

Full Length Research Paper

¹H and ³¹P–NMR monitored cross-metathesis reaction of octavinylsilsesquioxane hybrid nanocomposite with ruthenium carbene: possibility for multifunctional octasilsesquioxane derivatives

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Cross metathesis reaction of octavinylsilsesquioxane 1 with Grubb's carbene 2 in CDCl₃ has been monitored by ¹H – and ³¹P – NMR spectroscopy. Reaction in the presence of excess 1 afforded a ruthenium alkylidene resonance attributable to a monofunctional derivative of 1, while in the presence of excess 2, a tetrafunctional derivative resulted as determined by ¹H - , ³¹P – NMR and mass spectrometry.

Key words: Cross metathesis, octavinylsilsesquioxane, ruthenium carbene, nanocomposite.

INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) are well known hybrid molecules that have recently attracted extensive attention as possible nanomaterial (size, Si - Si 0.5 nm; R - R 1.5 nm) building blocks in the synthesis of various materials, such as ceramic and liquid crystalline supramolecular systems. Most metal- functionalized silsesquioxanes were synthesized from trisilanol using "end- capped" reaction (Feher et al., 1992; Maschmeyer et al., 1995; Field et al., 1994). The metallasil-sesquioxanes are noted for their high catalytic activities (Maschmeyer et al., 1995).

There are reports (Voronkov et al., 1979; Martynova et al., 1982; Yucks and Carrado, 1996) on cross-metathesis reactions of alkenes with readily available vinyl-substituted silsesquioxane and spherosilicates. However, investigations on metallasilsesquioxanes bearing ruthenium metal are often hampered by slow rates of cross-metathesis which limits its practicability. Moreover, there are reports on cross-metathesis of vinyl-substituted (vinyltrialkoxo) and (vinyltrisiloxy)-silanes catalyzed by a ruthenium carbene complex (Grubbs catalyst) with various olefins, such as styrene (Pietraszuk et al., 2000), terminal alkenes and p-substituted styrenes (Pietraszuk et al., 2001; Kujawa-Welton et al., 2002). However, the alkyl-substituted vinylsilanes appear to be quite inactive in ruthenium-catalyzed cross-metathesis (Kujawa-Welton et al., 2002). Recently, Itami et al. (2004) reported the

functionalization of octavinylsilsesquioxane by employing both types of reactions catalyzed by ruthenium carbene complexes silylative coupling and cross-metathesis on a wide range of substituted silsesquioxanes with diverse b-substituted vinyl (especially b-heteroatom-substituted) groups. It is noteworthy that multifunctionalization of octasilsesquioxane with ruthenium carbene (Schwabs et al., 1995) has not been achieved. Here, a report of ¹H – and ³¹P – NMR – monitored cross metathesis reactions of vinylsilsesquioxane 1 with [(Cy₃P)₂Cl₂Ru=CHPh] 2 (ruthenium or Grubb's carbene) (Schwabs et al., 1995) on a preliminary scale is presented.

NMR TUBE EXPERIMENTS

NMR tube was charged with 1 (0.04 g, 6.3 × 10⁻⁵ mole) and Grubb's carbene (0.009 g, 1.01 × 10⁻⁵ mole). CDCl₃ (1.0 mL) was added as fast as possible under nitrogen. The tube was sealed up and ¹H and ³¹P NMR signals were recorded.

Under nitrogen, a solution of 1 (0.02g, 3.16 × 10⁻⁵ mole) in CH₂Cl₂ (5.0 mL) was prepared. This solution was added to a stirred solution of Grubb's carbene. (0.104 g, 1.26 × 10⁻⁴ mole) at 0°C. Ice-bath was removed and the mixture was stirred for 5 h at 30°C. The solvent was removed giving shining black microcrystal, which was further washed with little dried methanol. ¹H-NMR (CDCl₃): δ: 6.0-6.25 ppm (m, H₂C=CH-, 12H), 1.23-2.15 ppm (m, -C₆H₁₁, 264H). ³¹P-NMR (CDCl₃): δ: 50.94 ppm (s, P(C₆H₁₁)₃). MS (FAB): 3505.8 (M⁺, parent ion).

