Ring-Closing Metathesis on an Allyl-Terminated Carbosilane Dendrimer

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Grubbs' catalyst was used to prepare a series of carbosilane dendrimers with silacyclopentene peripheral groups, suitable for further elaboration to functional dendrimers. The efficiency of the ring closing metathesis reaction was found to be strongly dependent on the reaction temperature and the amount of catalyst used, as shown by ^{1}H NMR monitoring.

Keywords: Grubbs' catalyst; Ring-closing metathesis; Carbosilane; Dendrimer; Silacyclopenten.

INTRODUCTION

Grubbs' catalyst has been extensively used in coupling reactions of olefins such as ring-closing metathesis,[1-4] cross-metathesis,[5] and ring-opening metathesis.[6] Although the activity of Grubbs' catalyst is lower than that of Schrock's molybdenum alkylidenes, it displays superior stability towards oxygen, water, and minor impurities in the solvents. As a result, Grubbs' catalyst has enjoyed widespread application in organic and polymer chemistry[7] as summarized in several review articles.[8-12] Most literature reports concentrate on the synthesis of natural products with large ring structures,[13-15] especially systems containing eight-membered rings that are unstable from a kinetic and thermodynamic point of view.[16] In short, Grubbs' catalyst offers a powerful method for the creation of chemical diversity, especially the cross-metathesis reaction that provides access to alkenes bearing a wide range of functional groups.[17-21]

Our initial goal in this research was to use cross-metathesis methods to attach different chelating functionalities to the periphery of a carbosilane dendrimer framework so that lanthanide ions could be bound at the dendrimer exterior. The high catalytic activity of lanthanide ions in Lewis acid catalyzed transformations, as well as some oxidations and reductions, make these metals attractive reaction centers.[22,23] Although cross metathesis proved difficult to achieve, ring-closing metathesis of the allyl-terminated carbosilane dendrimers resulted in a new kind of silacyclopentene terminated dendrimers in high yield using Grubbs' catalyst.

RESULTS AND DISCUSSION

Using the divergent method, carbosilane dendrimers with allyl terminal groups (**2**, **5** and **7**) can be easily synthesized using alternating Grignard reagent and hydrosilylation reactions (Scheme I).[24,25] It was expected that reaction of carbosilane dendrimers **2** or **5** with allyl phenol **3** or allyl oxazoline **X** using Grubbs' catalyst would produce the cross metathesis target dendrimers (**11** or **12**), especially in the presence of excess **3** or **X**.

However, no reaction was observed when **2** or **5** were stirred with a fourfold excess of **3** and Grubbs' catalyst at room temperature for several days. But, increasing the temperature of the reaction mixture and the amount of the catalyst resulted in formation of the ring-closing products **4** and **6** in > 90% yield. And in the same time, reaction of **3** with Grubbs' catalyst on its own under the same conditions resulted in self-metathesis to produce **9**,[26] so it is clear that intramolecular metathesis reactions of carbon silane den-

