Journal of Organometallic Chemistry 696 (2011) 1565–1569

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Diphenylphosphino functionalization of mesoporous silica using tripodal linker units

Takayuki Miyaji [a], Shun-ya Onozawa [b,*], Norihisa Fukaya [b], Masae Ueda [b], Yukio Takagi [a], Toshiyasu Sakakura [b], Hiroyuki Yasuda [b,*]

[a] N.E. CHEMCAT Corporation, 678 Ipponmatsu, Numazu, Shizuoka 410-0314, Japan
[b] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

ARTICLE INFO

Article history:
Received 28 October 2010
Received in revised form
17 December 2010
Accepted 24 December 2010

Keywords:
Immobilized catalysts
Mesoporous silica
Tripodal linker unit
Aryl phosphine
CP/MAS NMR spectroscopy

ABSTRACT

The immobilization of diphenyl phosphine onto ordered mesoporous silicas using a tripodal linker unit possessing one bromopropyl group and three anchoring silicon atoms was investigated. Solid-state ^{31}P, ^{29}Si, and ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectroscopic studies as well as isothermal nitrogen adsorption/desorption measurements revealed that grafting the tripodal linker unit and a subsequent reaction with potassium diphenylphosphide (the “bottom-up” method) successfully realized diphenylphosphino functionalization of silica while maintaining the mesoporous structure. In contrast, directly grafting tripodal diphenylphosphino ligands pre-synthesized from the tripodal linker unit onto silica (the “top-down” method) was unsuccessful.

1. Introduction

We have recently developed a tripodal linker unit possessing three leaving allylsilyl or isopropoxysilyl groups (**1a** and **1b** in Fig. 1) [1]. This linker unit can be tightly bound to a silica surface via three independent Si–O–Si bonds. In fact, organo-modified silica with a grafted tripodal linker unit exhibits a higher hydrothermal stability against leaching of organic moieties than silica modified with conventional trialkoxysilanes. Additionally, the tripodal linker unit contains a bromopropyl moiety to which various functional groups can be attached. Therefore, diverse organic functional molecules, including auxiliary ligands for metal complexes, can be firmly immobilized onto a silica surface employing the linker unit.

Immobilization of molecular catalysts like transition metal complexes onto inorganic porous supports such as ordered mesoporous silicas has been actively researched because immobilized catalysts are advantageous in terms of separating and recycling the catalyst [2–8]. Aryl phosphines are the most common ligands in transition metal complex catalyzed reactions, and numerous examples of immobilized metal aryl phosphine complex catalysts have been reported [9–13]. Therefore, it is interesting to investigate the immobilization of aryl phosphines onto silica via the tripodal linker unit. There are two preparative approaches to functionalize silica by diarylphosphino groups via the linker: the “bottom-up” (route 1 in Fig. 1) and “top-down” (route 2) methods [14]. In the former, the tripodal linker unit is grafted onto silica and the bromo group is subsequently converted into diaryl phosphine. In the latter, a phosphorous compound containing a diarylphosphinopropyl moiety and three allylsilyl or isopropoxysilyl groups (tripodal diarylphosphino ligand) is pre-synthesized from the tripodal linker unit, and then the compound is directly grafted onto silica. Herein we examine these two methods to determine an effective strategy to tightly bind aryl phosphine ligands to silica using the tripodal linker unit.

2. Results and discussion

2.1. Diphenylphosphino functionalization via route 1 (the “bottom-up” method)

Grafting of 3-bromopropyltris[3-(allyldimethylsilyl)propyl]silane (**1a**) onto an ordered mesoporous silica TMPS-4 (denoted as SIO-1) in heptane at reflux afforded bromopropyl-functionalized silica **2** (hereafter, **2** for SIO-1 is denoted as **2-1**) [15]. Likewise, grafting of **1a** onto another ordered mesoporous silica TMPS-7 (denoted as SIO-2)

---

* Corresponding authors. Tel.: +81 29 861 9399; fax: +81 29 861 4580.
E-mail addresses: s-onozawa@aist.go.jp (S.-y. Onozawa), h.yasuda@aist.go.jp (H. Yasuda).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.12.030

