

A NEW TYPE OF CROWN FUNCTIONALIZED POLYSILOXANE AND ITS PLATINUM COMPLEX

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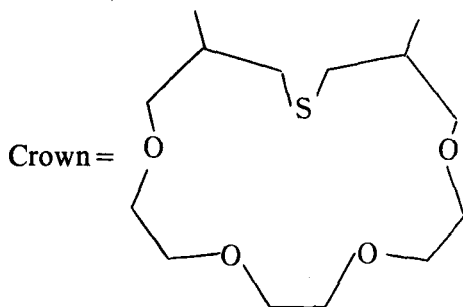
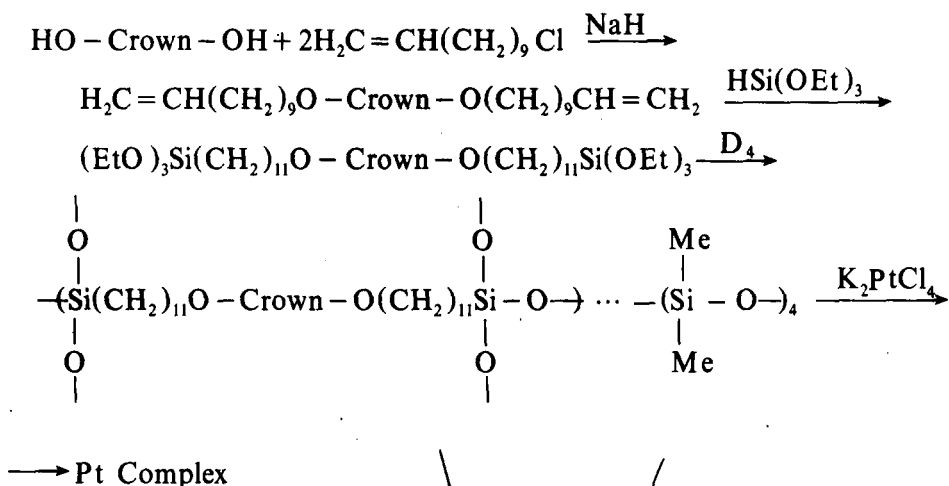
ABSTRACT

A new type of crown functionalized polysiloxane, in which the crown moieties were incorporated into main chain, and its platinum complex were synthesized. The polysiloxane was synthesized from 3, 16-dihydroxy-1-thia-5, 8, 11, 14-tetraoxacycloheptadecane via etherification with ω -chloroundecene, followed by hydrosilylation with triethoxysilane, cohydrolysis with D_4 , sequentially. Treating the polysiloxane with potassium chloroplatinite, the title complex was obtained. It was found that the platinum complex exhibited high catalytic activity in the hydrosilylation of olefins with triethoxysilane.

INTRODUCTION

Organosilicon compounds and crown ethers both have their own characters. It is interesting to see what will happen when these two kinds of compounds were combined. The first report on crown-modified silica gel was published in 1975 by Cram and his coworkers^[1]. They attached chiral bis-dinaphtho-22-crown-6 to silica gel and used the immobilized crown ethers as stationary phase in solid-liquid chromatography to totally resolve chiral amine salts. In 1982, we first realized the hydrosilylation of 3- or 4-allylbenzo-15-C-5 with trichlorosilane and methyl dichlorosilane, and obtained linear polysiloxane, polysilsesquioxane with pendant crown ether moieties and silica-bound crown ethers^[2]. In 1987, Lee et al. adopted a modified route, i.e. hydrosilylation of alkenyloxymethyl crown ether with polymethylhydrosiloxane directly, to synthesize the same type of linear silicone with pendant crown ether moieties^[3]. Besides, linear polysiloxane with pendant azacrown ether moieties^[4], silica gel-bound crown ethers^[5], azacrown ethers^[6], and thiocrown ethers^[7] have been also reported, although specific details of the silica gel-bound thiocrown ethers was not given. However, in all the published papers, the crowns were attached to the polysiloxane backbone via an alkyl spacer or grafted to silica, silica gel. No paper has reported yet the crown ether-containing polysiloxane in which the crowns were incorporated into the main chain.

