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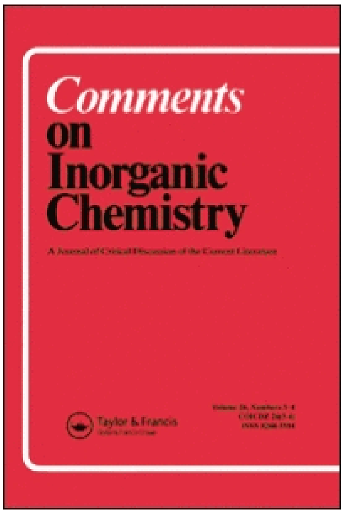

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Mechanistic Aspects of Transition-Metal Catalyzed Dehydrogenative Silane Coupling Reactions

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Dehydrogenative silane couplings to give Si–Si bonded compounds are catalyzed by a number of transition-metal complexes. A mechanism based on transition-metal silylene complexes, $L_nM=SiR_2$, seems possible for some of these reactions; however, little evidence exists to support their involvement in known systems. Based on precedents that exist in stoichiometric reactions, a more likely mechanism for late transition-metal catalysts consists of oxidative addition/reductive elimination cycles. For early transition metal (d^0) catalysts, evidence accumulated to date points toward a "σ-bond metathesis" mechanism based on concerted, 4-center transition states.

Key Words: *polysilane, silyl, silane coupling, silylene complex, σ-bond metathesis, polymerization*

INTRODUCTION

Dehydrogenative coupling reactions of hydrosilanes have attracted widespread interest as accessible routes to silicon–element bonds (Equation (1)).

$$R_3Si-H + H-X \longrightarrow R_3Si-X + H_2 \qquad (1)$$

These reactions are catalyzed by late transition-metal complexes, in some cases at convenient rates.[1] Examples include the alco-

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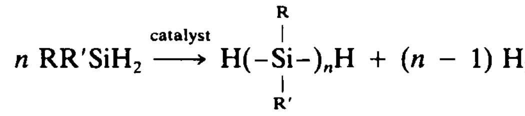
holysis of hydrosilanes to give alkoxysilanes,[2] and C–H activation processes leading to Si–C bonds.[3] Mechanisms for such reactions are not well-understood, and probably vary with the nature of H–X.

An intriguing reaction of this type is the dehydrogenative coupling of hydrosilanes with themselves to produce Si–Si bonds. In the case of a silane with more than one Si–H functionality, polymers with a silicon backbone are possible (Equation (2)).



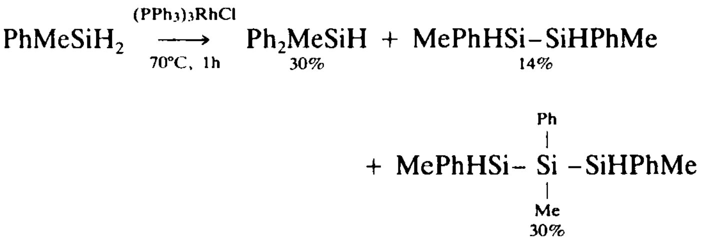
$$n\,\mathrm{RR'SiH_2} \xrightarrow{\text{catalyst}} \mathrm{H(-}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{Si}}}\mathrm{-)_{\it n}H} + (n-1)\,\mathrm{H_2} \qquad (2)$$

Generally reactions of this type could provide important routes to catenated species. Polysilanes have come under increased scrutiny as studies have shown that these polymers have unusual chemical properties and a number of potential applications, including their use as photoresist materials, preceramic fibers, photoconductors, dopable semiconductors, nonlinear optical materials, and photoinitiators for radical polymerizations.[4] This has increased interest in versatile synthetic routes to polysilanes that could be useful on a commercial scale. The only practical method available until now has been the Wurtz-type coupling of dichlorosilanes by an alkali metal.[4] This method suffers from some limitations that discourage commercial development, such as problems associated with handling large quantities of molten alkali metals and the difficulties in controlling molecular weight distributions. In addition, the highly reducing reaction conditions preclude introduction of many functional groups into the polymer chain.

