

Ring-closing Metathesis on an Allyl-terminated Carbosilane Dendrimer

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Abstract: Grubbs' catalyst was used to prepare a series of carbosilane dendrimers with silacyclopentene peripheral groups. It was found that ring closing metathesis reaction was influenced strongly by the reaction temperature and the amount of catalyst.

Keywords: Grubb's catalyst, carbosilane dendrimers, metathesis.

Grubbs' catalyst has been extensively used in coupling reactions of olefins such as ring-closing metathesis^{1,2}, cross-metathesis³ and ring-opening metathesis⁴. It offers a powerful method for the creation of chemical diversity, especially the cross-metathesis reaction that can make alkenes bearing various functional groups^{5,6}. Our initial goal of this research was to attach different chelating groups on the periphery of a carbosilane dendrimer with cross-metathesis methods. So that lanthanide ions could be bound at dendrimer exterior and target products could show high catalytic activity⁷. It was proved that the ring-closing metathesis of the allyl-terminated carbosilane dendrimers resulted in silacyclopentene terminated dendrimers in high yield by using Grubbs' catalyst.

Using the divergent method, carbosilane dendrimers with allyl terminal groups (**Scheme I, 2 and 5**) was easily synthesized by Grignard and hydrosilylation reactions⁸. It was expected that the reaction of carbosilane dendrimers **2** or **5** with allyl phenol **3** or allyl oxazoline **X** would produce the cross metathesis target dendrimers **9, 10** by Grubbs' catalyst, especially in the presence of excess **3** or **X**.

According to the experiment results, the expected reaction did not occur, when **2**⁹ or **5**¹⁰ were stirring with a fourfold of **3** or **X** in the presence of Grubbs' catalyst (0.5-5 mmol%) at room temperature for several days. However, increasing the temperature of the reaction and the amount of the catalyst resulted in formation of the ring-closing products **4**¹¹ and **6**¹² with >90% yield. No compounds **7, 8, 9** or **10** were found in the reaction system. Reaction of **3** with Grubbs' catalyst under the same conditions resulted in self-metathesis to afford **7**. It is clear that intramolecular metathesis reactions are

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dominant even with excess of **3** or **X**. Because the ring-closing reaction highly favored 5-membered ring, the cross metathesis products could not be observed¹³.

The structure of **4** was characterized by ¹H NMR. The signals at δ 5.4-5.7 and 4.75 ppm for alkenyl of **2** are replaced by a new single peak at δ 5.70 ppm that is assigned to vinyl protons of the silacyclopentene ring of **4**. Significantly, the ²⁹Si resonance shifted from 0.92 ppm in **2** to δ 18.07 ppm in **4** due to ring strain. Similarly, the SiMe resonance in the ¹³C NMR shifted from -5.60 ppm in **2** to -3.61 ppm in **4**. As expected, the ¹³C-DEPT spectrum showed that the methylene carbon of the terminal double bonds (δ 113.34 ppm) is disappeared. The MS also supported the structure of **4**.

The process of the ring-closing reaction can be conveniently monitored by the integral of ¹H-NMR at δ 5.4-5.7 and 4.75 ppm (the resonance of allyl groups) and the results were shown in the **Table 1**. It showed that the conversion primarily depended on the reaction temperature. Increase of the catalyst loading is also beneficial to the reaction. The reason might be that the catalyst degraded under the reaction conditions.

Scheme 1

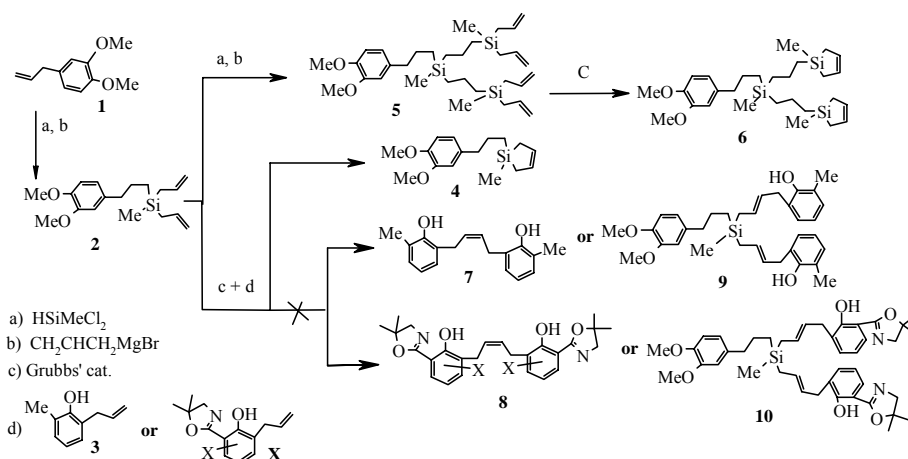


Table 1 The conditions and result of ring closed reaction

Entry	Temp.(°C)	Catalyst.(%mol)	Time (h)	Conver.(%) ^a
1 ^b	20	0.5	48	0
2	20	5.0	48	0
3	80	0.5	12	25
4	80	1.0	60	65
5	100	1.0	60	85
6	130	5.0	24	>99
7 ^c	130	5.0	24	>99

^a determined by integration of ¹H NMR the product and substrate alkenyl;

^b from entry 1 to 6, the substrate is compound **2**, and compound **5** was the only product;

^c entry 7, the substrate is compound **4**, compound **6** was the only product.

