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Dehydrogenative Polymerization of Silanes to Polysilanes by Zirconocene and Hafnocene Catalysts. A New Polymerization Mechanism

Hee-Gweon Woo and T. Don Tilley*

Chemistry Department, D-006
University of California at San Diego
La Jolla, California 92093-0506

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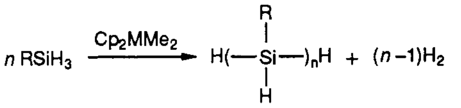
Polysilanes, $(-SiRR'-)_n$, represent a class of inorganic polymers that have unusual chemical properties and a number of potential applications.[1] Prospects for development of a coordination polymerization route to these polymers have improved dramatically with the recent discovery by Harrod and co-workers that titanocene and zirconocene alkyl derivatives are active catalysts for the dehydrogenative coupling of primary silanes $RSiH_3$ to linear polysilanes with ca. 10–20 Si atoms (eq 1, Cp = η^5-C_5H_5, M = Ti, Zr).[2] We have found that a number of zirconium and hafnium



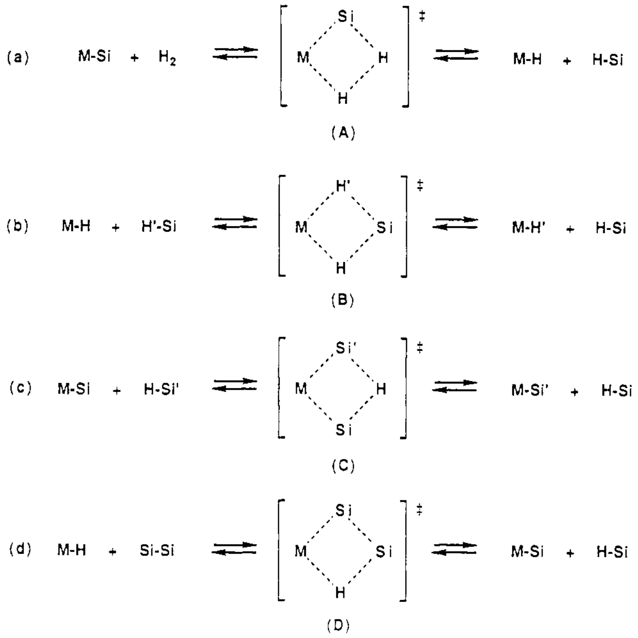
$$n\,RSiH_3 \xrightarrow{Cp_2MMe_2} H(-\overset{R}{\underset{H}{Si}}-)_nH + (n-1)H_2 \qquad (1)$$

silyl complexes of the type $Cp'_2M(SiR_3)R'$ (Cp′ = Cp, Cp* (η^5-C_5Me_5); M = Zr, Hf; R = Me, Ph, $SiMe_3$; R′ = Cl, alkyl, silyl) are catalyst precursors for this dehydrogenative coupling reaction and that polymer molecular weights can vary as a function of reaction conditions and catalyst.[3] Improvement of this method relies heavily on an understanding of the polymerization mechanism, which has remained obscure.[2] This report describes observations that suggest a mechanism for dehydrogenative silane polymerization by zirconocene and hafnocene catalysts.

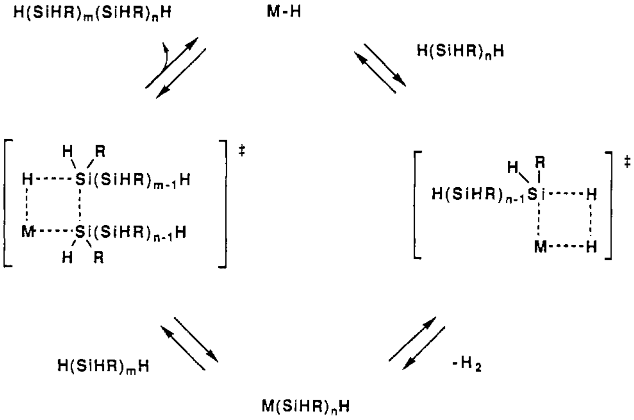
Our investigations of d^0 metal–silicon bond reactivity have revealed a number of processes that can be described as "σ-bond metathesis"[4a] reactions involving M–H, M–Si, Si–H, Si–Si, and H–H bonds. Similar reactions for d^0 M–C and M–H bonds have been described, and mechanistic studies indicate that they pass through concerted, four-center transition states.[4] Observation of the six unique processes represented by the equations in Scheme I suggests that silicon readily participates in σ-bond metathesis reactions with d^0 metal centers via four-center transition states A–D. These processes have been observed for zirconocene and hafnocene derivatives that are catalysts for the dehydrogenative coupling of silanes.