A coordination polymerization route to polysilanes has appeared feasible for some time, given the precedents of many reactions between transition metal complexes and silanes.[1] There could be a number of advantages to such a polymerization reaction, such as providing a clean route to polysilanes with hydrogen gas as the only side-product. Also, manipulation of chemical factors at the reacting metal center may allow control of polymer properties such as chain length, tacticity, etc. Two classes of transition-metal complexes have been reported to catalyze the dehydrogenative coupling of hydrosilanes: (1) complexes of the platinum group metals such as rhodium, palladium, and platinum, and (2) d^0 metal complexes, particularly those of titanium and zirconium. The following discussion addresses mechanistic aspects of both reactions.

DEHYDROGENATIVE SILANE COUPLING REACTIONS

Since 1970, it has been known that late transition-metal (platinum metal) complexes can catalyze Si–Si bond-formation. The original report describes a redistribution process in which $(\mathrm{PEt_3})_2\mathrm{PtCl_2}$ acts as catalyst for converting the disilanes $\mathrm{RMe_2SiSiMe_2H}$ (R = H or Me) to a mixture of oligomers $\mathrm{R(SiMe_2)}_n\mathrm{H}$ (n = 1–6).[5] In 1973 Ojima and co-workers described the use of Wilkinson's catalyst, $(\mathrm{PPh_3})_3\mathrm{RhCl}$, for low conversion of the secondary silanes $\mathrm{PhMeSiH_2}$, $\mathrm{Ph_2SiH_2}$, and $\mathrm{Et_2SiH_2}$ to mixtures of mono-, di-, and trisilanes (e.g., Equation (3)).[6]



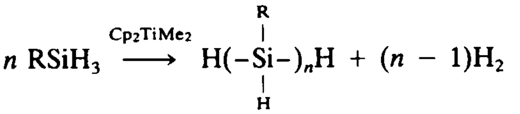
$$\mathrm{PhMeSiH_2} \xrightarrow[70^\circ\mathrm{C},\ 1\,\mathrm{h}]{(\mathrm{PPh_3})_3\mathrm{RhCl}} \underset{30\%}{\mathrm{Ph_2MeSiH}} + \underset{14\%}{\mathrm{MePhHSi{-}SiHPhMe}} + \underset{30\%}{\mathrm{MePhHSi{-}}\overset{\mathrm{Ph}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{{-}SiHPhMe}} \tag{3}$$

Note that a competing SiH/SiC redistribution process gives significant quantities of $\mathrm{Ph_2MeSiH}$ (along with trace quantities of $\mathrm{Ph_3SiMe}$). As pointed out by Curtis and Epstein,[7] this reaction must also produce a hydrogen-rich volatile fraction consisting of $\mathrm{H_2}$ and $\mathrm{MeSiH_3}$. A similar reaction was reported by Corey, who found that $(\mathrm{PPh_3})_3\mathrm{RhCl}$ also catalyzed dehydrocoupling of the secondary silane 9,10-dihydro-9-silaanthracene and related dibenzosilacycles to di- and trisilanes.[8] Lappert has reported conversion of $\mathrm{Ph_2SiH_2}$ to hydrogen and $\mathrm{Ph_2HSiSiHPh_2}$ with a rhodium carbene complex.[9] Interestingly Vaska's complex, $(\mathrm{PPh_3})_2\mathrm{Ir(CO)Cl}$, catalyzed redistribution of $\mathrm{PhMeSiH_2}$, but only to other monosilanes.[7]

Brown-Wensley investigated the activities of a number of platinum metal catalysts for the dimerization of diethylsilane, and found the following ordering (with relative reactivities): $(\mathrm{PPh_3})_3\mathrm{RhCl}$ (31) > $[\mathrm{Pd(allyl)Cl}]_2$ (12) > $[\mathrm{Rh(CO)_2Cl}]_2$ (5) > $(\mathrm{PPh_3})_2\mathrm{Pt(C_2H_4)}$, $[\mathrm{Rh(cod)Cl}]_2$ (1) > $\mathrm{Pt(cod)Cl_2}$ (0.7) > $\mathrm{RhCl_3}$ (0.3) > $\mathrm{CpRh(C_2H_4)}$,

