

Short communication

Synthesis of a novel fumed silica-supported bidentate arsine rhodium complex and its catalytic behavior in the hydrosilylation of olefins with triethoxysilane

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Received 10 February 2006; accepted 19 May 2006

Available online 7 July 2006

Abstract

A novel fumed silica-supported bidentate arsine rhodium complex was prepared by treatment of poly-4-oxa-6,7-dichloroheptylsiloxane with potassium diphenylarsenide in THF and then reaction with rhodium chloride. It was found that the title complex is an efficient catalyst for hydrosilylation reaction of olefins with triethoxysilane and can be reused several times without noticeable loss of activity.

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Keywords: Supported rhodium catalyst; Bidentate arsine rhodium complex; Hydrosilylation; Functional polysiloxane

1. Introduction

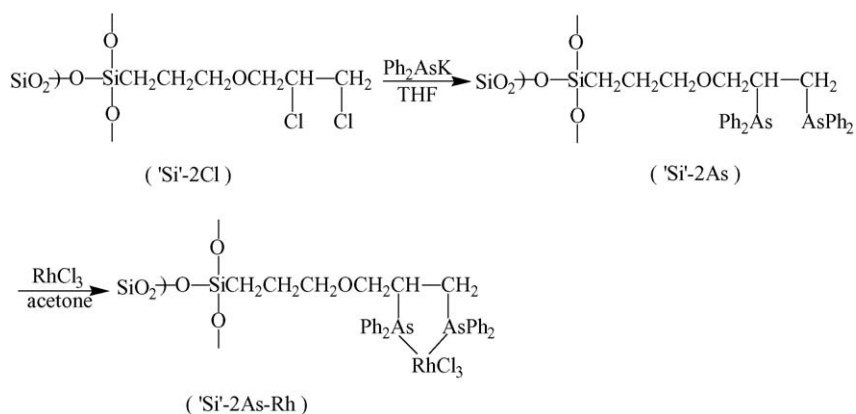
Polymer-supported transition metal complexes catalysts are currently attracting great interest because they have the advantages of both homogeneous and heterogeneous catalyzed processes [1,2]. These 'third generation' catalysts [1,3] have received much attention [4–14]. In the preparation of supported transition metal complexes catalysts a wide variety of support materials have been used including cross-linked polymer [9,13–16], silica [10–12], and high surface area glasses [17]. Inorganic supports possess a rigid structure which is not deformed by solvent swelling during catalytic reactions. Fumed silica is a better support because they have large surface area, high mechanical strength, heat and chemical stability. Polysiloxane grafted on fumed silica-supported sulfur platinum [18–21], phosphine platinum [22] complexes have been proved to be efficient catalysts for hydrosilylation of olefins with triethoxysilane. However, to date, the hydrosilylation of olefins catalyzed by polymer-supported rhodium complexes has received less attention [23–25].

Study of new types of polymer-bound rhodium complexes catalysts which might be suitable for hydrosilylation of olefins with triethoxysilane has theoretical and practical significance. Chen et al. described the synthesis of polysiloxane-supported bidentate phosphine rhodium [26], bidentate sulfur rhodium [27] complexes and their catalytic behavior in the hydrosilylation of olefins with triethoxysilane. However, to the best of our knowledge, no hydrosilylation of olefins with triethoxysilane catalyzed by a fumed silica-supported bidentate arsine rhodium complex has been reported until now. In this paper, we wish to report the preparation of a fumed silica-supported poly-4-oxa-6,7-bis(diphenylarsino)heptylsiloxane rhodium complex (abbreviation: 'Si'-2As-Rh) and its catalytic properties in hydrosilylation of olefins with triethoxysilane. The novel polymeric bidentate arsine rhodium complex could be easily prepared by treatment of poly-4-oxa-6,7-dichloroheptylsiloxane with potassium diphenylarsenide and then reaction with rhodium chloride (Scheme 1).