In the present work, we wish to report a general route for the synthesis of crown functionalized polysiloxane in which the crowns are incorporated into the main chain. The following synthetic route is adopted: (a) preparation of dialkenyl-substituted crown ether; (b) conversion of the crown ether to $(RO)_3Si(CH_2)_n$ -crown- $(CH_2)_nSi(OR)_3$; (c) cohydrolysis of the above-mentioned silicon monomer with D_4 . The synthetic scheme is shown below:



EXPERIMENTAL

PMR, IR, MS, and XPS spectra were obtained on EM 360L spectrometer, IR-440 spectrometer, KRATOS ZAB HF-HF mass spectrometer, and KRATOS XSAM 800 electron energy spectrometer, respectively. GLC was carried out on 102G model chromatography, using thermal conductivity detector, SE-30 stationary phase, and silylanized white matrix. 3,16-Dihydroxy-1-thia-5,8,11,14-tetraoxa-cycloheptadecane was synthesized according to Ref. [8].

Synthesis of 3,16-bis (undecenylloxy)-1-thia-5,8,11,14-tetraoxacycloheptadecane

A mixture of 3,16-dihydroxy-1-thia-5,8,11,14-tetraoxacycloheptadecane (2.96g, 0.01mol), ω -chloroundecene (4.2g, 0.022mol), sodium hydride (1.2g, 0.05mol), and diglyme (100mL) was stirred at 100 °C under nitrogen atmosphere for 24h. Insoluble matters were removed by filtration. The filtrate was distilled under reduced pressure to recover diglyme and chloroundecene, and the residue was passed through a neutral alumina column. The eluents with the same R_f value were combined and concentrated to give a slightly yellow viscous oil (3.97g, 66.1 %). Calcd. for $\text{C}_{34}\text{H}_{64}\text{O}_6\text{S}$: S 5.33; Found: S 5.04%. PMR: 1.20-1.60 (m, 28H), 1.80-2.20 (m, 4H), 2.60-2.90 (m, 4H), 3.30-3.80 (m, 22H), 4.60-5.10 (t, 4H), 5.40-6.00 (m, 2H) ppm. IR: 3079, 2878, 1640, 1351, 1150, 1100, 998, 920, 722 cm^{-1} . MS: m/z 599 (M-1) 623 (M+Na)^[9]. n_D^{25} 1.4810.

Synthesis of 3,16-bis (triethoxysilylundecyloxy)-1-thia-5,8,11,14-tetraoxacycloheptadecane

A mixture of 3,16-bis (undecenylloxy)-1-thia-5,8,11,14-tetraoxa-cyclo-

heptadecane (2.0g, 3.3mmol), triethoxysilane (5 mL, 27.4mmol), and tetrakis (triphenylphosphine) platinum complex (10mg, 0.008mmol) was stirred at 100°C for 15h. The cooled mixture was passed through a sintered glass filter in which alumina was packed to 3cm layer. The residue was washed three times with absolute ether. The combined filtrate was concentrated to give 3, 16-bis (triethoxysilylundecyloxy) - 1 - thia - 5, 8, 11, 14 - tetraoxa-cycloheptadecane, a slightly yellow viscous oil (2.83g, 92.3%). Its PMR spectra showed that no peak of proton attached to the double bond (δ , 4.6-6.0) was found and a new triplet peak around 0.5ppm due to the proton of Si-CH₂ in Si-CH₂-CH₂ appeared. Calcd. for C₄₆H₉₆O₁₂SSi₂: S 3.46; Found: 3.65%. IR: 2878, 1450, 1100, 795cm⁻¹.

Synthesis of the title polymer, crown functionalized polysiloxane

A mixture of 3,16-bis (triethoxysilyldecyloxy) - 1 - thia - 5,8,11,14 - tetraoxa-cycloheptadecane (1.03g, 1.11mmol), octamethylcyclotetrasiloxane(D₄) (0.66g,2.22 mmol), toluene(10mL), and 4% sulfuric acid (1mL) was stirred at ambient temperature for 15h. The reaction was continued at reflux temperature until the viscosity of the system stopped increasing. Three drops of trimethylchlorosilane were added to this system, and stirring was continued at reflux temperature for 5h. A slightly yellow elastomer was obtained. After removing toluene by vacuum the product was washed thoroughly with distilled water until the rinsed water remained neutral, and then washed with a small amount of acetone. Dried at 100 °C under reduced pressure, and ground in an agate mortar, a slightly yellow powder was obtained. Found: C 47.69, H 8.39%.