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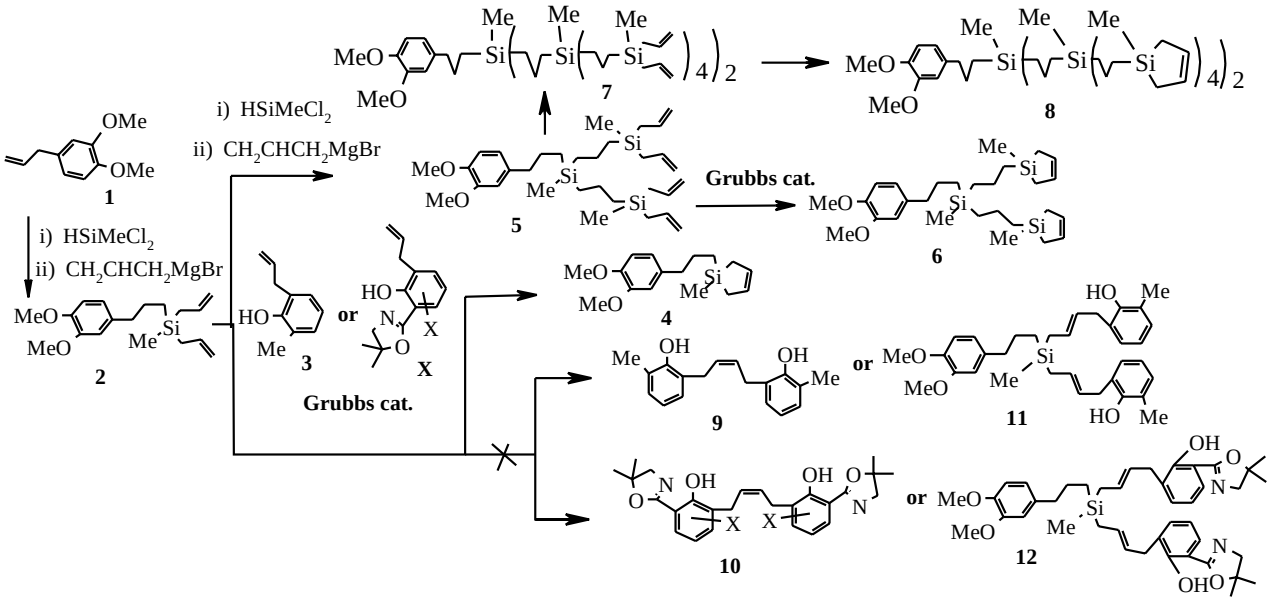
Scheme I The synthesis route of the preparation of the dendrimers and the ring-closing metathesis reaction under the Grubbs' catalyst



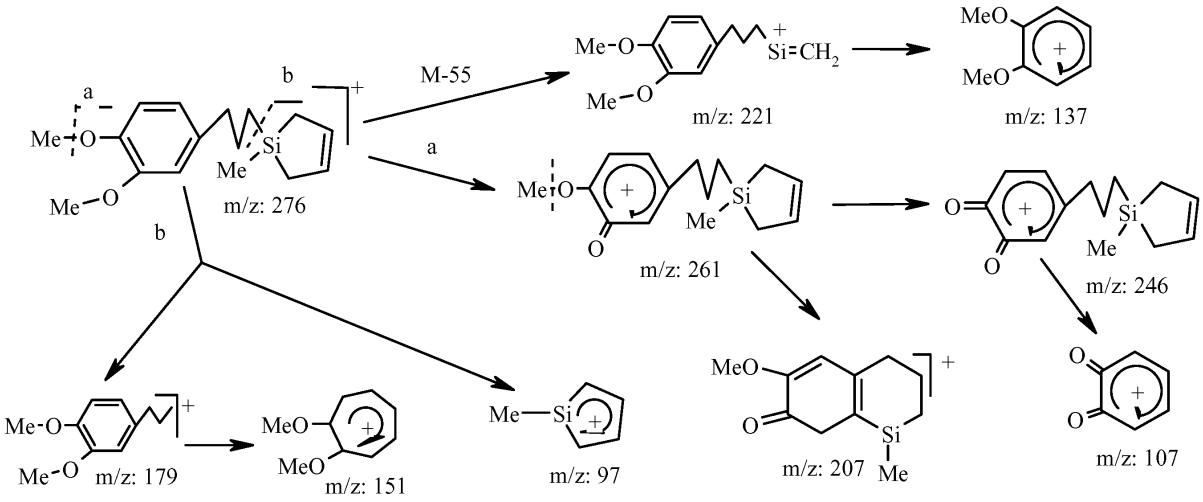
drimers are dominant even when a significant excess of **3** is present. The fact that the ring-closing reaction produces a highly favored 5-membered ring apparently precludes observation of the cross metathesis products.[27,28]

The assignment of **4** as the silacyclopentene is evident from the NMR spectrum. In the ^{1}H-NMR, the alkenyl signals at δ 5.4-5.7 and δ 4.75 ppm for **2** are replaced by a new singlet at δ 5.70 ppm due to the silacyclopentene ring vinyl protons of **4**.