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In conclusion, Grubbs' catalyst was used to prepare a new kind of dendrimer with silacyclopentenes terminal groups. It was showed that the efficiency of ring closing metathesis depended on the reaction temperature and the amount of the catalyst.

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9. Compound **2** was obtained 75% yield. IR (KBr, cm^{-1}): 3076 (CH), 1629 (C=C), 1253 (Si-CH₂), 813 (Ph); NMR(CDCl₃, δ ppm) ¹H: 6.82-6.79 (d, 1H, *J*=8.5Hz, ArH), 6.74-6.73 (d, 1H, *J*=8.5Hz, ArH), 6.71 (s, 1H, ArH), 5.82-5.76 (m, 2H, Si-CH₂CH=CH₂), 4.89-4.83 (d, 4H, *J*=9.9Hz, Si-CH₂CH=CH₂), 3.89-3.88 (s, 6H, OCH₃), 2.60-2.55 (t, 2H, *J*=7.1Hz, Ar-CH₂-CH₂CH₂Si), 1.57-1.55 (m, 6H, Si-CH₂CH=CH₂ and Ar-CH₂CH₂CH₂Si), 0.64-0.59 (t, 2H, *J*=7.8Hz, Ar-CH₂CH₂CH₂Si), 0.00 (s, 3H, Si-CH₃); ¹³C: 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; ²⁹Si: 0.92; MS(EI): *m/z* 304.
10. Compound **5** was obtained in 60% yield. IR (KBr, cm^{-1}): 3076 (CH), 1629 (C=C), 1252 (Si-CH₂), 813 (Ph); NMR(CDCl₃, δ ppm) ¹H: 6.81-6.78 (d, 1H, *J*=8.5Hz, ArH), 6.74-6.73 (d, 1H, *J*=8.5Hz, ArH), 6.70 (s, 1H, ArH), 5.86-5.68 (m, 4H, Si-CH₂CH=CH₂), 4.90-4.83 (d, 8H, *J*=9.9Hz, Si-CH₂CH=CH₂), 3.89-3.88 (s, 6H, O-CH₃), 2.60-2.57 (t, 2H, *J*=7.1Hz, Ar-CH₂-CH₂CH₂Si), 1.61-1.58 (d, 8H, *J*=5.0Hz, Si-CH₂CH=CH₂), 1.42-1.28 (m, 8H, CH₂), 0.98-0.96 (t, 2H, *J*=7.8Hz, CH₂), 0.61-0.42 (m, 8H, Si-CH₂), 0.00 (s, 9H, Si-CH₃); ¹³C: 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; ²⁹Si: 1.71, 0.22; MS(EI): *m/z* 566.
11. Spectroscopic data for **4**: IR (KBr, cm^{-1}): 3076 (CH), 1632 (C=C); NMR (CDCl₃, δ ppm) ¹H: 6.65-6.55 (m, 3H, ArH), 5.70 (s, 2H, CH=CH), 3.65-3.64 (s, 6H, OCH₃), 2.47-2.38 (t, 2H, *J*=7.8Hz, Ar-CH₂CH₂CH₂-Si), 1.58-1.39 (m, 2H, Ar-CH₂CH₂CH₂-Si), 1.15-1.05 (d, 4H, *J*=6.4Hz, CH₂CH=CH), 0.61-0.49 (t, 2H, *J*=7.1Hz, Ar-CH₂CH₂CH₂-Si), 0.02 (s, 3H, SiCH₃); ¹³C: 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; ²⁹Si: 18.07; MS(EI) *m/z* 276.
12. Spectroscopic data for **6**: IR (KBr, cm^{-1}): 3076 (CH), 1633 (C=C), 1252 (Si-CH₂); NMR (CDCl₃, δ ppm) ¹H: 6.68-6.56 (m, 3H, ArH), 5.72 (s, 4H, CH=CH), 3.70-3.69 (s, 6H, OCH₃), 2.58-2.56 (t, 2H, *J*=7.8Hz, Ar-CH₂CH₂CH₂Si), 1.42-1.28 (m, 8H, CH₂), 1.16-1.02 (d, 8H, *J*=6.2Hz, Si-CH₂CH=CH₂), 0.98-0.96 (t, 2H, *J*=7.1Hz, CH₂), 0.61-0.42 (m, 8H, Si-CH₂), 0.00 (s, 9H, SiCH₃); ¹³C: 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; ²⁹Si: 1.83, 19.68; MS(EI) *m/z* 566.
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