Cross-metathesis of alkenes with vinyl-substituted silsesquioxanes and spherosilicates: a new method for synthesizing highly-functionalized Si/O frameworks

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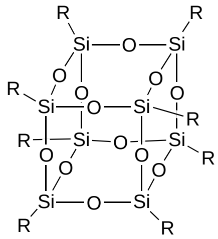
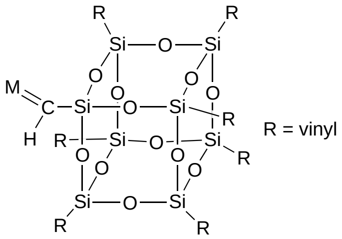
Highly functionalized silsesquioxanes and spherosilicates of the formulae [(RCH=CH)$_8$Si$_8$O$_{12}$] and [(RCH=CHSiMe$_2$-O)$_8$Si$_8$O$_{12}$] can be prepared by cross-metathesis reactions of alkenes with readily available vinyl-substituted silsesquioxane and spherosilicate frameworks, [(vinyl)$_8$Si$_8$O$_{12}$] 1 and [(vinylSiMe$_2$O)$_8$Si$_8$O$_{12}$] 2; the methodology is quite general and is not complicated by self-metathesis reactions of 1 or 2.

Topologically spherical silsesquioxanes {*i.e.* [RSiO$_{3/2}$]$_n$} and silicates {*i.e.* [ROSiO$_{3/2}$]$_n$} have attracted widespread attention as precursors to a variety of interesting compounds and materials, and the number of known frameworks bearing synthetically useful functional groups is growing at an increasingly rapid pace.[1] Numerous methods have been reported for preparing highly functionalized silsesquioxane and spherosilicate frameworks, but the four most common routes are: (i) direct synthesis *via* hydrolytic condensation of RSiX$_3$; (ii) hydrosilylation of hydridosilsesquioxanes; (iii) silylation of spherosilicates; and (iv) synthetic manipulation of organic substituents on other readily available frameworks.

Here, we report a general new strategy for preparing highly functionalized silsesquioxanes and spherosilicates based on cross-metathesis reactions of alkenes[2] with readily available vinyl-substituted silsesquioxane[3,4] and spherosilicate frameworks.[5,6] This strategy offers access to a wide range of synthetically useful compounds, and it provides an important alternative to traditional synthetic methods based on the hydrosilylation of hydridosilsesquioxanes and the silylation of spherosilicates.



1 R = vinyl
2 R = OSiMe$_2$vinyl



5 M = Ru{P(C$_6$H$_{11}$)$_3$}$_2$Cl$_2$
6 M = Mo(NAr){OCMe(CF$_3$)$_2$}$_2$

Vinylsilsesquioxane **1**[3] reacts with both [{(C$_6$H$_{11}$)$_3$P}$_2$Cl$_2$Ru=CHPh][7] **3** and [Mo(CHCMe$_2$Ph)(NC$_6$H$_3$-Pr$^i_2$-2,6){OCMe(CF$_3$)$_2$}$_2$][8] **4** to produce new compounds exhibiting ^{1}H NMR resonances consistent with the formation of new alkylidene complexes. In the case of **3**,† alkylidene resonances attributable to both **5** and [{(C$_6$H$_{11}$)$_3$P}$_2$Cl$_2$Ru=CH$_2$][7] grow in with nearly equal intensities at the expense of the resonance for **3**, but at longer reaction times, **5** is gradually consumed to produce [{(C$_6$H$_{11}$)$_3$P}$_2$Cl$_2$Ru=CH$_2$] as the major (>95%) ruthenium-containing species. In the case of **4**,‡ ^{1}H NMR resonances attributable to two new silyl-substituted alkylidenes grow in at the expense of the alkylidene resonance for **4**. The ratio of these resonances (*ca.* 2 : 1) remains constant at all times, suggesting that they are due to the *anti* (δ 13.50) and *syn* (δ 12.45) rotamers of **6**.[9]

Although it is reasonable to expect the self-metathesis of **1** to be thermodynamically favourable, ^{1}H NMR spectra of reaction mixtures containing **1** and either **3** or **4** never exhibit vinylic ^{1}H resonances attributable to the formation of products derived from the self-metathesis of **1**. It appears that steric demands by the Si/O framework prevent the formation of metallacyclobutanes containing two adjacent silsesquioxane frameworks. Similar results are observed for spherosilicate **2**.[5] From the standpoint of synthesizing highly functionalized silsesquioxanes and spherosilicates, the practical consequences of this situation are enormous: cross-metathesis of **1** or **2** with monofunctional alkenes should never be complicated by competing oligomerization or polymerization of the vinyl-substituted Si/O frameworks.

