

CROWN FUNCTIONALIZED LINEAR POLYSILOXANE PLATINUM COMPLEX AS HYDROSILYLATION CATALYST*

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ABSTRACT

A modified method of preparing crown functionalized linear polysiloxane has been described. 4'-allylbenzo-15-crown-5 was subjected to hydrosilylation with methyldichlorosilane, followed by polycondensation with silanol-terminated polydimethylsiloxane to give the title crown functionalized linear polysiloxane. It was found that the polysiloxane could be coordinated with platinum salt to form platinum complex, which could catalyze the hydrosilylation of olefins with triethoxysilane efficiently.

INTRODUCTION

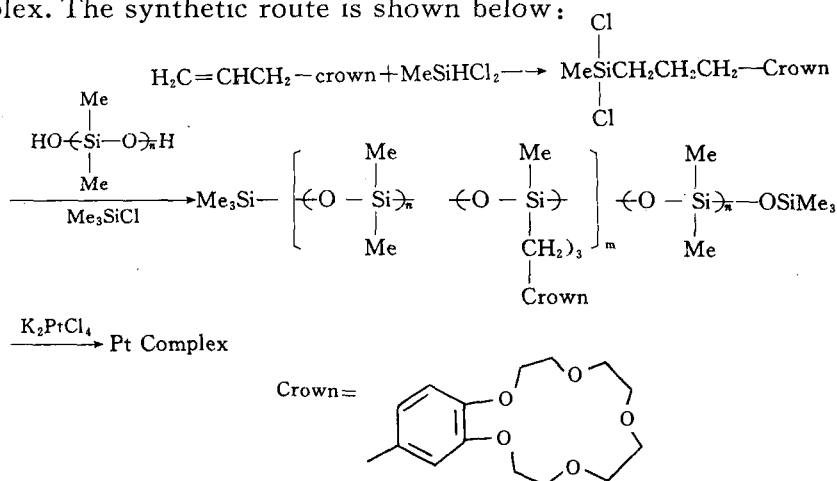
Crowns attached to silica, silica gel or polysiloxane backbone have attracted increasing attention recently^[1]. Polysiloxanes with pendant crown ether moieties were used as phase transfer catalysts^[2], excellent stationary phases for capillary chromatography^[3,4]. Polysiloxane-coupled crown ethers are able to facilitate the ion transport through a supported liquid membrane^[5]. As to the investigation of the complexation ability of this type of polymers toward heavy and noble metal ions and the catalytic behavior of the obtained metal complexes, it has not been reported in the literature yet.

In the published papers, there are several routes for the preparation of the crown functionalized linear polysiloxane. The first example was given by us in 1982. By hydrosilylation of 3'-or 4'-allylbenzo-15-crown-5 with methyldichlorosilane, the crown ether-containing silicon monomers were

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obtained. The monomers were subjected to hydrolysis with water to give the title polymers^[2]. There is one crown ether moiety per chain unit in such polymers. In 1987, Bayona et al. adopted a modified route, i. e. hydrosilylation of allyloxymethyl-18-crown-6 with polymethylhydrosiloxane, to synthesize the same type of linear polysiloxane directly^[3]. The density of crown ether moiety can be adjusted, but the hydrosilylation of alkenyl crown ether is incomplete, some decene must be added to completely substitute the residual Si—H in polymethylhydrosiloxane. Thus, the structure of the product is difficult to be characterized. Wienk et al. reported a third method; coupling hydroxymethyl crown ethers with 4-bromobutyl-terminated polydimethylsiloxane in THF in the presence of NaH as a base^[5]. However, the applications of this method are limited due to the multi-step synthesis of 4-bromobutyl-terminated polydimethylsiloxane and the type of the obtained polymers. With other applications in mind, we wish to design a general procedure to synthesize a range of crown ether functionalized linear polysiloxane through this procedure, the density of crown ether moiety and the length of the chain segment without crown ether moiety can be adjusted, the molecular weight of the polymer is easy to be controlled, and the structure of the polymer is easy to be characterized. In the present work, we wish to report the new synthetic route, i. e. polycondensing crown ether-containing silicon monomer with silanol-terminated polydimethylsiloxane in designed ratio, and also, the synthesis and catalytic property of its platinum complex. The synthetic route is shown below:



EXPERIMENTAL

PMR, IR, and XPS spectra were obtained on EM-360L spectrometer,

Nicolet 170 SX FT-IR spectrometer, and Kratos XSAM 800 electron spectrometer, respectively. GLC was carried out on 102G model chromatography, using thermal conductivity detector, SE-30 stationary phase, and silylanized white matrix. 4'-Allylbenzo-15-crown-5 was synthesized as reported^[2].