$[Ir(cod)Cl]_2$ (0.2) > H_2PtCl_6, $(PPh_3)_2PtCl_2$ (0.1). It was also observed that with respect to the monosilanes, reactivities follow the order $RSiH_3 > R_2SiH_2 > R_3SiH$.[10] Generally tertiary silanes R_3SiH are unreactive, but a recent report by Tanaka describes the dehydrogenative condensation of Me_2PhSiH to $(Me_2PhSi)_2$ with platinum catalysts.[11] Therefore, although some late transition-metal complexes catalyze the dehydrogenative condensation of Si–H bonds, this method does not appear encouraging with respect to production of high polymers.

A more promising class of catalysts discovered recently by Harrod and co-workers are based on d^0 metallocenes of titanium and zirconium. The most intensely studied catalyst precursor is the titanium alkyl Cp_2TiMe_2, which converts primary silanes to polysilanes according to Equation (4).[12]



$$n\,RSiH_3 \xrightarrow{Cp_2TiMe_2} H(-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{Si}}-)_nH + (n-1)H_2 \qquad (4)$$

This reaction produces mixtures of linear and cyclic oligomers with an average degree of polymerization of ca. 10 and narrow polydispersities. Zirconocene alkyl and hydride derivatives Cp_2ZrR_2 (R = alkyl, H) are also active catalysts, and can give higher molecular weight polysilanes (up to 20 Si atoms per chain). These coupling reactions are more selective than those based on late metal catalysts, since no side products from redistribution are formed. The catalysis is quite sensitive to steric factors, so that primary silanes react but tertiary silanes do not. In many cases secondary silanes react to give only disilane as product, but Corey has recently found that secondary silanes can be oligomerized by zirconocene catalysts at elevated temperature.[13] Nakano *et al.* find that under similar conditions Cp_2TiPh_2 couples $PhMeSiH_2$ to PhMeHSiSiHMePh and $H(PhMeSi)_3H$.[14] Also the secondary germane Ph_2GeH_2 is converted to a mixture of oligogermanes by Cp_2TiMe_2.[15] Other early transition-metal and uranium and thorium metallocene derivatives are not as active. In some cases, e.g., with Cp_2V and $Cp^*{}_2ThMe_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$), disilanes are the principle products.[16]

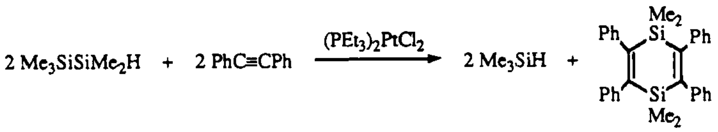
Addition of a primary silane to a d^0 titanocene or zirconocene alkyl complex results in a number of chemical processes, including transfer of the alkyl group to silicon, formation of metal hydrides, generation of the active catalyst, and polymerization. Induction periods lasting from a few seconds to a few hours are reported and a number of species have been identified in solution including $[Cp_2TiH]_2(\mu\text{-}H)$, $Cp_2Ti(\mu\text{-}H)(\mu\text{-}SiHPh)TiCp_2$, $Cp_2Ti(\mu\text{-}SiHPh)_2TiCp_2$, and $Cp_2(PhH_2Si)Zr(\mu\text{-}H)_2Zr(SiHPhMe)Cp_2$. These species are not directly involved in the catalysis, but there is evidence that catalytically active titanium complexes undergo monomer–dimer equilibria in solution.

