Polymer Bulletin 39, 573–579 (1997)

Polymer Bulletin

Effective catalysts for polymerization of cyclohexene oxide: Preparation of novel Martin-type pentacoordinate silicates

Masato Murakami, Shigeru Ikai, Takefumi Yano

Polymer Research Laboratory (Chiba), Ube Industries Ltd., 8-1 Goi-Minamikaigan,
Ichihara-shi, Chiba 290, Japan

Received: 18 August 1997/Accepted: 26 September 1997

Summary

The novel dialkylanilinium salts of pentacoordinate Martin-type silicates were prepared. They were found to be air stable catalysts for polymerization of cyclohexene oxide. The preparation of those silicates bearing a bulky substituent such as mesityl group was not successful.

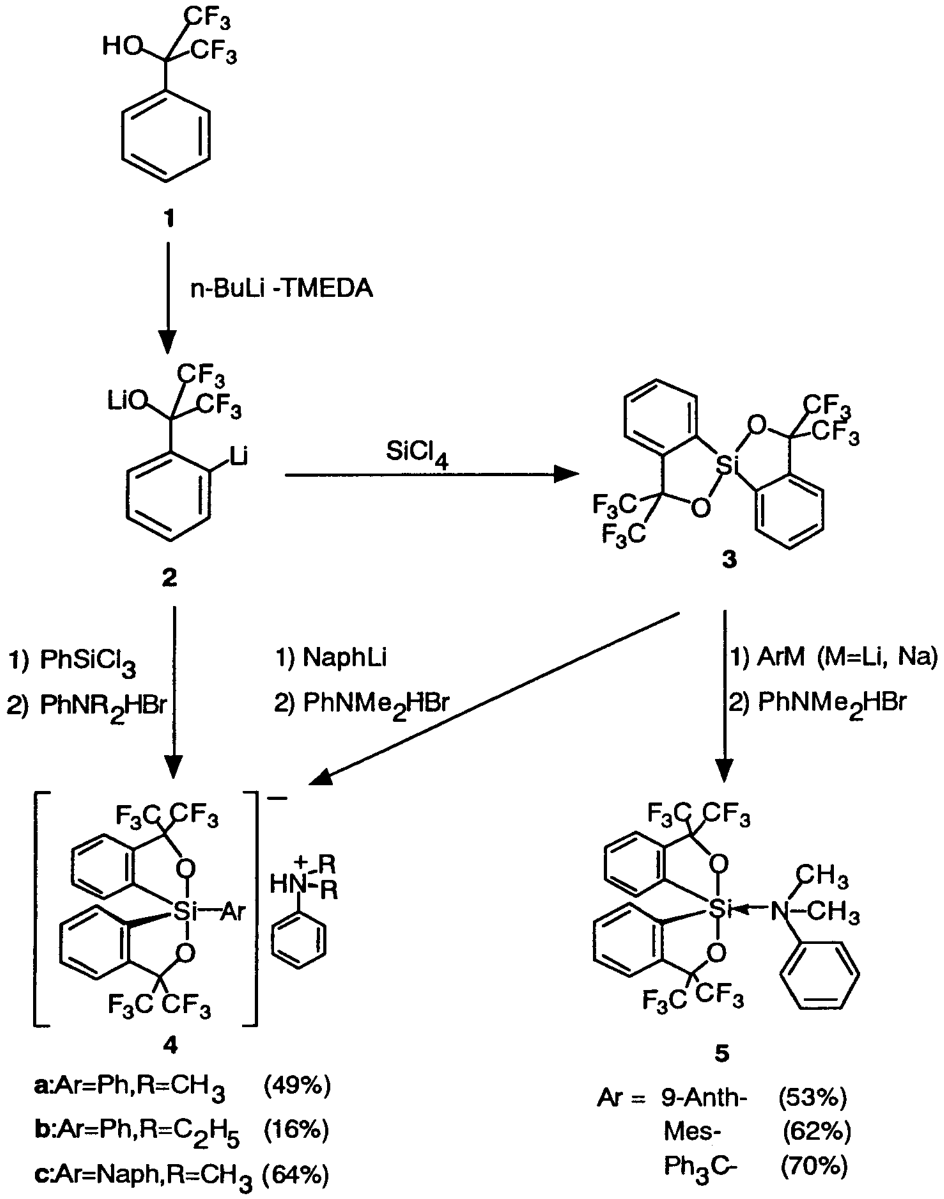
Introduction

Hypercoordinate silicon compounds have received much attention concerning reaction intermediates of some organic reactions.[1-3] The pentacoordinate silicates bearing 1,2-benzenediolato ligands have been known for several decades and their ammonium salts were structurally well studied.[4-6] Since the successful isolation of several hypercoordinate compounds using Martin ligands, which are easily derived from hexafluorocumyl alcohol **1**,[7] pentacoordinate silicates bearing the Martin ligands have been widely studied[8-10]. But there was no example of the application of such silicates to catalytic reactions. We wish to report here the first synthesis of dialkylanilinium salts of pentacoordinate Martin-type silicates **4** and their application to catalysts for the polymerization of cyclohexene oxide.

Experimental

Materials

Tetrahydrofuran(THF) and diethylether were distilled from sodium-benzophenone ketyl prior to use. Dichloromethane was distilled from calcium hydride. Dimethylanilinium bromide was prepared from dimethylaniline and hydrobromic acid. Bis(α,α-bis(trifluoromethyl)benzenemethanolato(2-)C^2,O)silane **3** and mesityltrichlorosilane were prepared according to the literatures[7,11]. Commercially available hexafluorocumyl alcohol **1**, phenyltrichlorosilane, tetramethylethylenediamine(TMEDA), 1-bromonaphthalene(Tokyo Kasei Kogyo Co.), 1.6M n-butyllithium solution in hexane and diethylanilinium chloride(Wako Pure Chem. Ind.) were used without further purification.