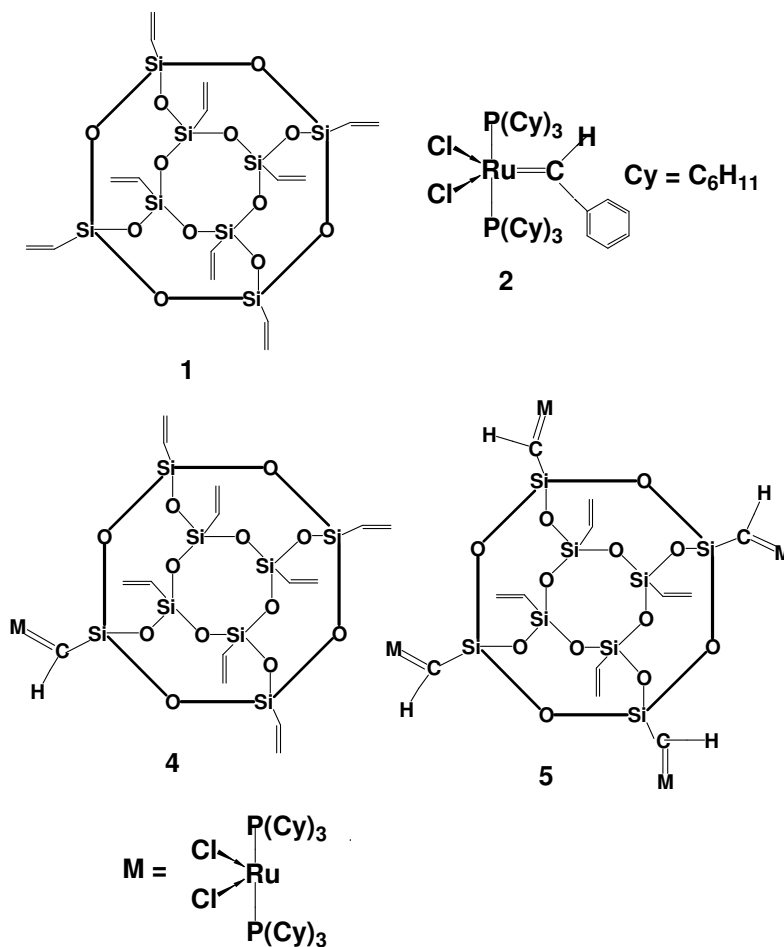


Figure 1. Structural representation of 1, 2, 4 and 5.

RESULTS AND DISCUSSION

In an NMR sample tube, treatment of 1 with 2 (6:1) in CDCl_3 afforded two products: $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CH}_2]$ 3 and 4 within the first 12 min of reaction. The latter is the monofunctional derivative of vinylsilsesquioxane as determined by ^1H -NMR spectroscopy while the former is the self metathesis product. Hence, the peaks at (^1H : δ 18.90, ^{31}P : δ 43.71) and (^1H : δ 23.93, ^{31}P : δ 45.36) are assigned to 3 and 4 respectively. This result conforms to a similar report [Feher et al., 1997] elsewhere (Figure 1).

After establishing the possibility for monofunctional formation of alkylidene complexes, the necessity to adopt a large excess of 2 arose. Within 20 min of reacting 1 with 2 (1:4) in CDCl_3 , three ruthenium-alkylidene proton resonances appeared (Figure 2). In addition to the reappeared 3 and 4, the smallest peak at δ 22.6 on proton NMR is assigned to 5 (tetrafunctional derivative of 1). ^{31}P -NMR of the mixture (Figure 3) also signified that indeed 3, 4, 5 and unreacted 2 were formed originally. The reaction was repeated on a preparative scale and 5 isolated as a shining black microcrystals with a clear ^{31}P -

NMR spectra indicating phosphorus signal at δ 50.94 (Figure 4).

The mechanism of cross metathesis reaction of alkenes and Grubb's catalyst has been proposed by Schwab et al. (1996). 1 reacted with Grubb's carbene to rapidly form a metallacyclobutane intermediate [Harrison and Chauvin, 1980]. Productive cleavage of the intermediate metallacycle leads to the formation of the alkylidene complexes 3, 4 and 5.