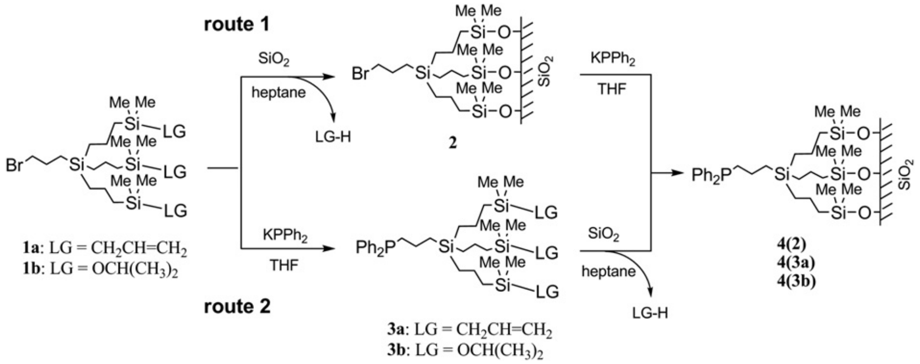

Fig. 1. Synthetic routes of diphenylphosphino-functionalized mesoporous silica using tripodal linker units.

Table 1
Summary of diphenylphosphino functionalization of mesoporous silica via route 1.

Entry	Modified silica	Silica	Conditions		Loading (mmol/g)[a]	S_{BET} (m^2/g)[b]	V_p (cm^3/g)[c]	D_{BJH} (nm)[d]
			$KPPh_2$	Temp.				
1	**2-1**	SIO-1	–	–	0.48	813	0.97	3.1
2	**4(2)-1**	SIO-1	7 equiv.	Reflux	0.32	570	0.58	2.7
3	**4(2)-1**	SIO-1	7 equiv.	RT	0.34	675	0.77	2.8
4	**4(2)-1**	SIO-1	5 equiv.	323 K	0.35	734	0.85	2.8
5	**2-2**	SIO-2	–	–	0.39	876	1.68	5.8
6	**4(2)-2**	SIO-2	5 equiv.	323 K	0.31	778	1.56	5.8

[a] Determined by elemental analysis of carbon.
[b] BET specific surface area.
[c] Pore volume determined at a relative pressure (P/P_0) of 0.99.
[d] Average pore diameter calculated by the BJH method from the adsorption branch.

gave **2** (hereafter, **2** for SIO-2 is denoted as **2**-**2**). Similar to **2**-**1** [1], the ^{29}Si and ^{13}C CP/MAS spectra of **2**-**2** confirmed successful grafting via three covalent Si—O—Si bonds (see Supplementary data, Figs. S1 and S2). The amounts of organic moieties in **2**-**1** (prepared in this study) and **2**-**2**, which were determined by elemental analysis of carbon, were 0.48 and 0.39 mmol/g (0.61 and 0.48 mmol/g-SiO_2), respectively (entries 1 and 5 of Table 1).

Next we examined the transformation of the Br group in **2** into a PPh_2 group. Reactions of **2**-**1** with varying amounts of $KPPh_2$ (5–7 equiv.) were carried out at several temperatures. Entries 2–4 of Table 1 list the amounts of organic groups loaded in the resulting PPh_2-functionalized SIO-1 (**4**(**2**)-**1**). Treatment of **2**-**1** with $KPPh_2$ reduced the loading amounts, presumably because the treatment partially eliminated the grafted tripodal linker unit. The bromine contents of all the **4**(**2**)-**1** samples were less than 0.1 wt% (corresponding to 0.013 mmol/g), indicating that the Br group was almost completely converted into PPh_2 groups. Fig. 2 shows the ^{31}P, ^{29}Si, and ^{13}C CP/MAS spectra of **4**(**2**)-**1** obtained under the condition in entry 4 of Table 1. In the ^{31}P CP/MAS spectrum, a major peak assigned to PPh_2 species was observed at δ −15 ppm, although a minor peak due to the oxidized PPh_2 species was also detected at δ 40 ppm. In addition to the silica peaks in the ^{29}Si CP/MAS spectrum, two signals corresponding to one tetraalkyl-coordinated silicon (δ 2 ppm) and three trialkylmonooxygen-coordinated silicon atoms (δ 14 ppm) [16] in **4**(**2**) were observed, suggesting that the tripodal anchoring structure of **2** was maintained even after phosphine was attached. The ^{13}C CP/MAS spectrum exhibited several peaks, which corresponded to the carbon skeleton of **4**(**2**). The peaks assigned to the carbons of the benzene ring in the PPh_2 group appeared near δ 130 ppm. The transformation of the Br group into a PPh_2 group caused the peak attributed to the carbon at the β-position to shift from δ 30 ppm (**2**-**1**) to approximately δ 20 ppm (**4**(**2**)-**1**). The CP/MAS spectra of **4**(**2**)-**1** (entries 2 and 3 of Table 1) as well as those of PPh_2-functionalized SIO-2 (**4**(**2**)-**2**) (entry 6) were essentially the same as Fig. 2 (see Supplementary data, Figs. S3–S5). Hence, the treatment of **2** with $KPPh_2$ efficiently introduced a PPh_2 group into **2** while maintaining the tripodal anchoring structure.

