

SYNTHESIS AND CATALYTIC HYDROSILYLATION PROPERTY OF POLYSILOXANE-SUPPORTED MERCAPTOSELENAETHER PLATINUM OR RHODIUM COMPLEX

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Abstract Silica-bound mercaptoselenaether-containing silsesquioxane and its platinum or rhodium complex were synthesized from γ -(2,3-epithiopropyl) propyltrimethoxysilane via ring-opening reaction with bis(2-hydroxyethyl) selenide, followed by hydrolysis and immobilization on fumed silica, and then reacting with potassium chloroplatinite or rhodium chloride in acetone under nitrogen atmosphere. It was found that two noble metal complexes can catalyze the hydrosilylation of olefins with triethoxysilane effectively. The influences of temperature, the amount of complex used, the nature of olefin on catalytic activity were investigated.

Keywords Polymer-supported catalyst; Hydrosilylation catalyst; Platinum; Rhodium

INTRODUCTION

Polysiloxane-supported selenacrown ether platinum complex^[1] and selenaether platinum complex^[2] are efficient hydrosilylation catalysts. This is also true for polysiloxane-supported mercaptan platinum complexes^[3,4]. How about mercaptoselenaether platinum or rhodium complex? Clark et al. reported that the catalytic hydrogenation activity of $\text{PtLL}'\text{Cl}_2$ ($\text{L}=\text{PPh}_3$, $\text{L}'=\text{sulfide, amine}$) is higher than that of PtL_2Cl_2 or $\text{PtL}'_2\text{Cl}_2$ ^[5]. It is interesting to see what happens when mercaptoselenaether is used as mixed-bidentate ligand. Herein we report the synthesis of the first example of mercaptoselenaether mixed-bidentate platinum or rhodium complex and their catalytic behavior exhibiting in the hydrosilylation of olefins with triethoxysilane. The synthetic route is depicted below:

sequentially, was dried at 80°C/67 Pa. The yield was 0.175 g. Elemental analysis (%): C 15.17, H 2.89, S 4.12, Se 10.3, Pt 6.04.

Rhodium complex (**4**) was prepared similarly. The product was a light yellow powder. Elemental analysis (%): C 16.12, H 3.18, S 3.80, Se 11.3, Rh 10.0.

Hydrosilylation

Hydrosilylation was carried out as report elsewhere^[1,2,4]

RESULTS AND DISCUSSION

Characterization of the structure of the platinum or rhodium complex

The XPS data of the silica-bound mercaptoselenaether (**2**) and its platinum complex (**3**), rhodium complex (**4**) are shown in Table 1.

Table 1 The binding energy of polymer ligand and Pt, Rh complex

Sample	Binding energy (eV)				
	Pt _{4f7/2}	Rh _{3d}	S _{2P}	Se _{3d}	Cl _{2P}
Pt foil	71.3				
K ₂ PtCl ₄	73.3				199.4
Rh		307.0			
RhCl ₃		310.0			199.2
Polymer Ligand			163.9	55.8	
3	72.8		163.8	55.4	198.3
4		309.5	164.0	55.7	198.8

The XPS data indicate that the binding energy of platinum in **3** is 0.5 eV less than that in K₂PtCl₄ and 1.5 eV more than that in Pt foil, the binding energy of rhodium in **4** is 0.5 eV less than that in RhCl₃ and 2.5 eV more than that in Rh. These can be interpreted as results of the formation of platinum and rhodium complex, and both metals play the roles of electron acceptor. The binding energy of selenium decreases 0.4 and 0.1 eV after the silica-bound mercaptoselenaether coordinated with platinum and rhodium, respectively. The binding energy of sulfur decreases 0.1 eV in platinum complex and increases 0.1 eV in rhodium complex. In general, the binding energies of selenium and sulfur ought increase after the polymer ligand coordinated with platinum or rhodium. However, in polysiloxane-supported selenather platinum complex, the binding energy of selenium decreases 0.7 eV after coordination^[2], in mercaptoamine platinum and rhodium complex, the binding energies of sulfur both decrease 0.3 eV^[4]. A possible explanation is that the σ bonding (S, Se→Pt, Rh donation) is balanced by the π bonding (Pt, Rh→S, Se donation), and

the total electron density on S or Se atom varied very small. The π bond feedback phenomenon was also observed in phosphine transitional metal complexes^[9].