The forward reaction represented by eq (a), M–Si bond hydrogenolysis, has previously been reported for $Cp_2Zr(SiR_3)Cl$ complexes and appears to be generally facile for d^0 silyl complexes.[5] The reverse, M–Si bond-forming process is observed in reactions between hydrides $[CpCp^*MHCl]_2$ (**1**, M = Zr; **2**, M = Hf)[6] and $PhSiH_3$ to produce $CpCp^*M(SiH_2Ph)Cl$ (**3**, M = Zr; **4**, M = Hf)[6] and H_2. Hydrogen/deuterium exchange, possibly via transition state B, occurs rapidly between **1** or **2** and $PhSiD_3$.

Scheme I. Possible σ-Bond Metathesis Processes Involving a d^0 Metal Center, Hydrogen, and One or Two Silyl Groups



Scheme II. Proposed Mechanism for Dehydrogenative Silane Polymerization by Zirconocene and Hafnocene Catalysts



We recently reported stoichiometric σ-bond metathesis reactions that are probably relevant to formation of the active catalyst (eq 2).[6] The thermal (dark) reaction between $CpCp^*Hf[Si(SiMe_3)_3]Cl$ (**5**) and $PhSiH_3$ is quantitative and was subjected to a kinetic study. Reaction rates were monitored by ^1H NMR spectroscopy in benzene-d_6 under pseudo-first-order conditions with excess silane and are consistent with a second-order rate law, rate = $k[\mathbf{5}][PhSiH_3]$, with $k(40\ °C) = 4.3\ (3) \times 10^{-5}\ M^{-1}\ s^{-1}$. The kinetic deuterium isotope effect for this reaction at 70 °C is 2.5 (1), and activation parameters determined for the temperature range 40–85 °C are $\Delta H^\ddagger = 16.4\ (7)$ kcal mol^{-1} and $\Delta S^\ddagger = -27\ (2)$ eu. These data are consistent with values reported for σ-bond metathesis reactions of d^0 M–X (X = H, C) bonds[4] and with a concerted mechanism for silyl group exchange (transition state C).

$$M-SiR_3 + R'SiH_3 \rightarrow M-SiH_2R' + HSiR_3 \qquad (2)$$

A stoichiometric Si–Si bond-forming reaction is observed in the thermal decompositions of **3** and **4** to the corresponding hydrides **1** and **2** and polysilane derivatives.[6] In benzene-d_6 disappearance of **4** follows a second-order rate law, rate = $k[CpCp^*Hf(SiH_2Ph)Cl]^2$, with $k(75\ °C) = 1.1\ (1) \times 10^{-4}\ M^{-1}\ s^{-1}$, $\Delta H^\ddagger = 19.5\ (2)$ kcal mol^{-1}, $\Delta S^\ddagger = -21\ (1)$ eu, and $k_H/k_D = 2.9\ (2)$ at 75 °C. These data suggest that Si–Si bonds may be formed via a transition state of type D, arising from bimolecular collisions of **4**. Significantly, conversion of **4** to **2** and polysilanes is ac-

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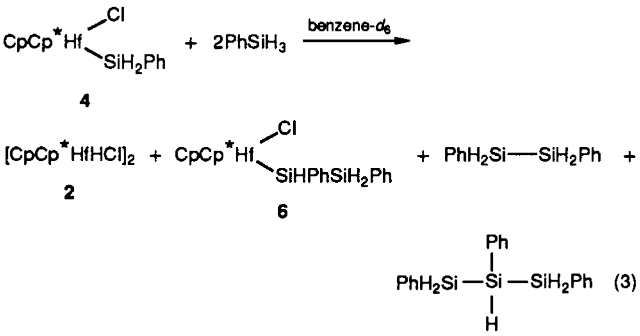
celerated by $PhSiH_3$. Under pseudo-first-order conditions with excess $PhSiH_3$, disappearance of **4** is first-order in both **4** and $PhSiH_3$ over three half-lives (k(70 °C) = $3.7\ (3) \times 10^{-4}\ M^{-1}\ s^{-1}$). The isotope effect, determined at 70 °C with use of excess $PhSiD_3$, is 2.7 (2). We propose that the latter conversion proceeds through concerted Si–Si bond-forming steps, as represented by eq (d). Presumably the acceleration effect of $PhSiH_3$ results from the better fit of $H–SiH_2Ph$ vs H–SiHPh(CpCp*HfCl) in the four-center transition state.

The σ-bond metathesis chemistry summarized above suggests a mechanism for the dehydrogenative polymerization of silanes by zirconocene and hafnocene derivatives (Scheme II). A coordinatively unsaturated hydride complex is implicated as an important intermediate, since Si–Si bond formation results in production of metal hydride species, and since hydride complexes themselves are active catalysts.[3] Such hydride species are readily formed in solution from catalyst precursors via σ-bond metathesis reactions (see Scheme I). Each catalytic cycle involves formation of a metal silyl derivative and free polysilane. Observed steric constraints on these σ-bond metathesis reactions suggest that the metal hydride interacts predominantly with the sterically less crowded $-SiH_2R$ end group of a polymer chain, giving linear chain growth. We also believe that steric constraints are such that one of the reacting silanes in a cycle must be primary (n or $m = 1$), resulting in chain growths of only one Si per cycle. Note that the mechanism proposed here involves reactions at only one M–X σ-bond, whereas a metal silylene-based mechanism[2] requires that two σ-bonds are used. Our results are consistent with involvement of only one σ-bond, since compounds **3**, **4**, and **5** are catalyst precursors for the polymerization of $PhSiH_3$, which quantitatively converts these chloro complexes to the corresponding hydrides $[CpCp^*MHCl]_2$.[3]