2. Experimental

All hydrosilylation products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were obtained using a Perkin-Elmer 683 instrument. ¹H NMR spectra were recorded on a JEOL FX-90Q (90 MHz)

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Scheme 1.

or a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in CDCl_3 as solvent. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyzer. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a KRATOS XSAM 800 electron energy spectrometer. Poly-4-oxa-6,7-dichloroheptylsiloxane ('Si'-2Cl) was prepared according to literature procedure [28], the chlorine content was 1.97 mmol/g. THF and acetone were distilled before use, other reagents were used as received without further purification.

2.1. Preparation of silica-supported poly-4-oxa-6,7-bis(diphenylarsino)heptylsiloxane ('Si'-2As)

A mixture of AsPh_3 (3.62 g, 11.83 mmol) and potassium (0.93 g, 23.66 mmol) in THF (60 ml) was stirred under nitrogen at 60°C for 16 h. After being cooled to room temperature, the mixture was treated with *t*-BuCl (1.10 g, 11.83 mmol) for 1 h to give a brown solution. Into the resulting solution was added 'Si'-2Cl (5.0 g) and the mixture was stirred at room temperature for 2 h and then heated at reflux for 24 h. The reaction mixture was cooled to room temperature and treated with *t*-BuCl (2 ml) for 2 h. The mixture was filtered and washed with 95% ethanol (4×40 ml), distilled water (5×40 ml), acetone (3×40 ml) and then dried under vacuum to give 4.97 g of silica-supported bidentate arsine ligand ('Si'-2As). The arsenic content was 1.52 mmol/g.

2.2. Preparation of silica-supported poly-4-oxa-6,7-bis(diphenylarsino)heptylsiloxane rhodium complex ('Si'-2As-Rh)

To a solution of RhCl_3 (0.159 g) in acetone (40 ml) was added 'Si'-2As (1.625 g). The mixture was heated at reflux under nitrogen for 72 h. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at $70^\circ\text{C}/26.7$ Pa under nitrogen for 3 h to give 1.544 g of the brown yellow polymeric rhodium complex ('Si'-2As-Rh). The arsenic and rhodium content was 1.27 and 0.38 mmol/g, respectively.

2.3. Hydrosilylation of olefins with triethoxysilane

Hydrosilylation was carried out in a 5 ml plane-bottomed flask equipped with a magnetic stirrer and a reflux condenser to the upper of which a drying system was attached. Olefin and rhodium complex were stirred at the reaction temperature for 30 min before triethoxysilane was added. The structure and yield of hydrosilylation products were determined based on a standard sample and a standard curve by GLC at regular intervals. Typical reaction conditions are as follows: olefin 5.0 mmol, triethoxysilane 5.0 mmol, rhodium complex 10^{-2} to 10^{-3} mmol Rh.

3. Results and discussion

A novel fumed silica-supported poly-4-oxa-6,7-bis(diphenylarsino)heptylsiloxane rhodium complex (abbreviation: 'Si'-2As-Rh) was conveniently prepared by treatment of poly-4-oxa-6,7-dichloroheptylsiloxane with potassium diphenylarsenide in THF and then reaction with rhodium chloride in acetone (Scheme 1). The polymer-bound rhodium complexes catalysts are very stable to air and moisture as a result of the isolation of the reactive species by the polymer matrix. As a result, this supported bidentate arsine rhodium catalyst can be stored for a long period and is very convenient to use. Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize this polymeric rhodium complex. The As:Rh mole ratio of the 'Si'-2As-Rh was determined to be 3.34. The XPS data for 'Si'-2As-Rh, 'Si'-2As, RhCl_3 and Rh foil are listed in Table 1. It can be seen that the binding energies of Si 2p and O 1s of 'Si'-2As-Rh are similar to those of 'Si'-2As, and the binding energy of Cl 2p of 'Si'-2As-Rh is

Table 1
XPS data for 'Si'-2As-Rh, 'Si'-2As, RhCl_3 and Rh foil (in eV)^a

Sample	Rh 3d _{5/2}	As 3d _{5/2}	Si 2p	O 1s	Cl 2p
'Si'-2As-Rh	308.3	42.5	103.3	532.6	199.4
'Si'-2As		42.0	103.3	532.5	
RhCl_3	310.4				199.5
Rh foil	307.0				

^a The binding energies are referenced to C 1s (284.6 eV), and the energy differences were determined with an accuracy of ± 0.2 eV.