Synthesis of platinum complex

A mixture of the above polymer ligand (1.6g), potassium chloroplatinite (0.2802 g, 0.675mmol), and acetone (40mL) was stirred under argon atmosphere at reflux temperature for 48h. The complex was filtered off, washed with distilled water, acetone and then dried under vacuum. Found: Pt 7.43, Cl 3.03%.

Hydrosilylation experiments

Hydrosilylation experiments were carried out in a 5mL plane-flask connected with a condenser to the upper end of which a drying system was attached. 5.0mmol of olefin and a weighed amount of platinum complex were stirred at the reaction temperature for 30min. 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

1. Characterization of the structure of the platinum complex

The structure of the platinum complex was characterized by elemental analysis and XPS. The result of elemental analysis shows that the molar ratio of platinum to chlorine is 1:2.2, a value approximates that in PtCl₂. The XPS data show that the binding energy of platinum is 72.55eV, 0.55eV less than that in K₂PtCl₄, and

1.25eV higher than that of platinum foil. On the other hand, the binding energy of sulfur is 163.8eV, 0.7eV higher than that in polymer ligand. The above data can be explained as the result of the formation of platinum-sulfide complex, and the platinum plays a role of electron-acceptor, and sulfur, a role of electron-donor as expected. The difference of Cl_{2p} binding energy of chlorine can be also explained in the same way. It was reported that the binding energy of chlorine is 197.6, and 197.8eV in *cis*- and *trans*-(Et_2S) $_2PtCl_2$, respectively^[9], nearly the same as that in the platinum complex, as shown in Table 1.

Table 1 The binding energy of platinum complex

Sample	Binding energy (eV)*			
	Pt4f7/2	S2p	Cl2p	O1s
Pt foil	71.3			
K ₂ PtCl ₄	73.1		199.2	
Polymer ligand		163.1		531.8
Platinum complex	72.55	163.8	197.65	531.8

* The binding energies are all relative to $C_{1s}=285.0eV$

It was reported that mercury can be used as a selective poison for heterogeneous (colloidal) catalysts while homogeneous ones (molecular compounds) are unaffected by $Hg^{[10]}$. The effect of mercury on the catalytic activity of the title catalyst was investigated. It was found that the hydrosilylation of decene with triethoxysilane proceeded equally smoothly with or without Hg in the presence of the catalyst. These results confirm that the active component of the hydrosilylation reaction is homogeneous in nature, i.e. platinum complex.

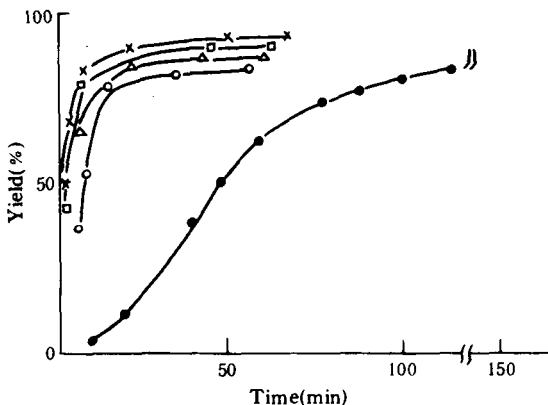


Fig. 1 Yield of decyltriethoxysilane vs. time at various temperature

Conditions: decene 5.0mmol; triethoxysilane 5.0 mmol; platinum complex, 3.3×10^{-4} mmol

(●) 60, (○) 70, (△) 80, (□) 90, (x) 100 °C

2. Influence of temperature on the activity of platinum complex

The reaction, hydrosilylation of dec-1-ene with triethoxysilane, is used to examine the influence of temperature

on the catalytic activity of platinum complex. The result is shown in Fig. 1.

As shown in Fig. 1, the platinum complex exhibits high catalytic activity in this reaction, especially, when temperature is above 70 °C. No obvious induction period is observed, and the yield of decyltriethoxysilane is more than 80% within 15min. At 60 °C, an induction period about 10min is observed. Increasing the temperature, the yield as well as the reaction rate of decyltriethoxysilane increases.

3. Influence of the amount of platinum complex used

The yield of decyltriethoxysilane is insensitive to the variation of the amounts of platinum complex used, as shown in Fig. 2. The turnover number amounts to 50,000 in the case of using 8.1×10^{-5} mmol of platinum complex.