Significantly, the ^{29}Si resonance shifts from 0.92 ppm in **2** to δ 18.07 ppm in **4** due to ring strain. Similarly, the Si-Me resonance in the ^{13}C{^{1}H} NMR shifts from -5.60 ppm in **2** to -3.61 ppm in **4**. As expected, the ^{13}C-DEPT spectrum shows that the methylene carbon of the terminal double bonds (δ 113.34 ppm) is no longer present. The MS also supports the structure of **4** as shown below (Scheme II).

The progress of the ring-closing reaction can be conveniently followed by the integral of the δ 5.4-5.7 (a) and δ 4.75 ppm (b) resonances (Fig. 1). Reaction of **2** and **3** (1:4 molar ratio) in the presence of 0.5 mol% Grubbs' catalyst did not re-

Scheme II The mass spectrum of compound **4**



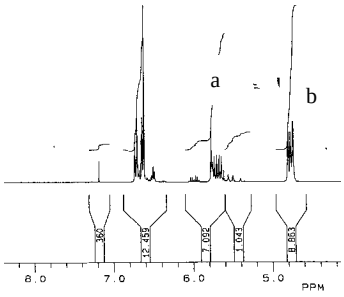
sult in the formation of **4** after stirring for 24 h at room temperature in toluene solution. Increasing the catalyst loading to 5 mol% also failed to produce any **4** under these conditions despite the fact that there are several reports indicating that metathesis should proceed readily at room temperature. However, heating the reaction mixture with 0.5 mol% Grubbs' catalyst at 80 °C did result in a 25% conversion of **2** to **4** in 12 h (Table 1, No. 3 and Fig. 1, ii). Increasing the time to 60 h and catalyst loading to 1 mol% increased the conversion to 65% (Table 1, No. 4 and Fig. 1, ii). Further increases in temperature to 100 °C at 1 mol% catalyst and 130 °C at 5 mol% catalyst resulted in 85 and > 99% conversion respectively (Table 1, No. 5 and 6 and Fig. 1, iii, iv). The conversion appears to be primarily dependent on reaction temperature, although increasing the catalyst loading also appeared to be beneficial; perhaps indicating that catalyst degradation was occurring under the reaction conditions employed.

Using the optimal conditions of No. 6 (in Table 1), we

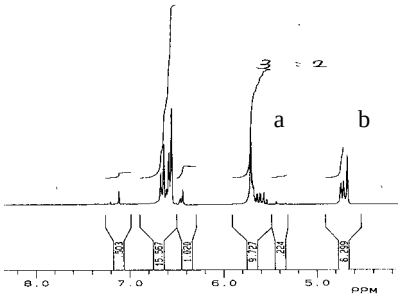
Table 1. The condition and result of the ring closed reaction

No.	Reactant	Product	Temp. (°C)	Catalyst (mol%)	Time (hr)	Yield[a] (%)
1	2	4	20	0.5	48	0
2	2	4	20	5.0	48	0
3	2	4	80	0.5	12	25
4	2	4	80	1.0	60	65
5	2	4	100	1.0	60	85
6	2	4	130	5.0	24	> 99
7	5	6	130	5.0	24	> 99
8	7	8	130	5.0	24	> 99

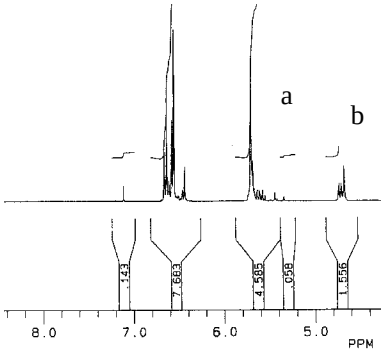
[a] Determined by integration of the product and substrate alkenyl ^{1}H resonances.