A mixture of 4'-allylbenzo-15-crown-5 (1.54 g, 5 mmol), methyldichlorosilane (2.3 g, 20 mmol), a drop of $\text{H}_2\text{PtCl}_6 \cdot i\text{-PrOH}$ (0.1 mol/L) and THF (20 mL) was stirred at ambient temperature for 2 h, and then at reflux temperature for 20 h. The solution was distilled under reduced pressure. 4'-Methyldichlorosilylpropylbenzo-15-crown-5 was obtained as slightly yellow oil in quantitative yield. ^1H NMR spectra showed that no peak of protons on double bond appeared, and a peak of 0.5 ppm (t, SiCH_2) appeared. It was used directly in the next step without further purification.

Synthesis of polysiloxane with pendant benzo-15-crown-5 moieties

A mixture of 4'-methyldichlorosilylpropylbenzo-15-crown-5 (5 mmol), silanol-terminated polydimethylsiloxane (6.0 g, 10.5 mmol), and benzene (45 mL) was stirred at reflux temperature for 10 h under nitrogen. 1.5 mL of trimethylchlorosilane was added to the above-mentioned solution, and the stirring was continued at reflux temperature for 10 h. After distilling off the solvent and surplus trimethylchlorosilane, a viscous oil residue was obtained. The residue was dissolved in 50 mL of dichloromethane, washed with distilled water until the pH value of the solution was 6–7. The solution was distilled under reduced pressure to remove dichloromethane. 7.25 g of crown functionalized linear polysiloxane was obtained as viscous oil in a yield of 89.6%. $\bar{M}_n$ was 3270 (VPO). ^1H NMR: 7.0–7.2 (s, ArH), 3.8–4.5 (m, OCH_2), 1.0–1.8 (m, $\text{Si}-\text{C}-\text{CH}_2\text{CH}_2$), 0.4–0.8 (t, SiCH_2), 0.1 (s, SiCH_3) ppm. IR (cm^{-1}): 2972, 2863 (C–H), 1557, 1511 (Ph), 1100–1000 (b, Si–O–Si, C–O–C). Elemental analysis: C 36.65, H 7.58. The crown ether content was 0.61 mmol per gram of polysiloxane.

Synthesis of platinum complex

A mixture of 1.0 g of the above mentioned polymer ligand, 0.137 g of K_2PtCl_4 , and 50 mL of acetone was stirred under argon at reflux temperature for 72 h. The solid product was filtered by suction, washed with acetone, distilled water, acetone successively and dried at $110^\circ\text{C}/0.27\text{ kPa}$ for 12 h. The platinum complex was obtained as slightly pale powder. Found: Pt 0.45%. Binding energy of $\text{Pt}_{4f7/2}$: 73.0 eV; O_{1s} 534.4 eV; Cl_{2p} 196.9 eV. The

binding energy of $\text{Pt}_{4f7/2}$ is 0.2 eV less than that in K_2PtCl_4 , 0.5 eV less than that in PtCl_2 , and 1.7 eV more than that in platinum foil. This can be explained as the result of formation of platinum complex, and the platinum atom plays a role of electron acceptor. The binding energy of O_{1s} increases 0.4 eV after polymer ligand coordinating with platinum, this fact is in accord with transferring electron pair from oxygen to platinum atom, as expected.

Hydrosilylation experiments

Hydrosilylation experiments were carried out in a 5 mL plane-bottomed flask connected with a condenser to the upper end of which a drying system was attached. 5.0 mmol of olefin and a weighed amount of platinum complex were stirred for 20 min before triethoxysilane was added. The reaction was monitored by GLC, and the yield of hydrosilylation product was determined by standard sample and standard curve.

