Transition Metal Catalyzed Dehydropolymerization of Silanes to Form Polysilanes: Reactions, Mechanism, and Applications

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Polysilanes have attracted considerable attention due to their novel electronic properties and their importance as polymeric SiC precursors [1,2]. However, it was not until the 1980's, that researchers found synthetic routes to soluble, high molecular weight polymers [3,4]. Until then, the synthesis of polysilanes involved the use of Wurtz-Fittig type coupling reactions using Na metal in toluene or xylene at a temperature greater than 100°C. This method is quite dangerous [5-7]. In 1985, Harrod's exciting discovery of the polymerization of primary silane monomers at room temperature using Cp_2TiR_2 (Cp = η^5-cyclopentadienyl, R = CH_3 or $C_6H_5CH_2$) catalysts with $H_2(g)$ as a by-product [8] has led to the interest in transition metal catalyzed dehydropolymerization reactions.

Several mechanisms have been proposed to describe the silane dehydropolymerization: silene intermediates [9, 10], oxidative addition-reductive elimination [11], and σ-bond metathesis [12, 13, 21] (Figure 1). σ-bond metathesis reactions via a four-center transition state have been studied intensely for the activation of C-H bonds in unsaturated and saturated hydrocarbons by group 3 and 4 transition metals [14-16]. Experimental evidence has led to the conclusion that σ-bond metathesis is the favored mechanism for dehydropolymerization of silanes [17-19]. The mechanism involves two steps: (1) dehydrometalation of a silane, $H(SiHR)_nH$ (R = alkyl or aryl), with an early transition metal hydride and (2) coupling of the metal silyl derivative with more hydrosilane, $H(SiHR)_mH$, to regenerate the early transition metal hydride catalyst.
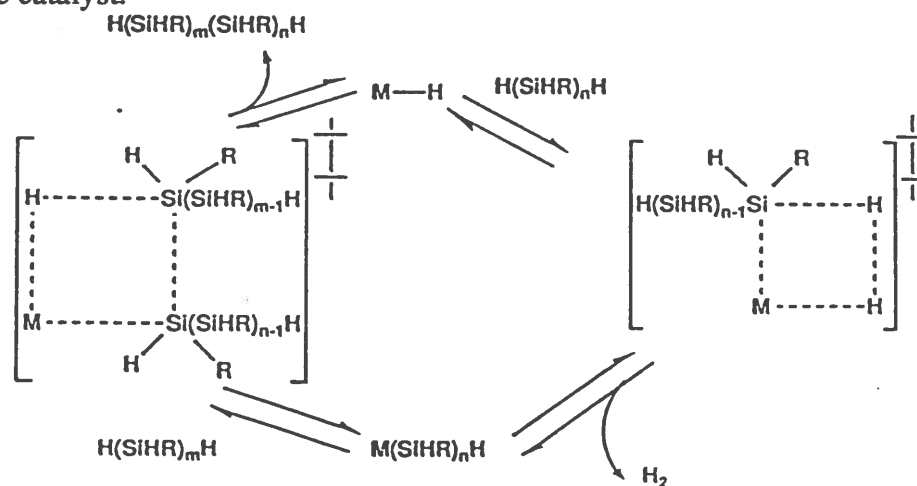

Figure 1. σ-bond metathesis mechanism (M = group 4 transition metal with CpCp*X or Cp_2X ligands where Cp = η^5-cyclopentadienyl, Cp* = η^5-pentamethylcyclopentadienyl, X = Cl or Me; R = alkyl, aryl, or silyl).

Mechanistic studies have been performed using ^{1}H NMR, ^{29}Si NMR, ^{13}C NMR, IR, and x-ray diffraction techniques. Treatment of CpCp*(Cl)MH, where Cp = η^5- cyclopentadienyl, Cp* = η^5-pentamethylcyclopentadienyl, and M = Zr or Hf, with $PhSiH_3$ formed $CpCp*(Cl)MSiH_2Ph$ [17, 18]. This reaction provided evidence for M-Si bond formation. Thermal decomposition of $CpCp*(Cl)HfSiH_2Ph$ and the reaction of $CpCp*(Cl)MSiH_2Ph$ with $PhSiH_3$ provided evidence for Si-Si bond formation [17,18]. This mechanistic study led to better understanding of how silane substituents, choice of transition metal, and choice of transition metal ligands affect the polymerization reaction.