Fig. 3 displays the N_2 adsorption/desorption isotherms of **2** and **4**(**2**). Table 1 includes the textural properties. All the samples provided type IV isotherms, which are typical for mesoporous structures. However, **4**(**2**)-**1**, which was prepared while refluxing (entry 2 of Table 1), showed a smaller step in the relative pressure (P/P_0) range of 0.3–0.5, suggesting the ordered mesopores were partially destroyed. This is also supported by the significant decrease in the surface area and the pore volume. On the other hand, the isotherms of **4**(**2**)-**1** (entries 3 and 4 of Table 1) as well as

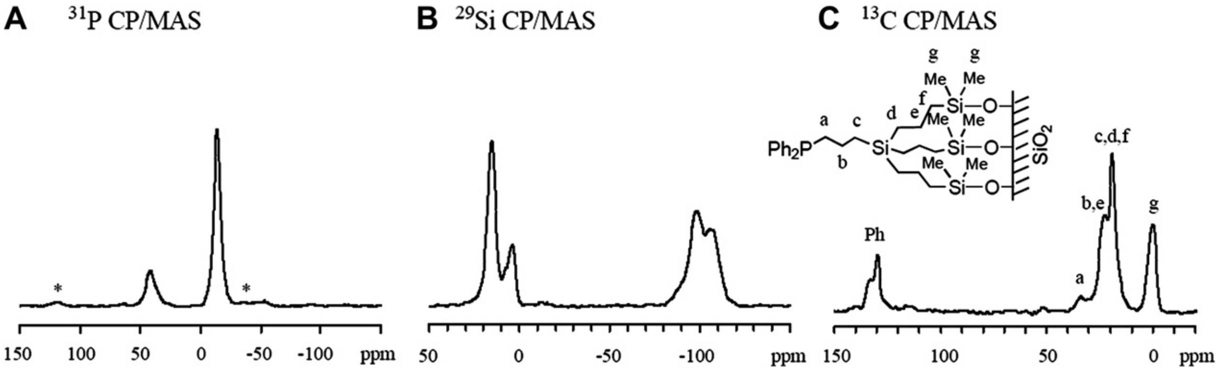

Fig. 2. (A) ^{31}P, (B) ^{29}Si, and (C) ^{13}C CP/MAS spectra of PPh_2-functionalized SIO-1 (**4**(**2**)-1) (entry 4 of Table 1). (*): spinning side band.