We have found that metallocene derivatives with Zr–Si or Hf–Si bonds are active catalysts for dehydrogenative coupling of primary silanes to polysilanes. As reported for Harrod's catalysts, the isolated polymers display bimodal molecular weight distributions and usually have degrees of polymerization of ca. 20. For the most active catalysts such as $CpCp^*Zr[Si(SiMe_3)_3]Me$ the dehydrogenative coupling of phenylsilane is violent at room temperature, and no induction periods are observed. An initial survey of early transition-metal silyl complexes revealed that those of the type $CpCp^*Zr(SiR_3)R'$ (R = Me, Ph, $SiMe_3$; R' = alkyl, silyl) gave the most active catalysts. After the mechanistic work described in the next section suggested that the real catalysts were hydride complexes, we determined that $CpCp^*ZrH_2$ is at least as active as $CpCp^*Zr[Si(SiMe_3)_3]Me$. These results imply that M–Si bonded species are converted more rapidly to the active catalysts than are analogous M–C bonded complexes.[17,18]

MECHANISMS

It appears that transition-metal catalyzed dehydrogenative couplings could provide useful synthetic means for selectively preparing desired disilanes, trisilanes, high molecular weight polysilanes, etc. A major goal is the development of catalysts that allow control of molecular weight and stereochemical properties. The key to the evolution of this chemistry in these directions is the elucidation of the mechanism(s) by which these Si–Si coupling reactions operate.

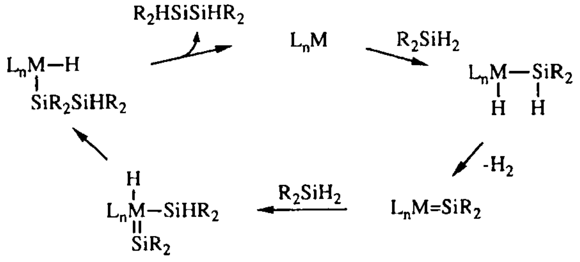
Early speculation about the mechanism of transition-metal catalyzed dehydrogenative silane coupling centered on intermediate silylene complexes, $L_nM{=}SiR_2$. These were originally proposed by Yamamoto *et al.*, who trapped silylene groups from the platinum-catalyzed reaction mixture (Equation (5)).[19]



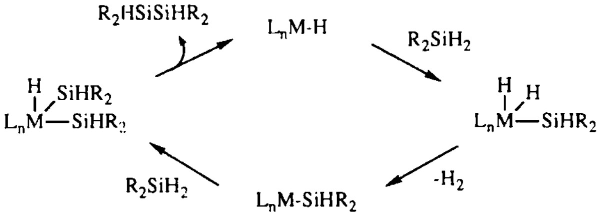
(5)

This proposal seems reasonable given the role of carbene complexes in various catalytic cycles, and since the metal centers are acting to shuttle silylene units to a growing silicon chain. A mechanism similar to those proposed by Yamamoto[19] and Ojima[6] is shown in Scheme 1.

The viability of such a silylene complex-based mechanism would improve drastically if reactivity studies with isolated silylene complexes could demonstrate Si–Si coupling processes. However, transition-metal silylene complexes have only recently become available as adducts with simple Lewis bases such as NCMe, THF, and HMPA.[20–22] The complex $[Cp^*(PMe_3)_2Ru{=}SiPh_2(NCMe)]^+BPh_4^-$ readily loses acetonitrile in solution and, as demonstrated by dynamic NMR experiments, is in equilibrium with the base-free complex $[Cp^*(PMe_3)_2Ru{=}SiPh_2]^+BPh_4^-$.[20b] Preliminary reactivity studies with this species indicate that it is relatively unreactive toward a variety of silanes. In related studies Zybill and co-workers have shown that the dimethylsilylene derivative $(CO)_4FeSiMe_2(HMPA)$ thermally decomposes to $Fe_3(CO)_{12}$ and polysilane of low molecular weight, but this process does not involve a dehydrocoupling.[21d] This reaction may involve dissociation of the silylene ligand, since free silylenes are known to condense into Si–Si bonded structures.[23] Another recent report relevant to this mechanism describes the dehydrogenative condensation of Me_2PhSiH to the disilane $(Me_2PhSi)_2$ with platinum catalysts. Silylene intermediates are unlikely for this reaction.[11]



SCHEME 1



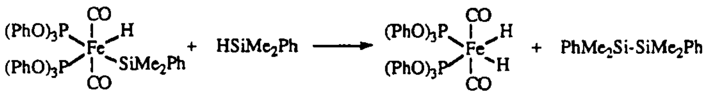
SCHEME 2

An alternative mechanism involving individual steps that have precedents in stoichiometric reaction chemistry has been proposed by Curtis and Epstein.[7] It consists of oxidative addition–reductive elimination cycles (Scheme 2).