The effectiveness of transition metal complexes as catalysts was determined from the molecular weight distributions of the polysilanes formed. The polysilanes created by σ-bond metathesis reactions were monitored using gel permeation chromatography (GPC) and a refractive index detector. Reactions of CpCp*Zr(Si(SiMe$_3$)$_3$)Me with PhSiH$_3$ and CpCp*Zr-(Si(SiMe$_3$)$_3$)Cl with PhSiH$_3$ demonstrated different molecular weight distributions [20]. The choice of ligand (L) in CpCp*Zr(Si(SiMe$_3$)$_3$)L affected the molecular weight distribution, with stronger π-donors decreasing the activity of the catalyst (Figure 2). The CpCp*Zr(Si(SiMe$_3$)$_3$)-Me and Cp$_2$Zr(Si(SiMe$_3$)$_3$)Me catalysts gave different molecular weight distributions, with the CpCp* ligand set being more effective than the Cp$_2$ ligand set [20]. Also, the molecular weight distributions were affected by the choice of early transition metal and silane monomer concentration [20].
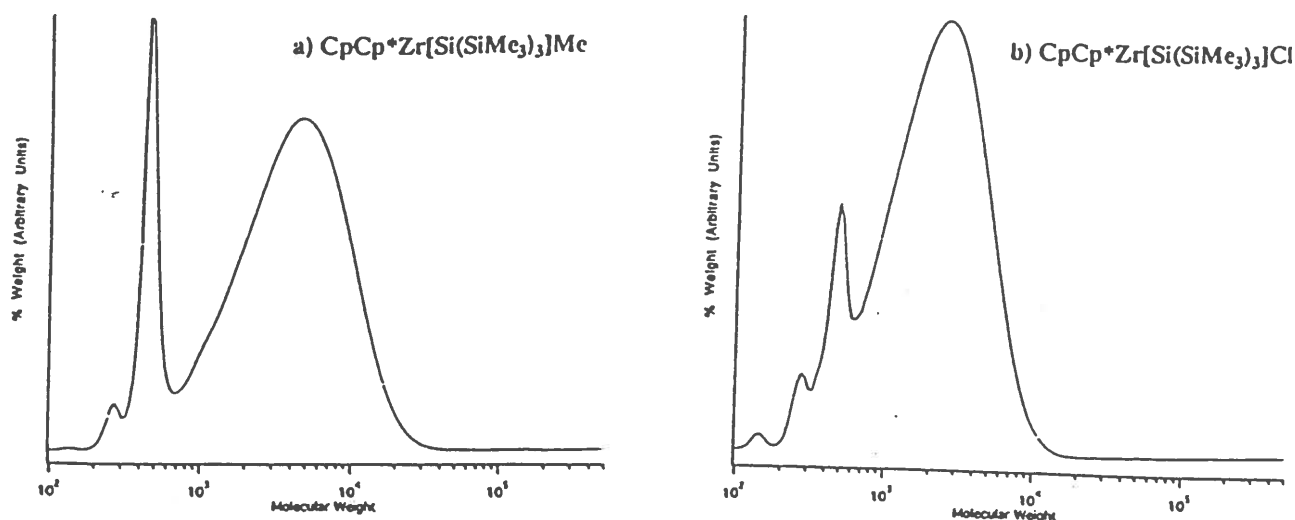

Figure 2. Molecular weight distributions for (SiHPh)$_n$ catalyzed by (a) CpCp*Zr[Si(SiMe$_3$)$_3$]Me and (b) CpCp*Zr[Si(SiMe$_3$)$_3$]Cl.

Room temperature syntheses of polysilanes are useful for several technological applications: (1) precursors to SiC, (2) microlithography, and (3) photoinitiation of vinyl polymerizations [6,7, 22]. However, the most interesting aspect of polysilanes is their ability to absorb light in the UV region (200-350 nm) with extinction coefficients that vary from 5,000 to 60,000 L mol^{-1} cm^{-1} [6,7]. The nature of these Si-Si σ-σ* electronic transitions is affected by the number and the type of substituents on the Si backbone [1,7].

Transition metal complexes as catalysts provide a room temperature route to polysilanes. The mechanism of the dehydropolymerization involves σ-bond metathesis reactions that occur via four-center transition states. The molecular weight distributions of the resulting polysilanes are dependent upon the choice of early transition metal, CpCp* or Cp$_2$ ligand set, π ligand on the metal, and concentration of silane monomer present.

References

1.   Gilman, H.; Atwell, W. H.; Schwebke, G. L. "Ultraviolet Properties of Compounds Containing the Silicon-Silicon Bond," *J. Organomet. Chem.* **1964**, *2*, 369-371.

3. Wesson, J. P.; Williams, T. C. "Organosilane Polymers. II. Poly(ethylmethyl-co-Dimethylsilylene) and Poly(methylpropyl-co-Dimethylsilylene)," *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 959-965.