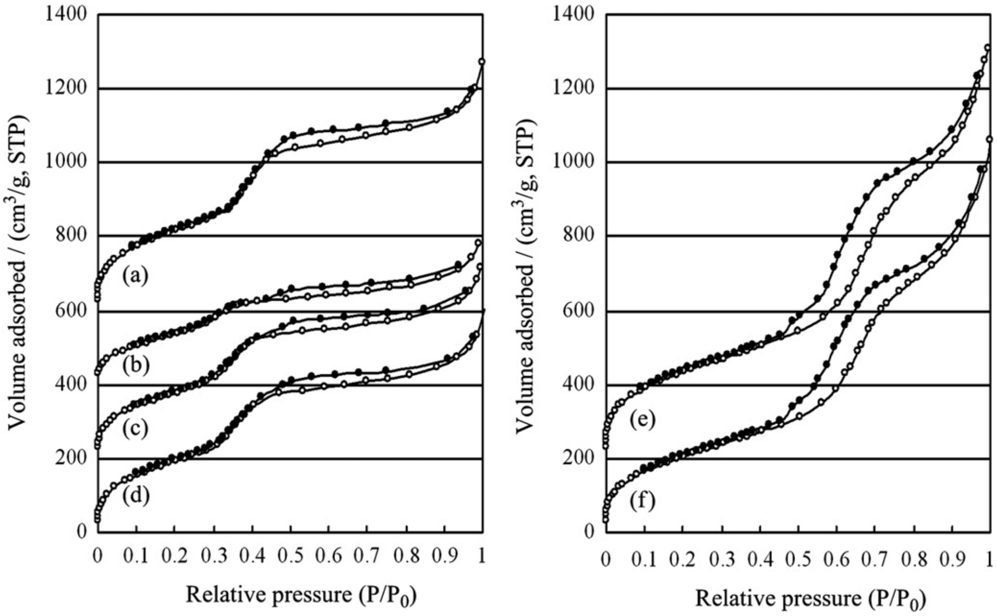

Fig. 3. Nitrogen adsorption/desorption isotherms of functionalized SIO-1 (left panel) and SIO-2 (right panel). (a) Bromopropyl-functionalized SIO-1 (**2**-**1**) (entry 1 of Table 1); (b) PPh$_2$-functionalized SIO-1 (**4**(**2**)-**1**) (entry 2); (c) PPh$_2$-functionalized SIO-1 (**4**(**2**)-**1**) (entry 3); (d) PPh$_2$-functionalized SIO-1 (**4**(**2**)-**1**) (entry 4); (e) bromopropyl-functionalized SIO-2 (**2**-**2**) (entry 5); (f) PPh$_2$-functionalized SIO-2 (**4**(**2**)-**2**) (entry 6). Open and closed symbols correspond to the adsorption and desorption branches, respectively. (a), (b), (c), and (e) are offset by 600, 400, 200, and 200 cm^3/g (STP), respectively.

4(**2**)-**2** (entry 6) demonstrate that the PPh$_2$ group was introduced while preserving the mesoporous structure. Thus, the diphenylphosphino functionalization via the tripodal linker unit was accomplished for both SIO-1 and SIO-2 using route 1 (the "bottom-up" method).

2.2. Diphenylphosphino functionalization via route 2 (the "top-down" method)

We initially grafted the tripodal diphenylphosphino ligand containing three allylsilyl moieties **3a** onto SIO-1 in heptane while refluxing. Entry 7 of Table 2 shows the loading amount and textural property of the resulting PPh$_2$-functionalized silica (**4**(**3a**)-**1**). Compared to **2**-**1**, less **3a** was loaded onto SIO-1. Fig. 4(a) shows the ^{31}P, ^{29}Si, and ^{13}C CP/MAS spectra of **4**(**3a**)-**1**. In addition to the PPh$_2$ (δ −15 ppm) and OPPh$_2$ (δ 40 ppm) peaks, a shoulder peak appeared near δ 25 ppm in the ^{31}P CP/MAS spectrum. The peak near δ 25 ppm might be due to the P—O—Si species formed by the interaction between the phosphorous group and the surface silanol group, similar to the findings of Blümel et al. [17,18]. In the ^{29}Si CP/MAS spectrum, the peak assigned to the tetraalkyl-coordinated silicon (δ 2 ppm) was detected, whereas the peak due to three trialkylmonooxygen-coordinated silicon atoms was negligible. The peaks assigned to the allyl group in **3a** were clearly observed in the ^{13}C CP/MAS spectrum. These observations suggest that the allyl groups in **3a** did not fully react with the surface silanol group. This is probably because the interaction of the phosphorous group in **3a** with the silica surface was preferential over the reaction between the allylsilyl groups and the silanol groups.

