained an intense, sharp peak at ca. 1.7 Å (without phase-shift correction) assigned to Ru–C or Ru–N bonds; curve-fitting analysis of EXAFS spectra revealed the different coordination environments, however (Table 1). For HMM–phRuCp and HMM–biphRuCp this peak could be assigned to bonds between the ruthenium atom and the neighboring carbon atoms of the phenylene (C_{ph}) and cyclopentadienyl (C_{Cp}) ligands. The bond lengths were determined to be



Fig. 3 Ru K-edge **a** XANES and **b** Fourier transform of EXAFS spectra of *a* HMM–phRuCp, *b* HMM–biphRuCp, *c* $[(C_6H_6)RuCp]PF_6$, and *d* $[(CH_3CN)_3RuCp]PF_6$

a Bond distance b Coordination number	Catalyst	Shell	$R^{\rm a}$ (Å)	CN ^b
	HMM–phRuCp	Ru–C _{ph}	2.23	6.2
		Ru-C _{Cp}	2.17	5.2
	HMM-biphRuCp	Ru-C _{ph}	2.23	6.1
		Ru-C _{Cp}	2.18	5.1
	[(C ₆ H ₆)RuCp]PF ₆	Ru-C _{ph}	2.24	6.0
		Ru-C _{Cp}	2.18	5.1
	[(CH ₃ CN) ₃ RuCp]PF ₆	Ru–N	2.10	3.4
		Ru–C _{Cp}	2.16	5.5

Ru–C_{ph} = 2.23 Å (coordination number (CN) = 6.2) and Ru–C_{Cp} = 2.17 Å (CN = 5.2) for HMM–phRuCp, and Ru–C_{Cp} = 2.23 Å (CN = 6.1) and Ru–C_{Cp} = 2.18 Å (CN = 5.1) for HMM–biphRuCp. These values were in good agreement with the bond lengths of [(C₆H₆)RuCp]PF₆ (Ru–C_{ph} = 2.24 Å (CN = 6.0), Ru–C_{Cp} = 2.18 Å (CN = 5.1)). The curve-fitting analysis for [(CH₃CN)₃RuCp]PF₆ revealed the existence of Ru–N bonding (2.1 Å, CN = 3.4) and Ru–C_{Cp} bonding (2.16 Å, CN = 5.5), which was different from that in HMM–phRuCp and HMM–biphRuCp. These results provide evidence that –[phRuCp]PF₆– and –[biphRuCp]PF₆– complexes are constructed within the respective HMM–ph and HMM–biph frameworks by the ligand-exchange reactions with [(CH₃CN)₃RuCp]PF₆. Furthermore, no other peaks were observed in the ranges of 2.0–3.0 Å, assigned to Ru–Ru bond, indicating that aggregated species and dimeric ruthenium complexes were not present in HMM–phRuCp and HMM–biphRuCp [28, 29].

The XANES data also provide information about the loading of the Ru complexes. On the basis of the peak intensity of the white line, the amounts of the -[phRuCp]PF₆- and -[biphRuCp]PF₆- complexes loaded were determined to be 1.1 and 1.7 % (w/w) Ru metal, respectively. Furthermore, from calculation based on these values, conversion of the organic moieties within the frameworks to the corresponding complexes was estimated to be 5.3 % for HMM-phRuCp and 9.5 % for HMM-biphRuCp. This difference is because the electron-donating ability of biphenylene moieties is greater than that of phenylene moieties, because arene ligands bearing electron-donating substituents can stabilize CpRu complexes [30]. Following successful formation of -[phRuCp]PF₆- and -[biphRuCp]PF₆- complexes within the HMMs, selective hydrosilylation of 1-hexyne with triethylsilane was performed in a solid-gas heterogeneous system at 523 K (Scheme 2). It is apparent from Fig. 4 that [(C₆H₆)RuCp]PF₆, HMM–phRuCp, and HMM–biphRuCp had catalytic activity in this hydrosilylation reaction, and gave α -vinylsilane with high selectivity. In contrast, HMM-ph and HMM-biph had almost no catalytic activity under the same reaction conditions. These results clearly indicate that -[phRuCp]PF₆- and -[biphRuCp]PF₆- complexes act as catalysts for the selective hydrosilylation reaction. Considering that [(C₆H₆)RuCp]PF₆ has no catalytic activity in the hydrosilylation reaction in a solid-liquid heterogeneous system at 298 K (data not shown), coordinatively unsaturated sites on the Ru(II) center could be formed by thermal activation of -[phRuCp]PF₆- and -[biphRuCp]PF₆complexes at 523 K. It was also found that [(C₆H₆)RuCp]PF₆ had less catalytic activity than HMM-phRuCp and HMM-biphRuCp, possibly because of aggregation of complexes, that is, the ligand-exchange reaction enabled immobilization of -[phRuCp]PF₆- and -[biphRuCp]PF₆- complexes on the HMMs in a highly dispersed state, resulting in improvement of the catalytic activity. Although the TON of HMM-biphRuCp (36.9) was lower than that of HMM-phRuCp (45.7), it was found that HMM-biphRuCp had greater catalytic activity than HMM-phRuCp



Fig. 4 Yields of products from selective hydrosilylation of 1-hexyne with triethylsilane on *a* HMM–ph, *b* HMM–biph, *c* $[(C_6H_6)RuCp]PF_6$, *d* HMM–phRuCp, and *e* HMM–biphRuCp. Reaction conditions: 1-hexyne and triethylsilane (527 µmol), catalyst (30 mg), 15 h, 523 K



Scheme 2 Hydrosilylation of 1-hexyne with triethylsilane

on the basis of the weight of catalyst used for the reaction. This could be because of the greater loading of the Ru complex, derived from the electron-donating ability of biphenylene moieties. This shows that organic moieties within HMMs that behave as framework ligands affect the chemical properties, herein stability, of the complexes constructed on them, resulting in a change in their catalytic activity.

Conclusion

Construction of the –[biphRuCp]PF₆– complex within HMM–biph was achieved by ligand-exchange reaction between [(CH₃CN)₃RuCp]PF₆ and the biphenylene moiety of HMM–biph. UV–visible and XAFS studies revealed that the –[biphRuCp]PF₆– complex was present in a highly dispersed state within the HMM–biph framework, and that aggregated and dimeric ruthenium species were not formed. HMM–biphRuCp catalyzed selective hydrosilylation of 1-hexyne in a solid–gas heterogeneous system and gave α -vinylsilane as the main product. It was also found that HMM–biphRuCp had greater catalytic activity than HMM–phRuCp. This high catalytic activity of HMM–biphRuCp was because of the greater loading of the Ru complex in HMM–biph, because of the high electron-donating ability of biphenylene moieties.

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