Scheme 1

Syntheses of dialkylanilinium salts of Martin-type silicates

Synthesis of dimethylanilinium bis(α,α-bis(trifluoromethyl)benzenemethanolato(2-) C^2,O)phenylsilicate 4a

To the stirred solution of butyllithium(49mmol) in hexane was added TMEDA(0.74ml 5 mmol) at room temperature. After stirring for 1 h, the mixture was cooled to 0°C and hexafluorocumyl alcohol **1** (5.35g 22mmol), dissolved in 3.5 ml of THF, was added dropwise to the mixture. After 30 min the mixture was allowed to warm to room temperaure and stirred for 21 hs. The orange suspension of lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide **2** thus obtained was cooled to 0°C and phenyltrichlorosilane(2.33g 11mmol), dissolved in 5 ml of THF, was added dropwise. The mixture was stirred for 1h at room temperature and quenched with water. The residue was dissolved in ether, washed with dilute HCl, twice with 30 ml of water, and dried on $MgSO_4$. The solvent was removed in vacuo to give lithium bis(α,α-bis(trifluoromethyl) benzenemethanolato(2-)C^2,O)phenylsilicate(5.44g 83%).

The mixture of thus obtained lithium silicate(1.80g 3mmol) and dimethylanilinium bromide(0.85g 4.2mmol) was dissolved in 50ml of dichloromethane and stirred at room temperature for 30 min. The suspension was washed with water and dried on $MgSO_4$. The solvent was removed in vacuo and the white residue was recrystalized from dichloromethane-pentane to give dimethylanilinium bis(α,α-bis(trifluoromethyl)benzene methanolato(2-)C^2,O)phenylsilicate **4a**(1.04g 49%) as colorless crystals. ^{1}H-NMR (400MHz, CD_3COCD_3, 23°C) : δ 10.43 (br s, 1H; NH), 8.38 (d,*J* = 7.3Hz, 2H; SiCCH), 7.90 (d,*J* = 6.8Hz, 2H; Si-Ph o-), 7.79 (d,*J* = 8.3Hz, 2H; N-Ph o-), 7.62 (t,*J* = 7.6Hz, 2H; N-Ph m-), 7.56 (t,*J* = 7.3Hz, 1H; N-Ph p-), 7.39 (d,*J* = 7.3Hz, 2H; SiCC(R)CH), 7.29 (t,*J* = 7.6Hz, 2H; SiCCCH), 7.21 (t,*J* = 7.1Hz, 2H; SiCCCCH), 6.92 (m, 3H; Si-Ph m,p-), 3.57 (s, 6H; N-CH_3); Anal.Found: C,53.85; H,3.60; N,2.05. Calcd. for $C_{32}H_{25}NO_2F_{12}Si$: C, 54.01; H, 3.54; N, 1.97; negative-ion FAB MS m/e -589

Synthesis of diethylanilinium bis(α,α-bis(trifluoromethyl)benzenemethanolato(2-) C^2,O)phenylsilicate 4b