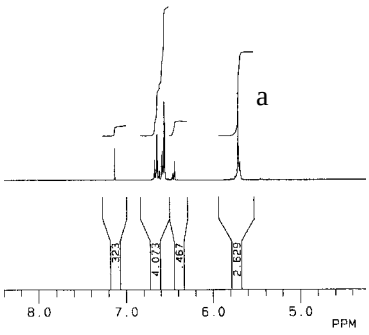
i): Temp: 80 °C, Cat%: 0.5%, Time: 12 h



ii): Temp: 80 °C, Cat%: 1%, Time: 60 h



iii): Temp: 100 °C, Cat%: 1%, Time: 60 h



iv): Temp: 130 °C, Cat%: 5%, Time: 60 h

Fig. 1. The ^{1}H-NMR of the alkeneyl region for the ring-closing reaction of **2**.

found that **5** and **7** also underwent smooth ring closing metathesis to afford the bis(silacyclopentene) **6** and **8** in excellent conversion (entry **7** and **8**).

CONCLUSION

Grubbs' catalyst was highly effective at ring closing metathesis on diallylsilane-terminated dendrimers to afford silacyclopentenes **4**, **6**, and **8** in extremely high conversions. The ideal reaction conditions for the RCM reaction were 130 °C in toluene using 5 mol% catalyst. No evidence for cross metathesis with allylphenol **3** or allyl oxazoline **X** was observed under any conditions, including a large excess of compound **3 or X**.

EXPERIMENTAL

General Method

All ^{1}H-NMR, ^{13}C-NMR, ^{13}C-DEPT spectra were recorded in $CDCl_3$ as solvent on Bruker AC-200 spectrometer, using 5 mm O.D. tubes at 303 K, no internal reference. ^{29}Si spectra were recorded in $CDCl_3$ as solvent on Bruker AC-500 spectrometer, using 5 mm O.D. tubes at 303 K. IR spectrum was obtained on Ni Cdet FT-IR 20SX spectrometer (KBr disk, 4000-400 cm^{-1}). Mass spectra were obtained by a FAB (fast atom bombardment) VG-70-250S Mass Spectrometer. Silica gel (silica gel 60, 230-400 mesh, Merck) was used for Column Chromatography and others reagents were purchased from Aldrich Company and were used without further purification.

The preparation of carbonsilane dendrimer G_0(OMe) (2)

3.56 g (20 mmol) 3-(1,2-methyoxylphenyl-4-)propylene and 5 mL dry hexane were added to a dry Kontes tube under inert atmosphere, and 5d Speirs catalyst was added to the solution. After 5.52 g (4.8 mL, 48 mmol) dichloromethylsilane was added; the tube was sealed and put in a 80 °C oil bath, and kept stirring overnight. (The mixture was cooled to room temperature (r.t.), and then the excess reagent and solvent were removed carefully under vacuum). Colorless oil was given. The oil was dissolved in 20 mL dry ether, and added slowly to an ether solution containing allylbromine Grignard reagent under ice-salt bath; then, after the ice-salt bath was removed, the reaction solution was warmed to r.t. slowly and kept stirring for 4 hr. At the end of the reaction, 50 mL 30% NH_4Cl solution was added slowly under ice-salt bath. The organic layer was separated, and the water layer was extracted with 3*20 mL ether. The combined organic lay was dried over anhydrous $MgSO_4$ overnight. After filtering, the solvent was removed under decompression, and the low boiling materials was got rid of under vacuum (100-140 °C/2 mmHg); then, the remainders were purified by column, Hexane:Ether = 40:1, colorless odorous oil was given. 4.56 g, yield 75.0%.

IR (cm^{-1}): 3076 (CH), 1629 (C=C), 1253 (Si-CH_2), 813 (Ph); NMR (δ ppm) ^{1}H: 6.82-6.79 (d, 1H, *J* = 8.5 Hz, ArH), 6.74-6.73 (d, 1H, *J* = 8.5 Hz, ArH), 6.71 (s, 1H, ArH), 5.82-5.76 (m, 2H, Si-CH_2CH=CH_2), 4.89-4.83 (s, d, 4H, *J* = 9.9 Hz, Si-CH_2CH=CH_2), 3.89-3.88 (s, 6H, OCH_3), 2.60-2.55 (t, 2H, *J* = 7.1 Hz, Ar-$CH_2CH_2CH_2$Si), 1.57-1.55 (m, 6H, Si-CH_2CH=CH_2 and Ar-$CH_2CH_2CH_2$Si), 0.64-0.59 (t, 2H, *J* = 7.8 Hz, Ar-$CH_2CH_2CH_2$Si), 0.00 (s, 3H, Si-CH_3); ^{13}C{^{1}H}: 148.9, 147.3, 135.4, 134.9, 120.4, 113.3, 112.0, 111.4, 56.1, 56.0, 39.7, 26.2, 21.5, 13.1, -5.6; ^{29}Si{^{1}H}: 0.92; MS (EI): *m/z* 304 (M^+).