4. West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. "Phenylmethylpolysilanes: Formidable Silane Copolymers with Potential Semi-conducting Properties," *J. Am. Chem. Soc.* **1981**, *103* (24), 7352-7354.

5. Harrod, J. F.; Mu, Y.; Samuel, E. "Catalytic Dehydrocoupling: A General Method for the Formation of Element-Element Bonds," *Polyhedron* **1991**, *10* (11), 1239-1245.

6. Miller, R. D.; Michl, J. "Polysilane High Polymers," *Chem. Rev.* **1989**, *89* (6), 1359-1410.

7. West, R. "The Polysilane High Polymers," *J. Organomet. Chem.* **1986**, *300*, 327-346.

8. Aitken, C.; Harrod, J. F. "Polymerization of Primary Silanes to Linear Polysilanes Catalyzed by Titanocene Derivatives," *J. Organomet. Chem.* **1985**, *279*, C11-C13.

9. Yamamoto, K.; Okinoshima, H.; Kumada, M. "Evidence for 'Silylenoid' Species in Disproportionation of Pentamethyldisilane Catalyzed by *trans*-[PtCl$_2$(Et$_3$P)$_2$]," *J. Organomet. Chem.* **1971**, *27*, C31-C32.

10. Ojima, I.; Inaba, S.-I.; Kogure, T. "The Action of Tris(triphenylphosphine)chloro-rhodium on Polyhydromonosilanes," *J. Organomet. Chem.* **1973**, *55*, C7-C8.

11. Curtis, M. D.; Epstein, P. S. "Redistribution Reactions on Silicon Catalyzed by Transition Metal Complexes," In *Advances in Organometallic Chemistry*, Vol. 19; Academic Press: New York, **1981**, pp 213-255.

12. Woo, H.-G.; Tilley, T. D. "σ-Bond Metathesis Reactions of Si-H and M-Si Bonds. New Routes to do Metal Silyl Compexes," *J. Am. Chem. Soc.* **1989**, *111*, 3757-3758.

13. Woo, H.-G.; Tilley, T. D. "Dehydrogenative Polymerization of Silanes to Polysilanes by Zirconocene and Hafnocene Catalysts. A New Polymerization Mechanism," *J. Am. Chem. Soc.* **1989**, *111*, 8043-8044.

14. Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. "Synthetic and Mechanistic Aspects of Intramolecular Aliphatic CH Bond Activation by Ti(IV) and Zr(IV) Metal Centers," *J. Am. Chem. Soc.* **1985**, *107*, 5981-5987.

15. Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. "'σ Bond Metathesis' for C-H Bonds of Hydrocarbons and Sc-R (R = H, alkyl, aryl) Bonds of Permethylscandocene Derivatives. Evidence for Noninvolvement of the π System in Electrophilic Activation of Aromatic and Vinylic C-H Bonds," *J. Am. Chem. Soc.* **1987**, *109*, 203-219.

16. Fendrick, C. M.; Marks, T. J. "Actinacyclobutanes. Implementation of Thermo-chemically Based Strategies for the Ring-Opening Stoichiometric C-H Function-alization of Saturated and Olefinic Hydrocarbons," *J. Am. Chem. Soc.* **1986**, *108*, 425-437.

17. Woo, H.-G.; Walzer, J. F.; Tilley, T. D. "A σ-Bond Metathesis Mechanism for Dehydropolymerization of Silanes to Polysilanes by d⁰ Metal Catalysts," *J. Am. Chem. Soc.* **1992**, *114*, 7047-7055.

18. Woo, H.-G.; Heyn, R. H.; Tilley, T. D. "σ-Bond Metathesis Reactions for d⁰ Metal-Silicon Bonds that Produce Zirconocene and Hafnocene Hydrosilyl Complexes," *J. Am. Chem. Soc.* **1992**, *114*, 5698-5707.

19. Pawlenko, S. In *Organosilicon Chemistry*; de Gruyter: Berlin, **1986**, pp 1-3.

20. Tilley, T. D. "The Coordination Polymerization of Silanes to Polysilanes by a 'σ-Bond Metathesis' Mechanism. Implications for Linear Chain Growth," *Acc. Chem. Res.* **1993**, *26*, 22-29.

21. Corey, J. Y.; Shaltout, R. M. "*Ansa*-Metallocenes: Catalysts for the Dehydrocoupling of Hydrosilanes," *Tetrahedron* **1995**, *51* (15), 4309-4320.

22. Roux, P.; Pillot, J.-P.; Birot, M.; Dunogues, J.; Lapouyade, P. "Synthesis of new poly(2,4-disilapentane) oligomers via dehydrocondensation reaction using Group IV metallocene catalysts," *J. Organomet. Chem.* **1995**, *499*, 199-204.