

SYNTHESIS OF POLYSILOXANE-SUPPORTED SELENAETHER PLATINUM COMPLEX AND ITS CATALYTIC PROPERTY FOR HYDROSILYLATION OF OLEFINS

LU Xueran (卢雪然) CHEN Zhen (陈臻) and DUAN Heping (段和平)

(Department of Chemistry, Wuhan University, Wuhan 430072)

CHEN Yifan (陈亦凡)

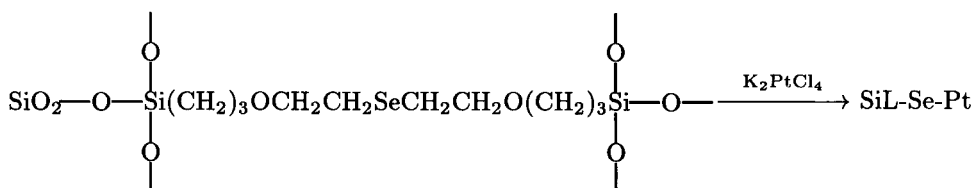
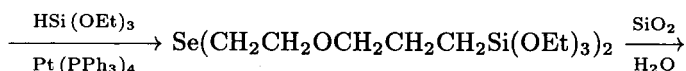
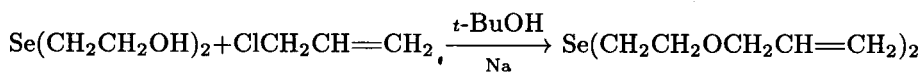
(The Center of Analysis and Measurement, Chinese Geology University, Wuhan 430074)

ABSTRACT

A new type of selenious polymer, silica-bound polybispropoxyethyl-selenidesilsesquioxane, and its platinum complex were synthesized from bis-allyloxyethyl selenide via hydrosilylation with triethoxysilane, followed by immobilized on fumed silica, and then reacting with potassium chloroplatinite under nitrogen atmosphere in acetone. It was found that the platinum complex can catalyze the hydrosilylation of olefins with triethoxysilane effectively. The effects of the nature of the substrate, the amount of complex used, and the reaction temperature on the catalytic activity were investigated.

INTRODUCTION

Recently, Yao et al. reported that 1,1'-bis(benzylseleno)-ferrocene platinum complex was an efficient hydrosilylation catalyst for olefins^[1]. We have also found that the selenacrown ether platinum complexes^[2,3] and the polysiloxane-supported selenacrown ether platinum complex^[4] are efficient hydrosilylation catalysts. No other paper concerning the selenious polysiloxane and its platinum complex has been published until now. In this paper, we report the synthesis of bis-allyloxyethylselenide, its hydrosilylation and immobilization on fumed silica, and the catalytic behavior of the platinum complex exhibiting in the hydrosilylation of olefins with triethoxysilane. The synthetic route is depicted below:



EXPERIMENTAL

Infrared spectra, proton nuclear magnetic resonance spectra, and X-ray photoelectron energy spectra were obtained from 170-SX FT-IR, EM-360L spectrometer, and Kratos XSAM 800 electron energy spectrometer, respectively. Elemental analyses were performed on a Model 1106 elemental auto-analyzer. Gas chromatographic analyses were carried out on a Model 102G chromatograph with a thermal conductivity detector, SE-30 stationary phase, silylanized 101 white matrix. $(\text{HOCH}_2\text{CH}_2)_2\text{Se}$ and $\text{Pt}(\text{PPh}_3)_4$ were prepared according to literatures [4] and [5], respectively. Other chemicals are C.P. or A.R. grade reagents.

1. Synthesis of bis-(allyloxyethyl) selenide

1.22 g (0.053 mol) of sodium metal was dissolved in 60 ml of *t*-BuOH, to this solution 4.0 g (0.0236 mol) $(\text{HOCH}_2\text{CH}_2)_2\text{Se}$ in 10 ml of THF was added slowly, and stirred continuously for 1.5 h at reflux temperature. 15 ml (0.184 mol) of allyl chloride was added with stirring, and the reaction was continued at 80°C for 6 h under nitrogen atmosphere. The mixture was stood overnight. After filtration, the solution was distilled under reduced pressure. 3.6 g of bis-(allyloxyethyl) selenide was obtained after passing the crude product through a silica column. The yield was 61%. Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{SeO}_2$: C 48.20, H 7.28, Se 31.69. Found; C 48.23, H 7.34, Se 30.90. ^1H NMR: 2.7 (t, 4H, SeCH_2), 3.6 (t, 4H, $\text{O—CH}_2\text{—C}$), 4.0 (b, 4H, $\text{O—CH}_2\text{—C=}$), 5.0–6.1 (m, 6H, CH=CH_2) ppm. IR (cm^{-1}): 3079, 2929, 2853, 1471, 1450 (C—H), 923, 997 ($\text{CH}_2=\text{CH}$), 1648 (C=C), 1272, 1089 (C—O).