The preparation of carbonsilane dendrimer G_1(OMe) (5)

Using the same method as above, the carbonsilane dendrimer G_1(OMe) was prepared at 60% yield. 3.04 (10 mmol) G_1(OMe) reacted with dichloromethylsilane and allylbromine Grignard reagent successively, and 3.36 g product was given after purification.

IR (cm^{-1}): 3076 (CH), 1629 (C=C), 1252 (Si-CH_2), 813 (Ph); NMR (δ ppm) ^{1}H: 6.80-6.77 (d, 1H, *J* = 8.5 Hz, ArH), 6.74-6.73 (d, 1H, *J* = 8.5 Hz, ArH), 6.69 (s, 1H, ArH), 5.86-5.68 (m, 4H, Si-CH_2CH=CH_2), 4.90-4.83 (d, 8H, *J* = 9.9 Hz, Si-CH_2CH=CH_2), 3.89-3.88 (s, 6H, O-CH_3), 2.60-2.57 (t, 2H, *J* = 7.1 Hz, Ar-$CH_2CH_2CH_2$Si), 1.61-1.58 (d, 8H, *J* = 5.0 Hz, Si-CH_2CH=CH_2), 1.42-1.28 (m, 4H, CH_2), 0.98-0.96 (t, 2H, 2H, *J* = 7.8 Hz, CH_2), 0.61-0.42 (m, 10H, Si-CH_2), 0.00 (s, 9H, Si-CH_3); ^{13}C{^{1}H}: 148.6, 146.9, 135.1, 134.6, 120.4, 113.1, 111.9, 111.0, 39.4, 25.99, 21.5, 18.6, 12.2, 17.9, 13.7, -5.1, -5.7; ^{29}Si{^{1}H}: 1.71, 0.22; MS: *m/z* 556 (M^+).

The preparation of carbonsilane dendrimer G_2(OMe) (7)

Using the same method as above, the carbonsilane dendrimer G_2(OMe) was prepared at 54% yield. 2.33 g (5 mmol) G_1(OMe) reacted with dichloromethylsilane and allylbromine Grignard reagent successively, and 2.86 g product was given after purification.

IR (cm^{-1}): 3076 (CH), 1629 (C=C), 1252 (Si-CH_2), 813 (Ph); NMR (δ ppm) ^{1}H: 6.81-6.78 (d, 1H, *J* = 8.5 Hz, ArH),

6.74-6.73 (d, 1H, J = 8.5 Hz, ArH), 6.70 (s, 1H, ArH), 5.88-5.71 (m, 8H, Si-CH_2CH=CH_2), 4.95-4.80 (m, 16H, Si-CH_2CH=CH_2), 3.88-3.87 (s, 6H, O-CH_3), 2.61-2.57 (t, 2H, J = 7.0 Hz, Ar-$CH_2CH_2CH_2$Si), 1.64-1.53 (d, 16H, J = 5.1 Hz, Si-CH_2CH=CH_2), 1.41-1.20 (m, 12H, CH_2), 1.028-0.80 (m, 4H, CH_2), 0.71-0.42 (m, 24H, Si-CH_2), 0.00 (s, 21H, Si-CH_3); $^{13}C\{^1H\}$: 148.5, 146.9, 135.1, 134.7, 120.7, 113.3, 112.1, 111.0, 39.2, 26.01, 21.5, 18.5, 12.2, 17.9, 13.7, -5.0, -4.98; $^{29}Si\{^1H\}$: 1.65, 0.98, 0.24; MS: *m/z* 1060 (M^+).