The above mentioned procedure was followed except for using diethylanilinium chloride instead of dimethylanilinium bromide. Diethylanilinium bis(α,α-bis(trifluoromethyl) benzenemethanolato(2-)C^2,O)phenylsilicate **4b** was obtained as colorless microcrystals in 16% yield. ^{1}H-NMR (400 MHz, CD_3COCD_3, 23°C): δ9.95 (br s,1H;NH), 3.90 (m,4H;NCH_2), 1.17 (t,6H;CH_3), Signals assigned to aromatic protons are identical with those of **4a**; Anal.Found: C, 55.70; H, 4.25; N, 1.85. Calcd. for $C_{34}H_{29}NO_2F_{12}Si$; C, 55.21; H, 3.95; N, 1.89; negative-ion FAB MS m/e -589

Synthesis of dimethylanilinium bis(α,α-bis(trifluoromethyl)benzenemethanolato(2-) C^2,O)naphthylsilicate 4c

The mixture of 1-naphthyllithium(0.41g 3 mmol) and bis(α,α-bis(trifluoromethyl) benzenemethanolato(2-)C^2,O)silane **3** (0.77g 1.5mmol) was dissolved in 10ml of diethylether and stirred at room temperature for 5 days. The suspension was quenched with dilute HCl and the solvent was removed in vacuo. To this pale yellow residue was added dimethylanilinium bromide(0.30g 1.5mmol) dissolved in 4ml of dichloromethane and stirred at room temperature for 1h. The suspension was washed with water and dried on $MgSO_4$. The solvent was removed in vacuo and the white residue was washed 4 times with pentane to give dimethylanilinium bis(α,α-bis(trifluoromethyl)benzene methanolato(2-)C^2,O)naphthylsilicate **4c** (0.73g 64%) as white powder. ^{1}H-NMR (400 MHz, CD_3COCD_3, 21°C):δ 10.65(br s, 1H;NH), 8.68 (d,*J* = 7.8Hz, 1H;Si-Nap), 8.58 (d,*J* = 7.3Hz, 2H;SiCCH), 7.77 (d,*J* = 7.1Hz, 2H;N-Ph o-), 7.70 (d,*J* = 6.8Hz, 1H;Si-Nap), 7.51-7.63 (m, 4H;N-Ph m-,p- and Si-Nap), 7.35-7.46 (m, 5H;SiCC(R)CH and Si-Nap), 7.28 (t,*J* = 7.3Hz, 2H;SiCCCH), 7.10 (t,*J* = 7.3Hz, 2H;SiCCCCH), 7.04 (m, 1H;Si-Nap), 3.53 (s, 6H;N-CH_3); Anal.Found: C, 56.55; H, 3.70; N, 1.85. Calcd. for

$C_{36}H_{27}NO_2F_{12}Si$; C, 56.77; H, 3.57; N, 1.84; negative-ion FAB MS m/e -639

Attempted synthesis of bulky arylsilicates

The reactions of mesityllithium, 9-anthryllithium, triphenylmethylsodium with bis(α,α-bis(trifluoromethyl) benzenemethanolato(2-)C^2,O)silane **3** were carried out according to the method for naphthylsilicate **4c**. In these cases, dimethylaniline adduct of Martin-type silane **5** was obtained in 62, 53, 70% yields, respectively, as colorless microcrystals. **5**:^{1}H-NMR (400 MHz, CD_3COCD_3, 23°C): δ 8.13 (m, 2H;SiCCH), 7.67 (m, 2H;N-Ph o-), 7.55 (br m,2H;SiCC(R)CH), 7.39-7.48 (m, 7H; other aromatic H), 3.20 (s, 6H;N-CH_3); Anal.Found: C,48.30;H,3.15; N,2.25. Calcd.for $C_{26}H_{19}NO_2F_{12}Si$; C, 49.29; H, 3.02; N, 2.21.

On the other hand, mesityltrichlorosilane was reacted with lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide **2** followed by the reaction with dimethylanilinium bromide according to the method for phenylsilicate **4a**. The dimethylaniline adduct of Martin-type silane **5** was obtained in 67% yield.

Polymerization procedure

The silicate **4** (12.5mmol) was dissolved in 5 ml of dichloromethane and 2.5 ml (25 mmol) of cyclohexene oxide was added with stirring. After 1h, the dichloromethane solution was poured into a large amount of acetone with vigorous stirring and precipitated polymer was separated and dried in vacuo.