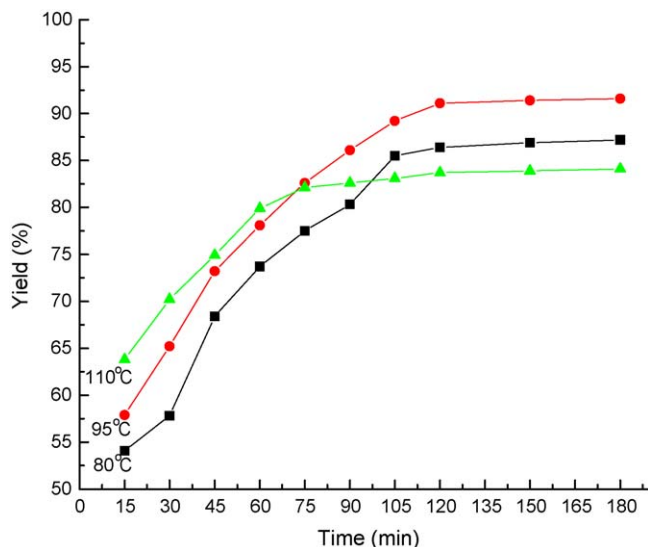


Fig. 1. Effect of reaction temperature on the yield of decyltriethoxysilane. Conditions: 1-decene, 5.0 mmol; HSi(OEt)₃, 5.0 mmol; catalyst, 1.0×10^{-2} mmol Rh.

similar to that of RhCl₃. However, the difference of As 3d_{5/2} binding energies between 'Si'-2As-Rh and 'Si'-2As is 0.5 eV. The binding energy of Rh 3d_{5/2} in 'Si'-2As-Rh is 2.1 eV less than that in RhCl₃, but 1.3 eV larger than that in Rh foil. These results show that a coordination bond between As and Rh is formed.

The hydrosilylation reaction of olefins with triethoxysilane was examined to evaluate the catalytic activity of the novel fumed silica-supported bidentate rhodium complex catalyst ('Si'-2As-Rh). At first, the catalytic activity of the rhodium complex at different temperatures was investigated using the hydrosilylation of 1-decene with triethoxysilane as the model reaction. The results are shown in Fig. 1. The experimental results show that no remarkable induction period was observed, and the reaction rate became faster with the increase in the temperature. When hydrosilylation reaction was carried out at 95 °C, decyltriethoxysilane was obtained in 91% yield after 2 h. So, for the temperatures evaluated [80, 95, 110 °C], 95 °C gave the best result. The effect of the amount of the 'Si'-2As-Rh on the hydrosilylation reaction was also examined using 5.0 mmol of

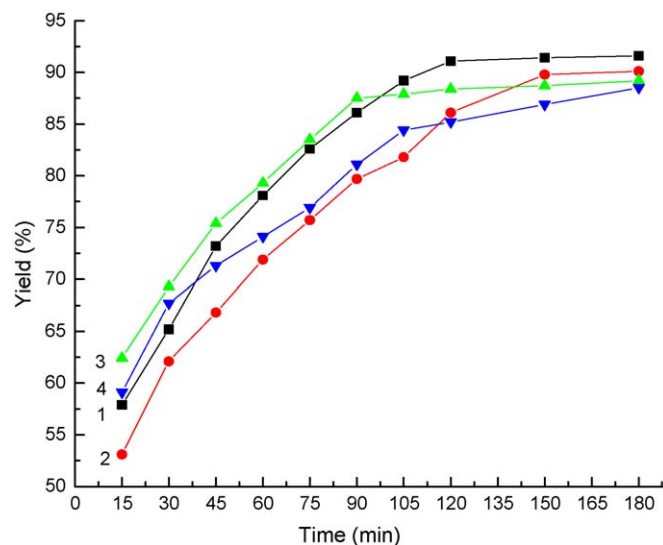


Fig. 2. Reuse of 'Si'-2As-Rh. Conditions: 1-decene, 5.0 mmol; HSi(OEt)₃, 5.0 mmol; catalyst, 1.0×10^{-2} mmol Rh.