Using model reactions, we have detected the expected intermediates for the proposed mechanism. Thus CpCp*Hf($SiHPhSiH_2Ph$)Cl (**6**), prepared independently from **1** and PhH_2SiSiH_2Ph and isolated as a 1:1 mixture of two diastereomers,[7] was identified (by ^1H NMR spectroscopy) in the slow oligomerization of $PhSiH_3$ by **4**. Addition of 2 equiv of $PhSiH_3$ to **4** resulted in formation of **2**, **6**, disilane, and trisilane after 24 h (33% conversion) (eq 3).[8] The latter three silicon-containing products were formed in a ratio of ca. 3:2:3. Free, oligomeric silanes are also observed during coupling reactions with $Cp^*_2HfH_2$ as catalyst. Presumably because of steric hindrance at the metal center, this hafnium hydride couples Si–H bonds very slowly. This allows observation (by ^1H NMR spectroscopy) of conversion of $PhSiH_3$ to disilane, which is followed more slowly by appearance of trisilane and finally, tetrasilane.[8] When heated to 120 °C for a day, the silane compounds are converted to higher molecular weight oligomers. These observations provide evidence for the stepwise nature of chain growth. Early in reaction of $Cp^*_2HfH_2$ with PhH_2SiSiH_2Ph, significant quantities of $PhSiH_3$ are detected, establishing reversibility of Si–Si bond formation.



This catalytic cycle appears to represent a new polymerization mechanism and is unusual as a coordination polymerization in that it involves step growth of polymer rather than chain growth. The mechanism accounts for the stringent steric requirements observed for catalysts and silane monomers, since the four-center transition states are inherently quite crowded. It is hoped that further investigation will produce a more complete understanding of factors controlling reactivity and that the proposed mechanism will lead to development of better catalytic systems that allow control of stereoregularity and molecular weights of the polysilanes.

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(7) For **6** (diastereomers A and B): Anal. C, H; IR (neat, CsI, cm^{-1}) ν(SiH) = 2040, 2100; ^1H NMR (benzene-d_6, 22 °C, 300 MHz) δ 1.79 (s, 30 H, Cp*, A, B), 4.65–4.92 (m, 6 H, SiH, SiH_2, A, B), 5.73 (s, 5 H, Cp, A), 5.76 (s, 5 H, Cp, B), 7.10 (m, 4 H, p-C_6H_5, A, B), 7.19 (m, 8 H, m-C_6H_5, A, B), 7.71 (m, 8 H, o-C_6H_5, A, B); ^{29}Si NMR (benzene-d_6, 22 °C, 59.6 MHz) δ −9.05, −9.86 (d, J_{SiH} = 152 Hz, HfSi*H*PhSiH$_2$Ph, A, B), −43.91, −50.43 (t, J_{SiH} = 183 Hz, HfSiHPhSi*H*$_2$Ph, A, B).

(8) Silanes were identified by mass spectroscopy and ^1H and ^{29}Si NMR spectroscopy: ^{29}Si NMR data (benzene-d_6, 22 °C, 59.6 MHz) PhH_2SiSiH_2Ph, δ −61.3 (t), $PhH_2SiSiHPhSiH_2Ph$, δ −68.0 (d), −58.6 (t), $PhH_2Si(SiHPh)_2SiH_2Ph$, δ −71.2 (d), −57.4 (t).

First Examples of Three-Coordinate Manganese(III) and Cobalt(III): Synthesis and Characterization of the Complexes $M[N(SiMe_3)_2]_3$ (M = Mn or Co)

Jeffrey J. Ellison, Philip P. Power,* and Steven C. Shoner

Department of Chemistry, University of California
Davis, California 95616

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In transition-metal complexes the coordination number three is often regarded as a rarity. Nonetheless, the number of three-coordinate compounds now known is considerable.[1] Among the better known examples are the series of M^{3+} compounds $M[N(SiMe_3)_2]_3$ (M = Sc, Ti, V, Cr, and Fe) which have been studied extensively.[2] For manganese and cobalt several three-coordinate species have also been reported.[1-7] Without exception, these involve the 2+ oxidation state, and three coordination remains unknown for the somewhat less stable 3+ oxidation state of these elements. For example, the great majority of Co^{3+} (d^6) complexes have a geometry based upon the octahedron. Moreover, they are almost always diamagnetic which gives maximized CFSE and kinetic stability. However, a small, but important, number of four- and five-coordinate Co^{3+} complexes have been reported.[8,9] Similarly, manganese(III) (and higher oxidation state) complexes are not as numerous as those of Mn^{2+}, but they have attracted considerable attention owing to their significance for biological systems.[10] Its d^4-electron configuration may, under certain

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