Conclusion

The possibility for the tetrafunctional derivative of 1 has been demonstrated by the cross metathesis reaction of octavinylsilsesquioxane and ruthenium carbene in an NMR tube as well as on a preparative scale. However, possibility for practicable octafunctionalization product still remains unsolved as proton NMR indicates complicated mixture of decomposed materials. The molecular orientation of the new organic-inorganic hybrid 5 may suggest its future application in catalysis. Full scale

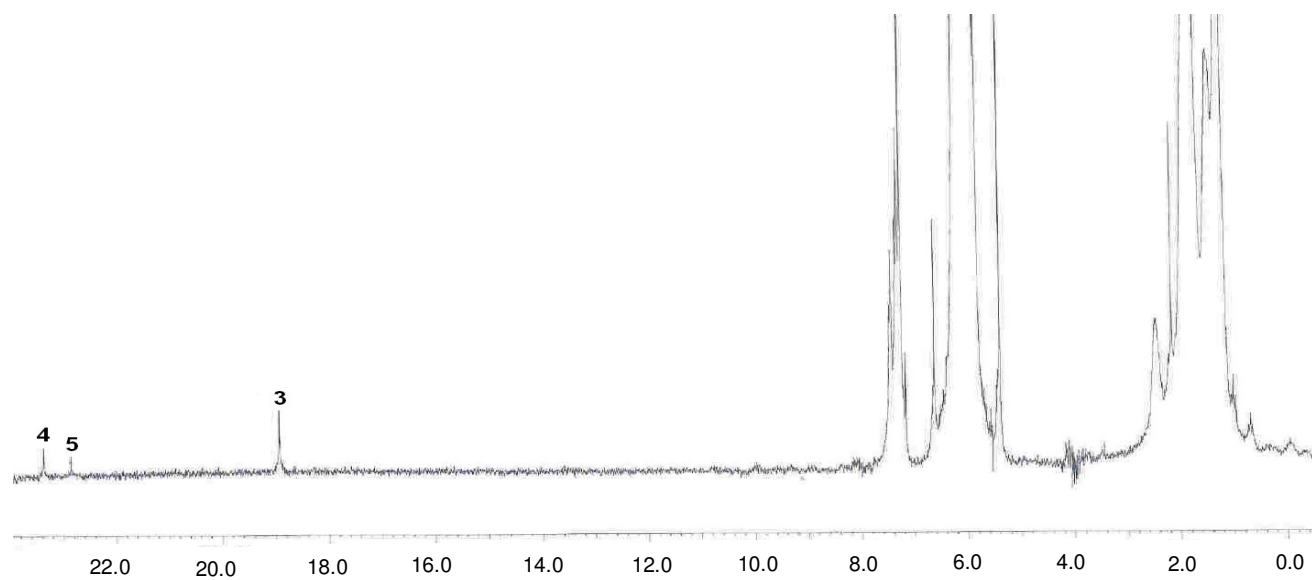


Figure 2. ^1H -NMR Spectra indicating ruthenium-alkylidene resonances of 3, 4 and 5.