1-decene as substrate at 95 °C. The experimental results show that the reaction rate became faster with the increase in the amount of the catalyst, for the amounts evaluated [5×10^{-3} , 1.0×10^{-2} , 2.0×10^{-2} mmol Rh], 1.0×10^{-2} mmol Rh gave the best result, decyltriethoxysilane was obtained in 91% yield. When 2.0×10^{-2} mmol of 'Si'-2As-Rh was used, the reaction rate was the fastest, but the final yield of decyltriethoxysilane was only 83% and tetraethoxysilane was formed in 8% yield.

Hydrosilylation reactions of a variety of olefins with triethoxysilane were studied at 95 °C using 2 mol% of 'Si'-2As-Rh as catalyst, the typical results are summarized in Table 2. As shown in Table 2, in the presence of catalytic amount of 'Si'-2As-Rh catalyst, hydrosilylation reactions of 1-decene, 1-dodecene and allyl glycidyl ether with HSi(OEt)₃ proceeded smoothly, the corresponding hydrosilylation products were obtained in 89–92% yields. Speier's catalyst was not so effective when HSi(OEt)₃ was used. It was reported that the yield of decyltriethoxysilane was only 40% in the case of using H₂PtCl₆ as catalyst [29]. Under the same conditions, hydrosilylation reactions of allyl phenyl ether, allyl acetate and allylbenzene with HSi(OEt)₃ could also proceed smoothly to give the correspond-

Table 2
Catalytic activity of 'Si'-2As-Rh for the hydrosilylation reaction of olefins with triethoxysilane

Olefin	Product ^a	Time (min)	Yield ^b (%)
CH ₃ (CH ₂) ₇ CH=CH ₂	CH ₃ (CH ₂) ₉ Si(OEt) ₃	120	91
CH ₃ (CH ₂) ₉ CH=CH ₂	CH ₃ (CH ₂) ₁₁ Si(OEt) ₃	140	89
C ₆ H ₅ OCH ₂ CH=CH ₂	C ₆ H ₅ O(CH ₂) ₃ Si(OEt) ₃	120	73
C ₆ H ₅ CH ₂ CH=CH ₂	C ₆ H ₅ (CH ₂) ₃ Si(OEt) ₃	140	71
CH ₃ CO ₂ CH ₂ CH=CH ₂	CH ₃ CO ₂ (CH ₂) ₃ Si(OEt) ₃	150	83
C ₆ H ₅ CH=CH ₂	C ₆ H ₅ (CH ₂) ₂ Si(OEt) ₃	130	70
$\begin{array}{c} \text{CH}_2-\text{CHCH}_2\text{OCH}_2\text{CH}=\text{CH}_2 \\ \diagdown \quad \diagup \\ \quad \quad \quad \text{O} \end{array}$	$\begin{array}{c} \text{CH}_2-\text{CHCH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OEt})_3 \\ \diagdown \quad \diagup \\ \quad \quad \quad \text{O} \end{array}$	180	92

Conditions: olefin, 5.0 mmol; triethoxysilane, 5.0 mmol; 'Si'-2As-Rh, 1.0×10^{-2} mmol; temperature, 95 °C.

^a The structure of product was further identified by ¹H NMR.

^b No increase in yield with increasing the reaction time.

ing addition products in good yields. Hydrosilylation of styrene with $\text{HSi}(\text{OEt})_3$ afforded α -adduct in 18% yield in addition to the β -adduct as a major product.

The hydrosilylation of 1-decene with triethoxysilane was examined to evaluate the reusable property of 'Si'-2As-Rh. The results are shown in Fig. 2. It was demonstrated that the novel fumed silica-supported bidentate arsine rhodium complex can be recovered by simple filtration and reused several times. The hydrosilylation of 1-decene with triethoxysilane was repeated four times using the same batch of supported catalyst, the yields of decyltriethoxysilane from the first to the fourth run were 91%, 90%, 88% and 87%. The good reusable property of 'Si'-2As-Rh may be due to the fact that Rh is chelated with As in 'Si'-2As-Rh.

Acknowledgement

This work was supported by the Natural Science Foundation of Jiangxi Province in China (Project no. 0420015).

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