Oxidative addition of silanes to metal hydride complexes is well known, and both $M(H)_2SiR_3$ and $MSiR_3$ complexes have been isolated from such reactions.[1,24] For example, iridium hydride $IrH(CO)(PPh_3)_3$ dissociates phosphine and adds a silane molecule to form $Ir(H)_2SiR_3(CO)(PPh_3)_2$ complexes.[25] Platinum dihydride *trans*-$PtH_2(PCy_3)_2$ reacts with silanes $XSiH_3$ ($X = H$, Cl, or SiH_3) to give hydrogen and *trans*-$PtH(SiH_2X)(PCy_3)_2$ complexes, and at low temperature the reaction intermediates $PtH_3(SiH_2X)(PCy_3)_2$ were detected by ^{31}P NMR spectroscopy.[26] Also, photolysis of the iridium(III) dihydrido silyl complex $Ir(Ph_2PCH_2CH_2SiMe_2)(PPh_3)(CO)H_2$ in the presence of CO induces reductive elimination of H_2 to give the first example of an iridium(I) silyl complex, $Ir(Ph_2PCH_2CH_2SiMe_2)(PPh_3)(CO)_2$.[27] It appears that few oxidative additions of Si–H bonds to transition-metal silyl complexes have been attempted, but such reactions are probably important in silyl exchange processes[1,24,28] and in the formation of bis(silyl) complexes $Cp^*(PMe_3)RuH(SiR_3)_2$ by addition of $HSiR_3$ to $Cp^*(PMe_3)_2RuCH_2SiMe_3$.[20b] One example is oxidative addition of $Ph_2PCH_2CH_2SiMe_2H$ to $Ir(Ph_2PCH_2CH_2SiMe_2)(PPh_3)(CO)HCl$ in the presence of triethylamine to give the bis(silyl) hydride $Ir(Ph_2PCH_2CH_2SiMe_2)_2(CO)H$.[29] Another significant observation is detection of the intermediates $R_3SiCo(CO)_3$ and $(R_3Si)(R'_3Si)(H)Co(CO)_3$ in silyl group exchange between $R_3SiCo(CO)_4$ and R'_3SiH. Note, however, that $(R_3Si)(R'_3Si)(H)Co(CO)_3$ undergoes reductive elimination to form Si–H, rather than Si–Si, bonds.[30]

The crucial Si–Si bond-forming step in the mechanism of Scheme 2 has been shown to be possible in at least a few circumstances.

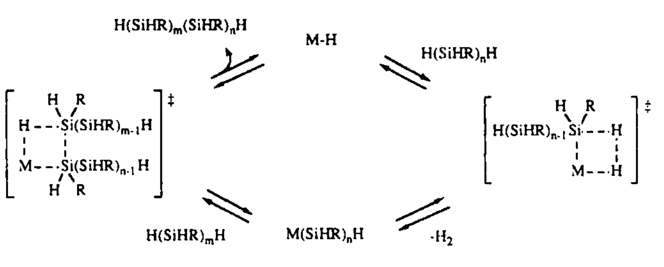
Formation of $Me_3SiSiMe_3$ in the reductive coupling of Me_3SiX (X = Cl, Br) by $Pd(PPh_3)_4$ has been reported.[31] Schubert has recently demonstrated formation of a disilane from an iron silyl complex and monosilane (Equation (6)).[32]



(6)

Schubert has also reported examples of spontaneous reductive elimination of disilane from bis(silyl) complexes of palladium, $(MePh_2P)_2Pd(SiR_3)_2$.[33] In summary, given the precedents that exist for the steps in Scheme 2, this mechanism currently appears to have more credibility. More support for this mechanism would of course be gained from observation of all the steps for a single metal system, so that a catalytic cycle was established.