Next, we grafted the tripodal diphenylphosphino ligand containing three isopropoxysilyl moieties **3b** onto SIO-1 and SIO-2 in heptane. Entries 8 and 9 of Table 2 show the results of the obtained PPh$_2$-functionalized silica **4**(**3b**) (hereafter, **4**(**3b**) for SIO-1 and SIO-2 are denoted as **4**(**3b**)-**1** and **4**(**3b**)-**2**, respectively). Several times the amount was loaded with **3b** than with **3a**. Fig. 4(b) shows the CP/MAS spectra of **4**(**3b**)-**2**. Besides the major peak from PPh$_2$ (δ −15 ppm) and the minor peak from OPPh$_2$ (δ 40 ppm), a peak around δ 25 ppm (possibly due to P—O—Si) was distinctly observed in the ^{31}P CP/MAS spectrum. Moreover, a new silicon peak arising from **3b** emerged near δ 20 ppm in the ^{29}Si CP/MAS spectrum, suggesting the existence of silicon species that did not participate in binding to silica. In the ^{13}C CP/MAS spectrum, the peaks assigned to an isopropoxy group were detected. It is assumed that the isopropoxy peaks resulted from the unreacted isopropoxy group in **3b** rather than from the isopropoxide species (iPrO—Si) formed by the reaction of the eliminated isopropyl alcohol and the surface silanol group because such iPrO—Si species were not observed when the tripodal linker unit containing leaving isopropoxy groups **1b** was grafted onto SIO-1 [1]. **4**(**3b**)-**1** gave the similar ^{31}P, ^{29}Si, and ^{13}C CP/MAS spectra as Fig. 4(b). These CP/MAS NMR results demonstrate that **3b** was not successfully grafted onto the silica surface via three covalent Si—O—Si bonds.

Furthermore, we attempted to graft **3b** onto SIO-2 in toluene and isopropyl alcohol (entries 10 and 11 of Table 2). Compared to grafting in heptane, less grafting occurred in toluene. In addition, there was little difference in the CP/MAS spectra between both solvents. The ^{13}C CP/MAS spectrum revealed that the surface of SIO-2 was isopropoxylated when isopropyl alcohol was used for the grafting (spectrum (c) in Fig. 4(C)). Thus, the loading amount could not be determined by carbon analysis, but a smaller loading amount than toluene was inferred from the fact that the signals

Table 2
Summary of diphenylphosphino functionalization of mesoporous silica via route 2.

Entry	Modified silica	Silica	Solvent	Loading (mmol/g)[a]	S_{BET} (m^2/g)[a]	V_p (cm^3/g)[a]	D_{BJH} (nm)[a]
7	**4**(**3a**)-**1**	SIO-1	Heptane	0.07	1002	1.33	3.7
8	**4**(**3b**)-**1**	SIO-1	Heptane	0.23	879	1.14	3.4
9	**4**(**3b**)-**2**	SIO-2	Heptane	0.30	802	1.79	5.8
10	**4**(**3b**)-**2**	SIO-2	Toluene	0.21	933	1.99	6.2
11	**4**(**3b**)-**2**	SIO-2	Isopropyl alcohol	–	945	2.01	6.2

[a] See Table 1.