The addition of an alkene to solutions containing **1** or **2** and an alkene metathesis catalyst quickly produces new ^{1}H resonances attributable to cross-metathesis products. In the case of **1**, **4** and *cis*-oct-4-ene, for example, prominent ^{1}H resonances are observed for free pent-1-ene and pent-1-enyl substituents on the Si$_8$O$_{12}$ framework, as well as the expected secondary metathesis products (*e.g.* C$_2$H$_2$ and PhCMe$_2$CH=CHBu). Similar results were observed upon addition of pent-1-ene, but the amount of ethene was much larger and the rate of productive cross-metathesis was slower.

Table 1 summarizes the results from a number of cross-metathesis reactions performed on a preparative scale using **3** and **4** as catalysts.§ Each reaction was performed under a slight vacuum in order to remove ethene, which greatly slows the rate of productive cross-metathesis and deactivates Schrock-type metathesis catalysts.[10,11] As expected,[12] Schrock's catalyst (*i.e.* **4**) is substantially more active than Grubbs' catalyst (*i.e.* **3**) in cases where the molybdenum alkylidene is compatible with functional groups attached to the alkene. However, the greater functional group tolerance of **3** allows the introduction of functional groups that deactivate **4**. Unfortunately, the rates of cross-metathesis with **3** are currently too slow to be of practical value for the preparation of pure octafunctional derivatives of **1** and **2**.

Both α-alkenes and internal alkenes can be used for the cross-metathesis reaction, but α-alkenes generally: (*i*) undergo cross-metathesis reactions much more readily than internal alkenes; (*ii*) offer a distinct cost advantage over internal alkenes; and (*iii*) undergo self-metathesis to internal alkenes at rates much greater than the rates of cross-metathesis with **1** or **2**. Nevertheless, internal alkenes are attractive starting materials because of their lower volatility and their inability to produce ethene. Except for reactions involving styrene, which appear to produce only *trans*-substituted products, it is important to note that the product in all cases is actually a complex mixture of substitutional isomers containing statistical distributions of *cis*- and *trans*-substituted double bonds. The same thermodynamic mixture of cross-metathesis products appears to form regardless

Table 1 Cross-metathesis reactions of **1** and **2** with alkenes

$$\mathbf{1}\text{ or }\mathbf{2}\ \xrightarrow[\text{RCH=CHR}]{\text{RCH=CH}_2\text{ or}}\ [\text{RCH=CHSiO}_{3/2}]_8\text{ or }[\text{RCH=CHSiMe}_2\text{OSiO}_{3/2}]_8$$

Entry	Si/O Framework	Alkene	Catalyst [amount (%)]^a	Conditions	Conv. (%)	Yield (%) (*trans*/*cis*)^b
1	**1**	*cis*-Oct-4-ene (3 equiv.)^c	**4** (1.6)	C_6H_6, 25 °C, 100 h	100	75^d (85/15)
2	**1**	*cis*-Oct-4-ene (3 equiv.)	**4** (5)	C_6D_6, 25 °C, 4.5 h	100	100^e (85/15)
3	**1**	Pent-1-ene (2 equiv.)	**4** (2.5)	Neat, 25 °C, 12 h	100	100^e (85/15)
4	**1**	Styrene (5 equiv.)	**4** (3)	C_6D_6, 25 °C, 12 h	100	81^d (All-*trans*)
5	**1**	Allyltrimethoxysilane (1.5 equiv.)	**4** (5)	C_6D_6, 25 °C, 12 h	100	100^d (88/12)
6	**1**	Ethyl undec-10-enylate (10 equiv.)	**4** (6)	C_6D_6, 25 °C, 22 h	100	100^e (80/20)
7	**1**	Oct-7-enyltrimethoxysilane (2 equiv.)	**4** (6)	C_6D_6, 25 °C, 6 h	100	100^e (84/16)
8	**1**	5-Bromopentene (12 equiv.)	**4** (6)	C_6H_6, 25 °C, 16 h	100	76^d (94/6)
9	**1**	Pent-4-en-1-ol (3 equiv.)	**3** (6)	CD_2Cl_2, 38 °C, 48 h	10	— (*ca.* 4/1)
10	**1**	5-Bromopent-1-ene (3 equiv.)	**3** (6)	CD_2Cl_2, 38 °C, 24 h	25	— (*ca.* 4/1)
11	**2**	Styrene (2 equiv.)	**4** (6)	C_6H_6, 25 °C, 24 h	100	70^d (All-*trans*)
12	**2**	Pent-1-ene (2 equiv.)	**4** (6)	C_6H_6, 25 °C, 24 h	100	100^e (86/14)