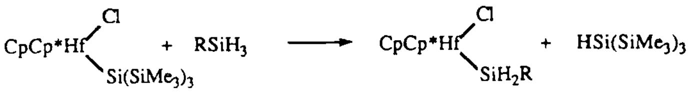
A mechanism based on addition/elimination cycles seems much less likely for dehydrocoupling reactions catalyzed by the early (d^0) metal catalysts. This is because the most stable oxidation state for these metals (e.g., M(IV) for group 4 metals) cannot undergo oxidation. Also the $M^{n+}/M^{(n+2)+}$ oxidation state cycles required by such a mechanism do not appear to be facile for these metals. A silylene-based mechanism does seem possible, however, especially given the role that carbene (or alkylidene) complexes play in catalysis by the early transition-metals.[34] Mechanisms based on silylene complexes of titanium have been considered,[12a,b,d-f,15] but in the absence of isolable early metal silylene complexes such mechanisms are difficult to test. Our work with zirconium and hafnium catalysts suggests that a mechanism consisting of concerted, σ-bond metathesis steps (Scheme 3) operates for d^0 metal catalysts.[17,18,35]



SCHEME 3

Our approach to investigating the mechanism by which group 4 transition-metal catalysts operate involves study of slow catalysts based on relatively non-labile complexes. The rate of reaction between a monosilane and a d^0 metal silyl complex is dramatically influenced by substituent effects. For example, chloro substitution at the metal center results in slower reactions of the silyl ligand. Also, hafnium derivatives react more slowly and yield more stable intermediates. Initially our investigations concentrated on reactions that model conversion of the metal complex to an active catalyst, and later our attention turned to reactivity more relevant to Si–Si bond formation.

Primary silyl groups are introduced into the coordination sphere of a d^0 metal center via a "σ-bond metathesis"[36] reaction (Equation (7)).

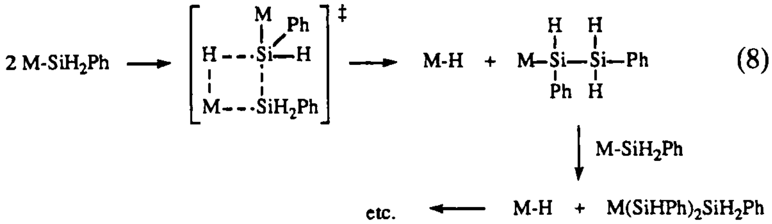


$$\mathrm{CpCp^{*}Hf(Cl)Si(SiMe_3)_3} + \mathrm{RSiH_3} \longrightarrow \mathrm{CpCp^{*}Hf(Cl)SiH_2R} + \mathrm{HSi(SiMe_3)_3} \qquad (7)$$

These reactions are quantitative by ^1H NMR spectroscopy, and isolated yields range from 65–75%. A kinetic study showed that the reaction with $PhSiH_3$ follows the rate law, rate = $k[CpCp^{*}ClHfSi(SiMe_3)_3][PhSiH_3]$, with activation parameters of $\Delta H^{\ddagger} = 16.4\ (7)\ \mathrm{kcal\ mol^{-1}}$ and $\Delta S^{\ddagger} = -27\ (2)$ eu, and a kinetic isotope effect of 2.5. This data is consistent with values reported for σ-bond metathesis reactions of d^0 M–X (X = H, C) bonds and with a concerted mechanism for silyl group exchange.[36] Further studies have shown that all possible σ-bond metathesis processes involving M–H and M–Si bonds with Si–H, Si–Si and H–H bonds can be observed as stoichiometric reactions. For example, the hydride $CpCp^{*}HfHCl$ reacts with $PhSiH_3$ to give hydrogen and $CpCp^{*}Hf(SiH_2Ph)Cl$. Therefore it appears that silicon readily takes part in such reactions via concerted, 4-center transition states, possibly because of its ability to expand its coordination sphere.[18]