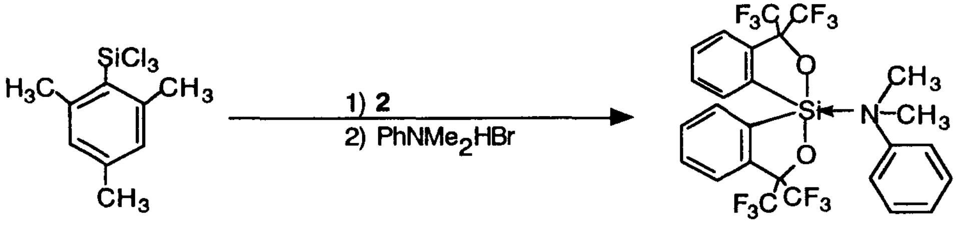
Measurements

^{1}H-NMR spectra were measured in acetone-d_6 at room temperature with a JEOL EX-400 spectrometer. The gel permeation chromatographic(GPC) analysis were made with Waters 150CV using Shodex KF-800D+KF805Lx2 column and tetrahydrofuran as solvent, and the molecular weight was calibrated with standard polystyrene. Elemental analysis were carried out with YANACO MT- 5 CHN CORDER.

Results and discussion

Dimethylanilinium and diethylanilinium bis(α,α-bis(trifluoromethyl)benzene methanolato(2-)C^2,O)phenyl silicates **4a-b** were prepared by the reaction of phenyltrichlorosilane with lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide **2** derived from hexafluorocumyl alcohol **1** in THF, followed by the treatment with corresponding anilinium bromide in dichloromethane in 49% and 16% yields as colorless microcrystals, respectively (Scheme 1). Dimethylanilinium bis(α,α-bis(trifluoromethyl) benzenemethanolato(2-)C^2,O)-1-naphthylsilicate **4c** was prepared by the reaction of 1-naphthyllithium with bis(α,α-bis(trifluoromethyl)benzene methanolato(2-)C^2,O) silane **3** in diethylether followed by the treatment with dimethylanilinium bromide in dichloromethane in 64% yield. These complexes are air stable and identified by ^{1}H-,^{13}C-NMR, negative-ion FAB Mass and elemental analysis.

In the case of the tertially ammonium silicates bearing o-phenylenedioxy ligands, the acidic proton of the ammonium cations has shown to be hydrogen bonded to oxygen atom of the ligand[6]. Such hydrogen bond formation reduces the acidity of proton and may cause the lower polymerization activity. Stimulated by the successful synthesis of triphenylsilylsilicate[10], we attempted to introduce a bulky substituent to the Martin-type silane **3** in order to avoid the hydrogen bond formation. The reactions of **3** with bulky organolithium reagent ArLi (Ar = 9-Anthryl, Mesityl (= 2,4,6-trimethylphenyl)) or triphenylmethylsodium were carried out in diethylether followed by the treatment with



5

(67%)

Scheme 2

dimethylanilinium bromide in dichloromethane (Scheme 1). In these cases, dimethylaniline adduct of Martin-type silane **5** was obtained in 53-70% yield instead of the desired dimethylanilinium bis(α,α-bis(trifluoromethyl)benzenemethanolato(2-)C^2,O) arylsilicate. It would be caused by the difficulty of nucleophilic attack of such bulky groups toward sterically hindered silicon atom. To reduce the steric difficulty, mesityl group was introduced at first to silicon atom, and then, the introduction of two Martin ligands was carried out following the synthetic method of the silicates **4a-b**. Surprisingly, dimethylaniline adduct of Martin-type silane **5** was obtained in 67% yield instead of the dimethylanilinium salt of mesitylsilicate (Scheme 2). This result indicates the elimination of mesityl group. From these results, the preparation of the tertially ammonium salts of Martin-type silicates bearing a bulky substituent such as mesityl group is impossible although quaternary ammonium salt of triphenylsilylsilicate has been reported[10].