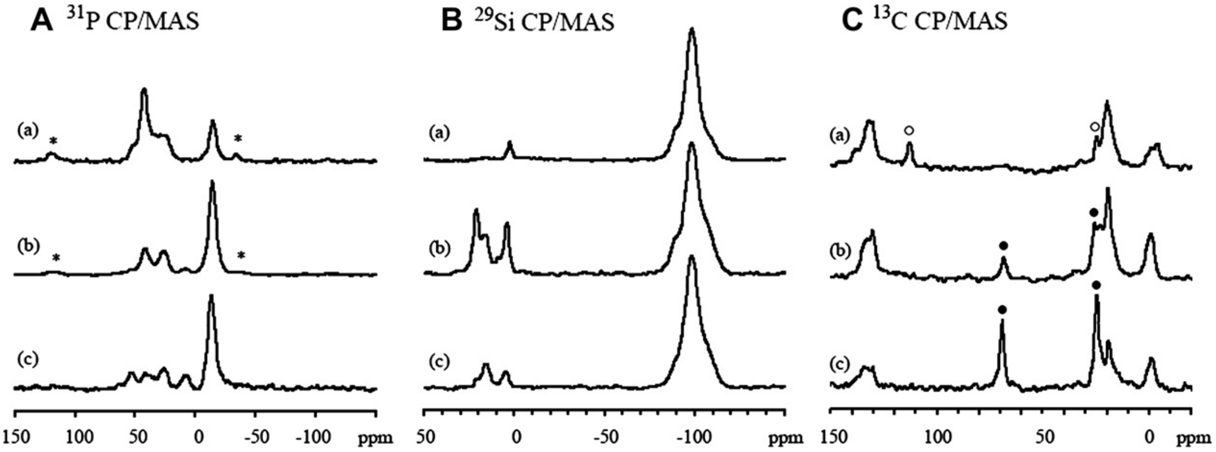

Fig. 4. (A) ^{31}P, (B) ^{29}Si, and (C) ^{13}C CP/MAS spectra of PPh_2-functionalized silica. (a) PPh_2-functionalized SIO-1 (**4**(**3a**)-**1**) (entry 7 of Table 2); (b) PPh_2-functionalized SIO-2 (**4**(**3b**)-**2**) (entry 9); (c) PPh_2-functionalized SIO-2 (**4**(**3b**)-**2**) (entry 11). (○): allyl group; (●): isopropoxy group; (*): spinning side band.

derived from **3b** were weaker in the ^{29}Si CP/MAS spectrum (spectrum (c) in Fig. 4(B)).

3. Conclusions

The diphenylphosphino functionalization of ordered mesoporous silicas via the tripodal linker unit could be realized by grafting of **1a** and a subsequent reaction with $KPPh_2$ under the appropriate conditions (7 equiv. at room temperature or 5 equiv. at 323 K) (the “bottom-up” method). On the other hand, directly grafting the tripodal diphenylphosphino ligands (**3a** and **3b**) (the “top-down” method) suffered from PPh_2 functionalization, probably because the interaction of the phosphorous groups with the silica surface was preferential over the reaction between the leaving groups and the silanol groups. Applications of the resulting PPh_2-functionalized mesoporous silica to transition metal complex catalyzed reactions are currently underway.

4. Experimental

4.1. General

All chemicals were reagent grade and used without further purification. Two types of ordered mesoporous silicas [19] (Taiyo Kagaku Co., Ltd., TMPS-4 and TMPS-7, denoted as SIO-1 and SIO-2, respectively) were used as supports. The surface area, pore volume, and average pore diameter were 1039 m^2/g, 1.46 cm^3/g, and 3.8 nm for SIO-1 and 1050 m^2/g, 2.39 cm^3/g, and 6.4 nm for SIO-2, respectively. SIO-1 and SIO-2 were dried at 353 K under a vacuum for 3 h prior to use. All experiments were performed under inert gas using standard Schlenk techniques.

4.2. Preparation of tripodal linker units and tripodal diphenylphosphino ligands

3-Bromopropyltris[3-(allyldimethylsilyl)propyl]silane (**1a**) and 3-bromopropyltris[3-(dimethylisopropoxysilyl)propyl]silane (**1b**) were prepared according to the previously described procedure [1]. 3-Diphenylphosphinotris[3-(allyldimethylsilyl)propyl]silane (**3a**) and 3-diphenylphosphinotris[3-(dimethylisopropoxysilyl)propyl] silane (**3b**) were prepared by reacting **1a** and **1b**, respectively, with potassium diphenylphosphide in tetrahydrofuran at room temperature for 20 h.

4.3. Diphenylphosphino functionalization via route 1 (the “bottom-up” method)

To a suspension of silica (1.0 g) in dry heptane (25 cm^3) was added **1a** (0.45–0.55 mmol), and the mixture was refluxed for 20 h. The resulting solid was filtered, washed successively with THF, ethyl acetate, and hexane (five times for each solvent (10 cm^3)) to remove unreacted **1a**, and then dried at 353 K under a reduced pressure for 3 h to give bromopropyl-functionalized silica (**2**). $KPPh_2$ (5–7 equiv.) in THF (0.5 M) was added, dropwise, to a suspension of **2** (1.0 g) in dry THF (30 cm^3), and the mixture was stirred for 20 h. The resulting solid was filtered, washed successively with THF, methanol, and hexane (five times for each solvent (10 cm^3)) to eliminate unreacted $KPPh_2$ as well as any by-products, and then dried at 353 K under a reduced pressure for 3 h to give PPh_2-functionalized silica (**4**(**2**)).