RESULTS AND DISCUSSION

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

Influence of temperature on the activity of platinum complex

The hydrosilylation of 1-decene with triethoxysilane is used to test the catalytic activity at a series of selected temperature. The result is shown in Fig. 1. The platinum complex exhibits high catalytic activity in the range of 70 to 100°C. The induction period decreases with the increasing of temperature, but the yield of decyltriethoxysilane varies little or nothing within the temperature from 80 to 100°C, i. e. $89 \pm 1\%$.

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

Decene, dodecene, allyl phenyl ether, and allyl glycidyl ether were used as substrates to test the catalytic activity and selectivity of the platinum complex. The results indicate that the

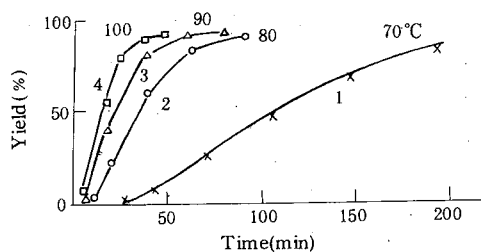


Fig. 1 Plot of the yield of decyltriethoxysilane vs. time at selected temperature
1) 70; 2) 80; 3) 90; 4) 100°C
Conditions: Decene 5 mmol; $\text{HSi}(\text{OET})_3$ 5 mmol; Platinum complex 2.3×10^{-4} mmol of Pt

catalyst is very effective for the hydrosilylation of allyl phenyl ether and the two aliphatic alkenes, the yields of adducts are more than 90%, even more than 95% in the case of allyl phenyl ether as shown in Fig. 2, but for allyl glycidyl ether, no reaction takes place within 120 min.

Recovery and reuse of the platinum complex

The platinum complex can be recovered and reused for several times. However, the induction period becomes longer with increasing run, and the yield of decyltriethoxysilane at each run is almost the same, as shown in Fig. 3

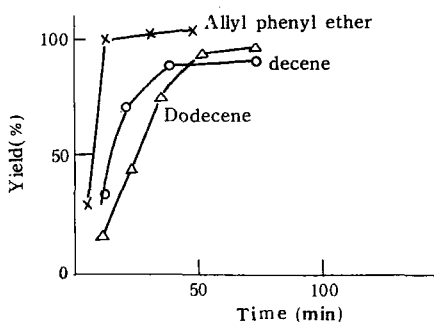


Fig. 2 Plot of the yield of hydrosilylation adduct vs. time at 90°C Conditions: Pt complex 2.31×10^{-4} mmol of Pt

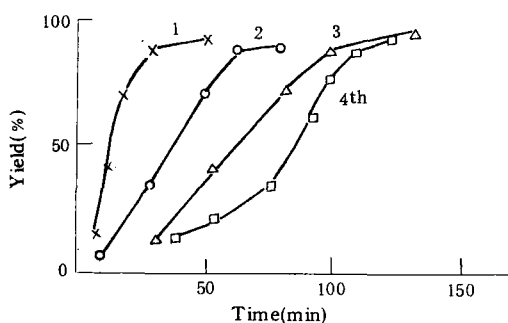


Fig. 3 Plot of the yield of decyltriethoxysilane vs. time with 2.31×10^{-4} mmol of Pt at 90°C in sequential run

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^[6]. It was found that the hydrosilylation of decene with triethoxysilane proceeded equally smoothly with or without Hg in the presence of the catalyst, as shown in Fig. 4. This fact confirms that the active component of the hydrosilylation is homogeneous in nature, i. e. platinum complex.

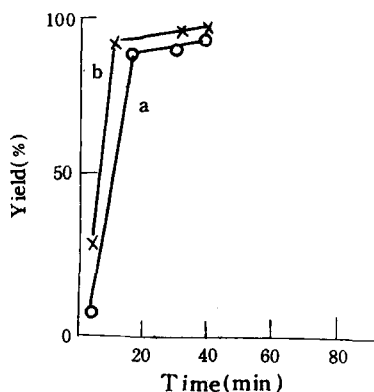


Fig. 4 Plot of the yield of decyltriethoxysilane vs. time (a) with or (b) without Hg at 90°C

Keywords:

Functionalized polysiloxane; Crown ether; Platinum complex; Hydrosilylation catalyst; Polymeric crown ether

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