The preparation of the dendrimers with silacyclopentene terminal groups (4, 6, 8)

General method: 0.1 mmol allyl terminal carbonsilane dendrimers 2, 5 or 7 and 0.5%-5% (based on the mol of allyl groups) Grubbs' catalyst 5 mL dry toluene were added to a dry Kontes tube under inert atmosphere, and kept stirring for several hours at the temperatures that are shown in Table 1. After the reaction, the solvent was removed under vacuum and then purified by column chromatography (Ether:Hexane = 1:20).

Spectroscopic data for compound 4

IR (cm^{-1}): 3076 (CH), 1632 (C=C); NMR (δ ppm) ^1H: 6.65-6.55 (m, 3H, ArH), 5.70 (s, 2H, CH=CH), 3.65-3.64 (s, 6H, OCH_3), 2.47-2.38 (t, 2H, J = 7.8 Hz, Ar-$CH_2CH_2CH_2$-Si), 1.58-1.39 (m, 2H, Ar-$CH_2CH_2CH_2$-Si), 1.15-1.05 (d, 4H, J = 6.4 Hz, CH_2CH=CH), 0.61-0.49 (t, 2H, J = 7.1 Hz, Ar-$CH_2CH_2CH_2$-Si), 0.02 (s, 3H, $SiCH_3$); $^{13}C\{^1H\}$: 148.2, 142.3, 135.3, 131.1, 120.3, 111.9, 111.2, 55.9, 55.8, 39.25, 26.38, 16.48, 14.48, -3.61; $^{29}Si\{^1H\}$: 18.07; MS: *m/z* 276 (M^+).

Spectroscopic data for 6

IR (cm^{-1}): 3076 (CH), 1633 (C=C), 1252 (Si-CH_2); NMR (δ ppm) ^1H: 6.68-6.56 (m, 3H, ArH), 5.72 (s, 4H, CH=CH), 3.70-3.69 (s, 6H, OCH_3), 2.58-2.56 (t, 2H, J = 7.8 Hz, Ar-$CH_2CH_2CH_2$Si), 1.42-1.28 (m, 4H, CH_2), 1.16-1.02 (d, 8H, J = 6.2 Hz, Si-CH_2CH=CH), 0.98-0.96 (t, 2H, J = 7.1 Hz, CH_2), 0.61-0.42 (m, 10H, Si-CH_2), 0.00 (s, 9H, $SiCH_3$); $^{13}C\{^1H\}$: 148.6, 143.7, 135.1, 120.4, 111.9, 111.0, 56.5, 56.4, 39.4, 25.99, 21.5, 18.6, 12.2, 17.9, 13.7, -3.59, -5.7; $^{29}Si\{^1H\}$: 1.83, 19.68; MS: *m/z* 501 (M^++1).

Spectroscopic data for 8

IR (cm^{-1}): 3076 (CH), 1633 (C=C), 1253 (Si-CH_2); NMR (δ ppm) ^1H: 6.69-6.56 (m, 3H, ArH), 5.71 (s, 8H, CH=CH), 3.71-3.70 (s, 6H, OCH_3), 2.60-2.57 (t, 2H, J = 7.8 Hz, Ar-$CH_2CH_2CH_2$Si), 1.44-1.27 (m, 12H, CH_2), 1.18-1.04 (d, 16H, J = 6.3 Hz, Si-CH_2CH=CH), 0.99-0.96 (t, 2H, J = 7.0 Hz, CH_2), 0.63-0.41 (m, 26H, Si-CH_2), 0.00 (s, 21H, $SiCH_3$); $^{13}C\{^1H\}$: 148.6, 143.7, 135.1, 120.4, 111.9, 111.0, 56.5, 56.4, 39.4, 25.99, 21.5, 18.6, 12.2, 17.9, 13.7, -3.59, -5.7; $^{29}Si\{^1H\}$: 1.83, 19.68; MS: *m/z* 947 (M^+-1).

ACKNOWLEDGMENT

The project was sponsored by the Scientific Research Foundation of Shandong University.

Received January 30, 2004.

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