2. Synthesis of platinum complex

A mixture of bis-(allyloxyethyl) selenide (1.16 g, 0.0046 mol), triethoxysilane (10 ml, 0.055 mol), and tetra-(triphenylphosphine) platinum complex (0.030 g, 0.024

mmol) was stirred at 80°C for 72 h. The cooled mixture was passed through a sinter glass filter in which alumina was packed to the height of 2 cm to remove the platinum complex. 3.0 g of bis-(triethoxysilylpropoxyethyl) selenide was obtained as a red oil in 89% yield. Its ^1H NMR spectra showed that no peak of protons attached on the double bond appeared, and a peak of 0.5 ppm (t, SiCH_2) appeared. The adduct was added to a suspension of 3.5 g of fumed silica (150–200 m^2/g) in 60 ml of toluene, stirred at 110°C for 10 h under nitrogen, and then for another 5 h after the addition of 5 ml of distilled water. The solid product was filtered, dried at 120°C/67 Pa for 4 h, and then ground in an agate mortar. After extracting with acetone in a Soxhlet apparatus for 24 h, 3.5 g of grey powder was obtained. Found; C 4.82, H 0.75, Se 3.16. The selenather content in the immobilized product was 0.40 mmol/g calculated from the selenium content.

A mixture of the above mentioned polymer ligand (0.96 g), potassium chloroplatinite (0.12 g), and acetone (30 ml) was stirred under nitrogen at reflux temperature for 72 h. The light yellow powder after being washed with acetone three times, twice with distilled water, and again with acetone was dried at 120°C/67 Pa for 4 h. Found: Pt 3.52%. The XPS data of the silica-bound selenather (ligand) and its platinum complex are shown in Table 1.

Table 1 The binding energy of ligand and its platinum complex

Sample	Binding energy (eV)			
	Pt 4f 7/2	Se 3d	O 1s	Cl 2p
Pt foil	71.3			
K_2PtCl_4	73.1			199.2
Ligand		55.9	533.2	
Sil-Se-Pt	72.5	55.2	533.45	195.6

The XPS data indicate that the binding energy of platinum in Sil-Se-Pt is 0.6 eV less than that in K_2PtCl_4 , and 1.2 eV more than that in Pt foil. This can be interpreted as a result of the formation of platinum complex, and the platinum atom plays a role of electron acceptor. The binding energy of selenium decreases 0.7 eV after the silica-bound selenather is coordinated with platinum. It is striking that the selenium atom is the softest base among the coordinated atoms. A possible explanation is that the π bonding ($\text{Pt} \rightarrow \text{Se}$ donation) is superior to σ bonding ($\text{Se} \rightarrow \text{Pt}$ donation) and the total electron density on Se atom increases. A similar phenomenon was observed by Blackburn in triphenylphosphine transition metal complex^[6]. The decrease of Cl 2p is not very surprising, because similar variation was reported when

PtCl_2 was coordinated with Et_2S [7]. The binder energy of oxygen increases 0.25 eV after the ligand coordinated with platinum, this fact is in accord with transferring electron pair from oxygen to platinum atom. As the increase is small, whether or not the oxygen atoms participate in the formation of platinum complex is not so certain.

3. Hydrosilylation

Hydrosilylation experiments were carried out as reported elsewhere [2-4].

RESULTS AND DISCUSSION

It was found that the platinum complex exhibited high catalytic activity in the hydrosilylation of olefins with triethoxysilane. The catalytic activity of the platinum complex was evaluated via the following respects:

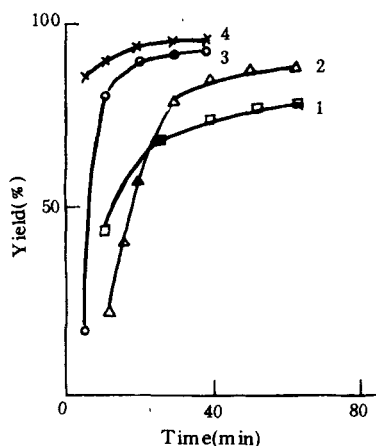


Fig.1 Plot of the yield of decyltriethoxysilane vs. time at various temperatures. Decene 5.0 mmol, $\text{HSi}(\text{OEt})_3$ 5.0 mmol, complex 9×10^{-4} mmol of Pt. Curves for: 1) 60°C; 2) 80°C; 3) 100°C; 4) 120°C