^{a} Mol% catalyst based on available $SiCH{=}CH_2$. ^{b} *trans*/*cis* ratio for SiCH=CHR groups determined by ^1H NMR spectroscopy. ^{c} Mol equiv. per $SiCH{=}CH_2$. ^{d} Isolated yield (quantified by NMR). ^{e} NMR yield.

of the alkene (*i.e.* internal alkene *vs.* α-alkene) used to prepare a particular octafunctional silsesquioxane. This inseparable mixture of isomers is unavoidable, but it can be transformed into a single octasubstituted product *via* catalytic hydrogenation [Pd/C, 25 °C, 160 psig) (1 psig = Pa). For example, catalytic hydrogenation of the product mixture obtained *via* cross-metathesis of **1** with pent-1-ene affords a high overall yield of (n-pentyl)$_8$Si$_8$O$_{12}$ **7**.¶

We have only begun to explore the generality of this cross-metathesis procedure, but it is already clear that it offers an important new route to functionalized silsesquioxanes. It also offers intriguing possibilities for the preparation of new hybrid inorganic/organic materials, such as network polymers derived from metathesis reactions of vinyl-substituted Si/O frameworks with cyclic alkenes (ROMP) and/or dienes (ADMET). These and other potential applications are currently under investigation.

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Footnotes

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† Within 8 min of mixing at 25 °C, the reaction of **3** with a large excess of **1** in CD_2Cl_2 exhibits three ruthenium–alkylidene resonances with nearly equal integrated intensities: δ 20.03 (unreacted **3**), δ 18.96 $\{[(C_6H_{11})_3P\}_2Cl_2Ru{=}CH_2]\}$ and 23.35 (assigned to **5**). Characteristic resonances for styrene and both *cis* and *trans*-stilbene (derived from self-metathesis of styrene) are also observed. Within 60 min, the resonance for **3** vanishes; after 17 h, only the resonance at δ 18.96 remains.

‡ Within 15 min of mixing at 25 °C, the reaction of **4** with a large excess of **1** in C_6D_6 exhibits three major molybdenum alkylidene resonances with relative integrated intensities of 2 : 1 : 2: δ 13.50 (assigned on the basis of chemical shift[9] to the *anti*-rotamer of **6**), 12.45 (assigned to the *syn* rotamer of **6**) and 12.12 (unreacted **4**). Characteristic resonances for $PhCMe_2(CH{=}CH_2)$ are also observed. Within 45 min, the resonance for **4** vanishes. Provided that air is rigorously excluded from the sample, the resonances at δ 13.50 and 12.45 persist indefinitely.

§ All new compounds in Table 1 exhibited satisfactory analytical and spectroscopic data; full details will be reported elsewhere.

¶ Catalytic hydrogenation of $[CH_3CH_2CH_2CH{=}CHSiO_{3/2}]_8$ (19 mg, obtained *via* the cross-metathesis of **1** with pent-1-ene) was performed over 10% Pd/C (7 mg) in ethyl acetate (2 ml) at 160 psi H_2 for 2 d at 25 °C. The catalyst was removed by filtration through a short column of silica gel and washed with CH_2Cl_2. Rotary evaporation of the filtrate gave **7** in quantitative yield as a colourless oil. For **7**: ^1H NMR (500 MHz, C_6D_6, 25° C) δ 1.69–1.63 (m, 16 H, CH_2), 1.40–1.27 (m, 32H, CH_2), 0.88 (t, 40 H, $SiCH_2$ and CH_3, J 7.3 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25° C) δ 35.08 (CH_2), 22.84 (CH_2), 22.49 (CH_2), 14.12 (CH_3), 12.55 ($SiCH_2$). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 25° C) δ −68.2. MS (70 eV, direct inlet; rel int.): m/z 984 (M^+, 9%).

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