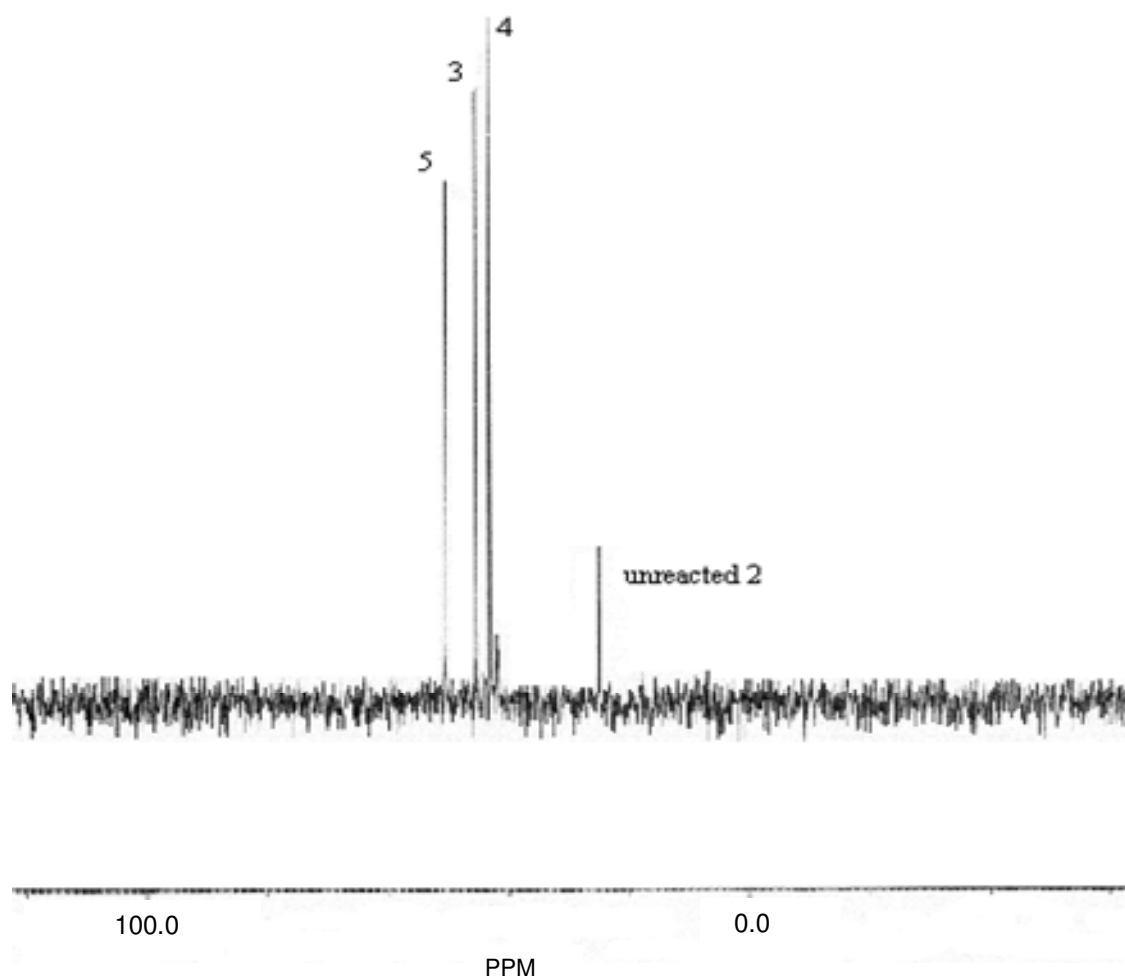


Figure 3. ^{31}P -NMR of the original mixtures of 2, 3, 4 and 5.

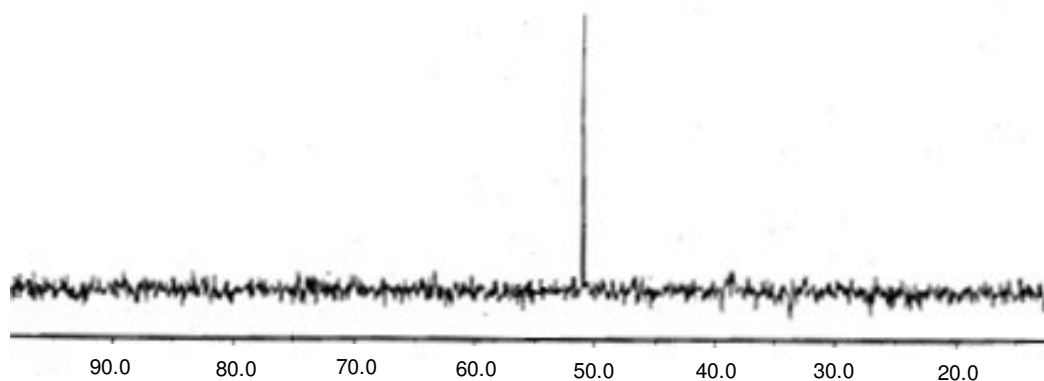


Figure 4. ^{31}P -NMR of isolated cross-metathesis product 5.

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