With a stable monomeric primary silyl derivative in hand, we were interested in examining its chemistry to discover how $M-SiH_2R$ species react or rearrange to deliver RSiH silylene units to a polymer chain. These studies led to observation of a Si–Si bond-forming reaction. Thermal decomposition of $CpCp^{*}Hf(SiH_2Ph)Cl$ leads cleanly to $CpCp^{*}HfHCl$ and polysilane, as determined by

NMR spectroscopy. Disappearance of the silyl complex follows a second order rate law, rate = $k[\mathrm{CpCp^*Hf(SiH_2Ph)Cl}]^2$, with $k(75°\mathrm{C}) = 1.1\ (1) \times 10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$, $\Delta H^{\ddagger} = 19.5\ (2)$ 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 are formed in this reaction by the process shown in Equation (8).



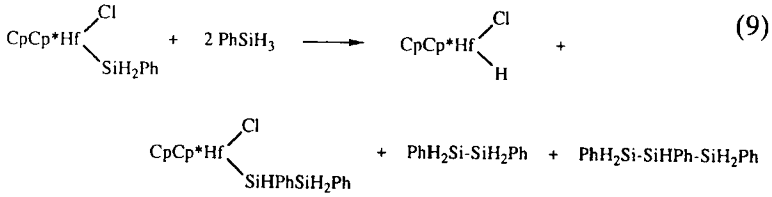
(8)

To test for the possible intermediacy of silylene species, the decomposition was carried out in the presence of efficient silylene traps, such as Et_3SiH and Ph_2SiH_2. The presence of these traps did not effect the rate or course of decomposition.[17] Our results are consistent with only one M–X σ-bond of a complex being involved in catalysis, since $\mathrm{CpCp^*M(SiR_3)Cl}$ complexes are catalyst precursors for the polymerization of $PhSiH_3$, which quantitatively converts these chloro complexes to the corresponding hydrides CpCp*MHCl. A metal silylene-based mechanism can be ruled out since it requires that two σ-bonds are used by the catalyst complex. Significantly, addition of $PhSiH_3$ speeds up the conversion of $\mathrm{CpCp^*Hf(SiH_2Ph)Cl}$ to CpCp*HfHCl and polysilane. This is presumably because the Si–H bond of $PhSiH_3$ and the Hf–Si bond of $\mathrm{CpCp^*Hf(SiH_2Ph)Cl}$ fit better in the transition state (see Scheme 3).[18]

The proposed mechanism in Scheme 3 features a coordinatively unsaturated hydride complex of a d^0 metal as the active catalyst. This suggests that silanes convert the catalyst precursor to a hydride complex in the initial phase of reaction. The greater catalytic activity of silyl complexes compared to analogous alkyls is probably related simply to the higher reactivity of M–Si bonds toward σ-bond metathesis. Evidence for the role of hydride complexes as the real catalysts comes from comparing molecular weight data (based on gpc traces) for polysilanes produced by both $\mathrm{CpCp^*Zr[Si(SiMe_3)_3]Me}$ and $\mathrm{CpCp^*ZrH_2}$ under comparable conditions. These two reactions give polysilanes with identical molecular weight properties.[17] Note that a possible consequence of this mechanism is that hydride complexes with higher d^n counts ($n \geq 1$) may be less effective as catalysts, since the metal center will be less electrophilic and therefore less effective in coordinating an Si–H bond.

The σ-bond metathesis mechanism of Scheme 3 is unusual for a metal-catalyzed polymerization in that it involves step growth of the polymer rather than chain growth. This feature of the reaction was independently established by using a sterically hindered and slow catalyst, $Cp^*_2HfH_2$. This allows observation of free oligomeric silanes during the course of reaction. As the $PhSiH_3$ concentration decreases, disilane appears and is more slowly followed by the appearance of trisilane. Finally, after a significant build-up of trisilane, tetrasilane accumulates. The time dependence of the concentrations of these species clearly establish the step growth nature of the polymerization. If the disilane PhH_2SiSiH_2Ph is added to $Cp^*_2HfH_2$, $PhSiH_3$ is seen to grow in rapidly. This shows that the Si–Si bond-forming step is reversible in this system.