4.4. Diphenylphosphino functionalization via route 2 (the “top-down” method)

To a suspension of silica (1.0 g) in dry solvent (25 cm^3) was added **3a** or **3b** (0.40–0.45 mmol), and the mixture was refluxed for 20 h. Dry heptane, toluene, and isopropyl alcohol were used as the solvents. The resulting solid was filtered, washed successively with THF, ethyl acetate, and hexane (five times for each solvent (10 cm^3)) to remove unreacted **3a** or **3b**, and then dried at 353 K under a reduced pressure for 3 h to give PPh_2-functionalized silica (**4**(**3a**) or **4**(**3b**)).

4.5. Characterization

Solid-state ^{31}P, ^{29}Si, and ^{13}C CP/MAS NMR spectra were recorded on a Bruker AVANCE 400WB spectrometer equipped with a 4 mm MAS probehead. Isothermal nitrogen adsorption/desorption measurements were carried out at 77 K on a BEL Japan BELSORP mini II after the sample was degassed at 353 K for 3 h. Elemental compositions of carbon and bromine were determined using a CE Instruments EA 1112 elemental analyzer and a DIONEX ICS-2000 ion chromatograph, respectively.

Acknowledgment

This research was financially supported by the Project of “Development of Microspace and Nanospace Reaction Environment

Technology for Functional Materials" of New Energy and Industrial Technology Development Organization (NEDO), Japan.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.12.030.

References

[1] N. Fukaya, S. Onozawa, M. Ueda, K. Saitou, Y. Takagi, T. Sakakura, H. Yasuda, Chem. Lett. 39 (2010) 402–403.
[2] A.P. Wight, M.E. Davis, Chem. Rev. 102 (2002) 3589–3614.
[3] D.E. de Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615–3640.
[4] J.Y. Ying, C.P. Mehnert, M.S. Wong, Angew. Chem. Int. Ed. 38 (1999) 56–77.
[5] A. Corma, H. Garcia, Adv. Synth. Catal. 348 (2006) 1391–1412.
[6] D. Brunel, A.C. Blanc, A. Galarneau, F. Fajula, Catal. Today 73 (2002) 139–152.
[7] J.H. Clark, D.J. Macquarrie, Chem. Commun. (1998) 853–860.
[8] X.S. Zhao, X.Y. Bao, W. Guo, F.Y. Lee, Mater. Today 9 (2006) 32–39.
[9] M. Cai, G. Zheng, L. Zha, J. Peng, Eur. J. Org. Chem. (2009) 1585–1591.
[10] S.-G. Shyu, S.-W. Cheng, D.-L. Tzou, Chem. Commun. (1999) 2337–2338.
[11] W. Zhou, Y. Li, D. He, Appl. Catal. A 377 (2010) 114–120.
[12] C. Kang, J. Huang, W. He, F. Zhang, J. Organomet. Chem. 695 (2010) 120–127.
[13] K. Melis, D.D. Vos, P. Jacobs, F. Verpoort, J. Mol. Catal. A: Chem. 169 (2001) 47–56.
[14] L. Bemi, H.C. Clark, J.A. Davies, C.A. Fyfe, R.E. Wasylishen, J. Am. Chem. Soc. 104 (1982) 438–445.
[15] A method that modifies the silica surface utilizing deallylation of allylsilane derivatives has been reported, see (a) T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, S. Inagaki, T. Hayashi, J. Am. Chem. Soc. 125 (2003) 4688–4689;
(b) K. Aoki, T. Shimada, T. Hayashi, Tetrahedron: Asymmetry 15 (2004) 1771–1777.
[16] G. Engelhardt, H. Jancke, E. Lippmaa, A. Samoson, J. Organomet. Chem. 210 (1981) 295–301.
[17] J. Sommer, Y. Yang, D. Rambow, J. Blümel, Inorg. Chem. 43 (2004) 7561–7563.
[18] J. Blümel, Coord. Chem. Rev. 252 (2008) 2410–2423.
[19] M.P. Kapoor, W. Fujii, M. Yanagi, Y. Kasama, T. Kimura, H. Nanbu, L.R. Juneja, Microporous Mesoporous Mater. 116 (2008) 370–377.