The polymerization of cyclohexene oxide was performed with the pentacoordinate silicates. The polymer yields and the molecular weights of the obtained polymers are summarized in Table 1. The number-average-molecular-weights (Mn) of the polymers were 13000-20000. These values are comparable to that of the $Ti(OiPr)_4$-PhOH catalyst system[12]. To our knowledge, this is the first example of the application of such hypercoordinate silicates to polymerization catalyst. Almost no polymerization was observed when dimethylanilinium bromide was used instead of the silicates. These results clearly show that the Martin-type arylsilicate moieties play important roles in the polymerization reaction. On the other hand, molecular-weight-distributions (Mw / Mn) depend on the structure of the anilinium cations rather than the silicate anions. When the

Table 1 Polymerization of cyclohexene oxide by penta-coordinate silicates.[a)]

Run	Catalyst	Polymer yield (mg)	Mn	Mw / Mn
1	**4a**	944	13300	5.48
2	**4b**	1280	16400	2.55
3	**4c**	1128	19200	5.81
4	$PhNMe_2HBr$	27	-	-

a)Reaction conditions: Solvent; CH_2Cl_2 5ml, Catalyst; 12.5 x 10^{-6}mol, Temperature; 20°C, Polymerization time; 1h, Monomer / Catalyst=2000.

Table 2. Effects of solvent on polymer yield[a)]

Run	Catalyst	moles of catalyst x10^6	Solvent	Polymer yield(mg)
1	**4a**	12.5	CH_2Cl_2	944
2	**4a**	13.4	Toluene	171
3	**4a**	13.4	THF	100

a)Reaction conditions: Solvent: 5ml, Temperature; 20°C, Polymerization time; 1h, Monomer / Catalyst =2000.

diethylanilinium salt **4b** was used as catalyst, narrower molecular-weight-distributions were observed. The tacticity of the polymer obtained from the catalyst **4a** (68% syndiotactic diad, 13.2% isotactic triad and 49.2% syndiotactic triad) was similar to those from $ZnEt_2$ or $(EtZnOMe)_4$ which are known to catalyse cationic polymerization of cyclohexene oxide[13]. The anilinium cations seem to be the active species of this polymerization reaction.

Polymerization also took place when other solvent was used. But the activity was lower in toluene or THF than in dichloromethane as shown in Table 2. It is assumed that the initiation of polymerization reaction is an attack of highly acidic proton of the ammonium cations to oxygen atom of the cyclohexene oxide. In THF, acidic proton may be coordinated by solvent reducing its activity. In non-polar solvent such as toluene, the ionization of the silicate may be difficult.

In conclusion, the novel dialkylanilinium salts of pentacoordinate Martin-type silicates **4a-c** were prepared. They were found to be air stable catalysts for the polymerization of cyclohexene oxide. The preparation of the Martin-type silicates bearing a bulky substituent such as mesityl group was proved to be impossible because of the formation of dialkylaniline adduct of Martin-type silane **5** .

The authers acknowledge Ube Industries.co.,Ltd.for permission to publish this paper.

References

1. M.Kira, K.Sato, and H.Sakurai (1988) J.Am.Chem.Soc.110: 4599
2. T.Kawashima, N.Iwama and R.Okazaki (1992) J.Am.Chem.Soc.114: 7598
3. C.Breliere, F.Carre, R.Corriu, and M.Wong Chi Man (1994) J.Chem.Soc., Chem. Commun.: 2333
4. C.L.Frye (1964) J.Am.Chem.Soc.86: 3170
5. F.P.Boer, J.J.Flynn and J.W.Turley (1968) J.Am.Chem.Soc.90: 6973
6. R.R.Holmes, R.O.Day, J.J.Harland, A.C.Sau, and J.M.Holmes (1984) Organometallics, 3: 341 and references therein
7. E.F.Perozzi, R.S.Michalak, G.D.Figuly, W.H.Stevenson III, D.B.Dess, M.R.Ross, and J.C.Martin (1981)J.Org.Chem.46: 1049

8. W.H.Stevenson III, S.Wilson, J.C.Martin, and W.B.Farnham (1985) J.Am.Chem Soc. 107: 6340
9. W.B.Farnham and R.L.Harlow (1981) J.Am.Chem.Soc. 103: 4608
10. M.Kira, K.Sato, C.Kabuto and H.Sakurai (1989)J.Am.Chem.Soc.111: 3747
11. G.R.Gillette, H.B.Yokelson and R.West (1988) Organometallic syntheses.vol. 4, ed. by R.B.King and J.J.Eisch. Elsevier:529
12. Y.Fukuchi, T.Takahashi, H.Noguchi, M.Saburi, and Y.Uchida (1988) J.Polym.Sci.: Part C: Polym.Lett., 26: 401
13. Y.Hasebe, and T.Tsuruta (1987)Makromol.Chem. 188: 1403