The catalytic behavior exhibiting in the hydrosilylation of olefins with triethoxysilane

It was found that the complexes both exhibit high catalytic activity in the hydrosilylation of olefins with triethoxysilane. The catalytic activity was evaluated via the following ways:

Influence of temperature and the amount of complex used. The addition of triethoxysilane to decene-1 was used to test the catalytic activity at a series of selected temperature. The results are shown in Table 2.

Table 2 Influence of reaction temperature

T (°C)	Sil—Se—S—Pt			Sil—Se—S—Rh		
	IP ^a (min)	t ^b (min)	Yield (%)	IP (min)	t (min)	Yield (%)
60	45	90	80	55	45	72
70	25	50	88	20	40	80
80	10	40	84	5	20	84
90	5	35	88	0	40	62

a. Induction Period; b. Yield is not increased with the increase of time

Conditions: Sil—Se—S—Pt 1.24×10^{-3} mmol of Pt; Sil—Se—S—Rh 4.86×10^{-3} mmol of Rh; Decene-1 5.0 mmol; Triethoxysilane 5.0 mmol

Table 2 shows that the platinum complex exhibits higher activity than rhodium complex does. Except rhodium complex at 90°C, the higher the temperature, the shorter the induction period, and the higher the yield of decyltriethoxysilane (the yield of decyltriethoxysilane is somewhat lower at 80°C using Sil—Se—S—Pt). In comparison with the selenaoether platinum complex at 80°C^[2] and mercaptoamine platinum complex at 100°C^[4], its yield at 70°C is almost the same, but it exhibits higher activity at lower temperature. The catalytic activity is also higher than that of other bidentate thioether platinum complex^[10]. The same conclusion can be made for Sil—Se—S—Rh in comparison with mercaptoamine rhodium complex^[4].

The yield of decyltriethoxysilane increases with the increase of the amount of platinum complex used. When the amount of platinum complex used was 1.55×10^{-4} , 3.10×10^{-4} and 1.24×10^{-3} mmol of Pt, the yield was 78, 82 and 88% at 70°C, respectively. The yield of decyltriethoxysilane was 92, 94, and 84%, at 80°C in the present of 1.26, 2.43 and 4.86×10^{-3} mmol of Rh in Sil—Se—S—Rh. This can be attributed to the side reaction of transformation of triethoxysilane to tetraethoxysilane and it is more sensitive to the amount of rhodium complex used. The similar phenomenon was

observed when poly-4,7-dithiadecen-9-ylsilsesquioxane rhodium complex was used as hydrosilylation catalyst^[11].

Influence of various kinds of olefins on the yield of hydrosilylation adduct. When the amount of platinum complex used was 6.20×10^{-4} mmol of Pt, the yield of hydrosilylation adduct of phenylallylether, allylbenzene and allylglycidylether at 70°C was 86, 74, 40 and 24%, respectively. For rhodium complex (80°C, 4.86×10^{-3} mmol of Rh), the yield was 84%, —, 82% and 80%, respectively. The rhodium complex was not so sensitive to the nature of substrate.

The recovery and reusability of platinum and rhodium complex.

The recovery and reusability property of platinum complex is excellent. The yield of decyltriethoxysilane (70°C, 4.7×10^{-3} mmol of Pt) was almost the same from the first run to sixth run, and decreased from about 82 to 50% at the seventh run. When the rhodium complex was reused, the yield (80°C, 2.4×10^{-2} mmol of Rh) decreased from 80 at first run to 20%.

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