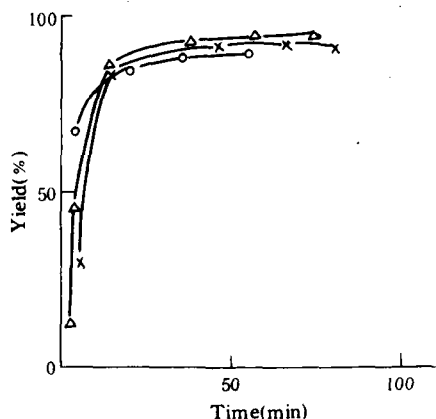


Fig. 2 Yield of decyltriethoxysilane vs. time using various amount of platinum complex

Conditions: decene, 5.0 mmol; $\text{HSi}(\text{OEt})_3$, 5.0 mmol; 80 °C
(○) 3.8×10^{-4} , (△) 2×10^{-4} , (×) 8.1×10^{-5} mmol of Pt

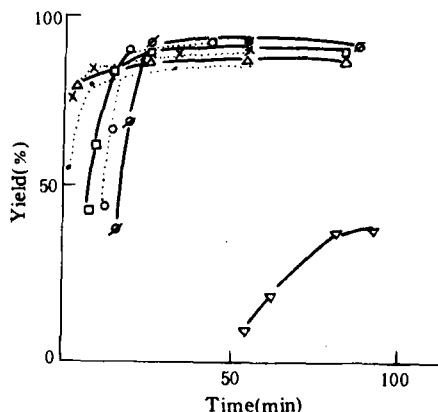


Fig. 3 Yield of decyltriethoxysilane vs. time at various runs

(●) 1st-3rd; (△) 4th-7th; (×) 8th-9th;
(□) 10th-11th; (○) 12th; (○) 13th; (△) 14th.
Others are as given in Fig. 2

The recovery and reused properties of platinum complex

The platinum complex can be used at least thirteen runs and the yield of decyltriethoxysilane is unchanged in the region of experimental error, as shown in Fig. 3.

Keywords:

Functionalized polysiloxane, Thiocrown ether, Platinum complex, Hydrosilylation catalyst

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REFERENCES

- [1] Dotsevi, G.; Sogah, Y. and Cram, D. J., *J. Am. Chem. Soc.*, **1975**, 97, 1358.
- [2] Chen, Y. Y., Yuan, G. P., 2nd China-Japan-USA Symposium on Organometallic and Inorganic Chemistry, Shanghai, China, B 11c, **1982**, p.135.
- [3] Bayona, J.M.; Tarbet, B.J.; Chang, H.C.; Schregenberger, C.M.; Nishioka, M.; Markides, K.E.; Bradshaw, J.S. and Lee, M.L., *Intern. J. Environ. Anal. Chem.* **1987**, 28, 263.
- [4] Abed-ali, S.S.; Brisdon, B.J. and England, R., *Macromolecules*, **1989**, 22, 3969.
- [5] Bradshaw, J.S.; Bruening, R.L.; Krakowiak, K.E.; Tarbet, B.J.; Bruening, M.L.; Izatt, R.M. and Christensen, J.J., *J. Chem. Soc., Chem. Commun.*, **1988**, 812.
- [6] Bradshaw, J.S.; Krakowiak, K.E.; Tarbet, B.J.; Bruening, R.L.; Biernat, J.F.; Bochenska, M.; Izatt, R.M. and Christensen, J.J., *Pure & Appl. Chem.*, **1989**, 61, 1619.
- [7] Bradshaw, J.S.; Krakowiak, K.E.; Izatt, R.M.; Bruening, R.L. and Tarbet, B.J., *J. Heterocyclic Chem.*, **1990**, 27, 347.
- [8] Ikeda, I.; Tsuji, Y.; Nakatsuji, Y. and Okahara, M., *J. Org. Chem.*, **1986**, 51, 1128.
- [9] Clark, D.T.; Briggs, D. and Adams, D.B., *J. Chem. Soc., Dalton Trans.*, **1973**, (2), 169.
- [10] Lewis, L.N. and Lewis, N., *J. Am. Chem. Soc.*, **1986**, 108, 7228.