The other proposed intermediate is a metal silyl species, $M(SiHPh)_nH$. A complex of this type, $CpCp^*Hf(SiHPhSiH_2Ph)Cl$, was prepared independently from $CpCp^*Hf[Si(SiMe_3)_3]Cl$ and PhH_2SiSiH_2Ph, and isolated as a 1:1 mixture of two diastereomers. This complex is clearly identified (by ^1H NMR spectroscopy) in the slow oligomerization of $PhSiH_3$ as catalyzed by $CpCp^*Hf(SiH_2Ph)Cl$. The addition of 2 equivalents of $PhSiH_3$ to $CpCp^*Hf(SiH_2Ph)Cl$ results in formation of the products shown in Equation (9) after 24 hours and 33% conversion.



(9)

Steric constraints on the dehydrocoupling of silanes can be quite pronounced, and for the d^0 metal catalysts this can be explained by the inherently crowded 4-center transition states. Observed steric constraints on σ-bond metathesis reactions suggest that the catalyst reacts predominantly with the polysilane $-SiH_2R$ end groups, giving linear chain growth. It also appears that steric factors limit the types of coupling reactions that can occur, so that one of the reacting silanes in a cycle must be primary (n or $m = 1$). This leads to growth of the chain by only one silicon atom per cycle. Steric hindrance at the metal center is also important; for example, $Cp^*_2MH_2$ catalysts are much slower than analogous $CpCp^*MH_2$ catalysts. However, it appears that some degree of steric bulk at the metal center is beneficial for creating active and long-lived catalysts by stabilization of monomeric species. Thus, whereas catalyst precursors that are Cp_2Zr derivatives eventually die out due to their conversion to the inactive dimer $Cp_2(PhH_2Si)Zr(\mu\text{-}H)_2Zr(SiHPhMe)Cp_2$,[12c] $CpCp^*Zr$-based catalysts do not form stable dimeric species in solution and stay active indefinitely.[17]

Similarities in the mechanisms of Schemes 2 and 3 are intriguing. Both involve a coordinatively unsaturated metal hydride as the active catalyst and a metal silyl species that is formed by reaction of a silane with the hydride. Also in both mechanisms it is reaction of the silyl complex with silane that eventually results in Si–Si bond formation and regeneration of the hydride. The major difference in these mechanisms is the formation in Scheme 2 of intermediates that arise from oxidative additions $MH_2(SiHR_2)$ and $MH(SiHR_2)_2$). Such processes are not possible for d^0 M–H and $M\text{–}SiR_3$ species, because these complexes are already in their highest oxidation state. However, formally the same types of exchange processes can occur in the d^0 systems via the 4-center transition states.

CONCLUSION

Dehydrogenative silane coupling reactions that form Si–Si bonds represent a challenging area for future research in catalysis. Much of this research must focus on cataloging reactivities of silanes toward different transition-metal systems and defining mechanistic possibilities. Various studies have so far implicated mechanisms based on transition-metal silylene complexes, addition/elimination cycles, and concerted σ-bond metatheses. All of these processes appear to present viable means for carrying out Si–Si bond-forming reactions. Other mechanisms can be envisioned, for example ones involving two metal centers.[7,37] Much more work is needed to extend the chemistry discussed above to the development of novel and useful syntheses of silicon-containing materials. Potentially useful applications include selective syntheses of small molecules, oligomers, and polymers, and fundamentally different approaches may prove useful depending on the nature of the desired product. It is worth noting here that useful syntheses of Si–Si bonded compounds based on transition-metal catalysis already exist. For example, a good method for the preparation of PhH_2SiSiH_2Ph is the dehydrocoupling of $PhSiH_3$ catalyzed by vanadocene.[16,38] More generally, mechanisms related to those discussed here may prove useful in the development of transition-metal catalyzed routes to other element–element bond-forming reactions.

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