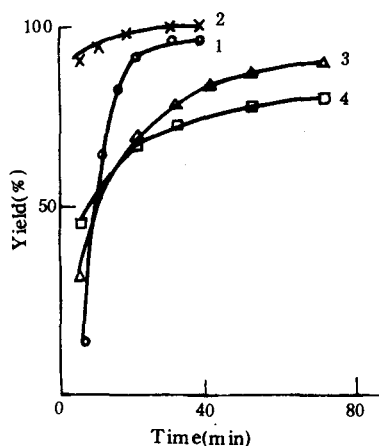


Fig.2 Plot of the yield of decyltriethoxysilane vs. time with various amounts of Pt complex at 80°C. Curves for: 1) 9.0×10^{-5} ; 2) 1.8×10^{-4} ; 3) 4.5×10^{-4} ; 4) 9.0×10^{-4} mmol of Pt. Other conditions are the same as in Fig.1

1. Influence of temperature

The hydrosilylation of 1-decene with triethoxysilane was used to test the catalytic activity at different selected temperatures. The result is shown in Fig.1. At 80°C, the yield of decyltriethoxysilane reached 95%, and decreased with further increasing temperature. In other words, the most suitable temperature is 80°C. For the silica-supported selenacrown ether platinum complex, the yield of decyltriethoxysilane is increased with the increase of temperature from 50 to 110°C [4].

2. Influence of the amount of platinum complex used

The yield of decyltriethoxysilane increases with the increase of the amount of platinum complex used. When the amount of platinum complex used was 9.0×10^{-5} mmol, the turnover number was about 44,000.

3. Influence of various kinds of olefins on the yield of hydrosilylation adduct

Dodecene, decene, and allylphenyl ether were used as probes to explore the catalytic activity of the platinum complex on various olefins. The results are shown in Fig.3. It indicates that the catalyst is very effective for the hydrosilylation of decene, as the yield of adduct is more than 95%. The relative activity of substrates is in the order of decene > allylphenyl ether > dodecene taking the final yield of adduct as comparative standard. It is obvious that the steric effect may play an important role, but other factors, such as the polarity of substrate, can not be ignored.

4. The recovery and reusability of platinum complex

The platinum complex can be used for several runs, however, the induction period for each run becomes longer, and the yield of decyltriethoxysilane decreases remarkably at the fifth run.

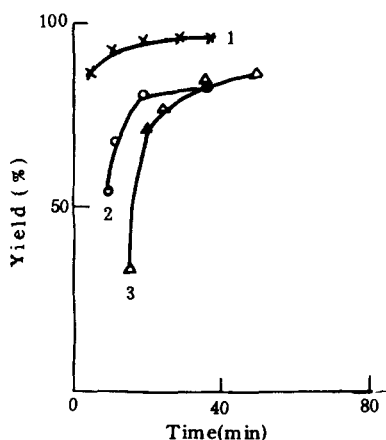


Fig.3 Plot of the yield of hydrosilylation adduct vs. time at 80°C with 9.0×10^{-4} mmol of Pt. Other conditions are the same as in Fig.1. Curves for: 1) decene; 2) dodecene; 3) allyl phenyl ether

5. Effect on adding of mercury

It was reported that mercury can be used as a selective poison for heterogenous (colloidal) catalysts while homogenous ones (molecular compounds) are unaffected

by Hg^[8]. It was found that the hydrosilylation of decene with triethoxysilane proceeds smoothly when Hg is added, although the yield drops to 80%. This fact confirms that the active component of the hydrosilylation catalyst is homogeneous in nature, i.e. platinum complex.

Keywords:

Selenaether; Platinum; Hydrosilylation catalyst; Hydrosilylation; Polysiloxane

REFERENCES

- [1] Yao, J.Z.; Tian, B.S. and Chen, Y.Y., *Chin. Chem. Letts.*, **1993**, 4: 601.
- [2] Liu, X.F.; Li, W.P.; Zhang, L.F., et al., *Chin. Chem. Letts.*, **1992**, 3: 255.
- [3] Li, W.P.; Liu, X.F.; Lu, X.R., et al., *Chin. Chem. Letts.*, **1994**, 5: 49.
- [4] Lu, X.R.; Zhang, L.F.; Wang, Z.X., et al., *Chem. Res. Chin. Univ.*, **1994**, 10(2): 126.
- [5] Malatesta, L. and Cariello, C., *J. Chem. Soc.*, **1958**, June, 2323.
- [6] Blackburn, J.R.; Nordberg, R.; Stevie, F., et al., *Inorg. Chem.*, **1970**, 9: 2374.
- [7] Clark, D.T.; Briggs, D., and Adawis, D.B., *J. Chem. Soc., Dalton Trans.*, **1973**, (2): 169.
- [8] Lewis, L.N. and Lewis, N., *J. Am. Chem. Soc.*, **1986**, 108: 7228.