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Gerald L. Larson, Editor
VP, Research Products
Gelest, Inc.
11 East Steel Road
Morrisville, PA 19067

DEHYDROGENATIVE COUPLING REACTIONS OF HYDROSILANES

Joyce Y. Corey

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1. INTRODUCTION

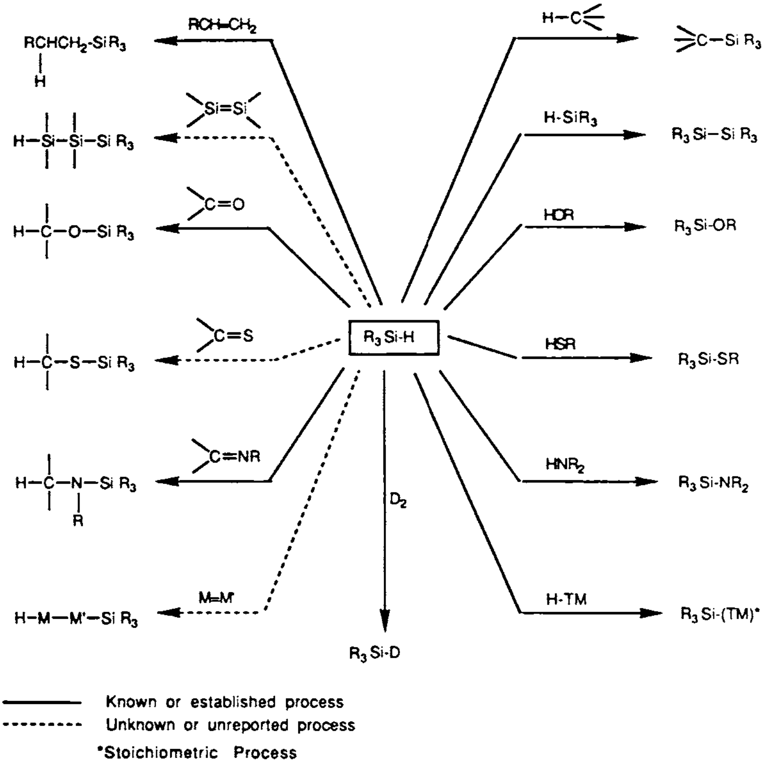
The addition of hydrosilanes to multiple bonds, referred to as hydrosilation or hydrosilylation, is a well-known process in organosilicon chemistry.[1] The most important uses of the hydrosilation reaction include formation of silicon–carbon bonds and reduction of carbonyl groups. The addition reactions are most conveniently carried out in the presence of a transition metal catalyst. From a synthetic standpoint hydrosilation provides one of the few alternatives to coupling of an active organometallic to a chlorosilane for silicon–carbon bond formation. Selective reduction of carbonyls by hydrosilanes is more a part of the repertoire of organic chemists than a method for silicon–oxygen bond formation.[1] The catalyzed addition of hydrosilanes to non-carbon containing multiple bonds has not yet been reported.

Less established are the transition metal catalyzed condensation reactions of hydrosilanes. This class of reactions involves the formation of Si–El (El = main group element) bonds through elimination (actual or formal) of HX between SiH and XEl. At present the only process that appears to have general application is the dehydrogenative coupling between SiH and HEl. The observed addition and condensation reactions of hydrosilanes are shown in simplified form in Scheme 1.

As can be seen from Scheme 1, dehydrogenative coupling has the potential to introduce a variety of functional groups to a silicon center without employing a chlorosilane, the common starting point for many of the products from the condensation reactions shown in Scheme 1. Probably the most important dehydrogenative coupling reaction is that which leads to the formation of silicon–silicon bonds. Although first reported in 1973,[2] this reaction was not developed until the mid-1980's and may represent the first reasonable alternative to the Wurtz coupling reaction for formation of oligosilanes and polysilanes.

The purpose of this chapter is to provide a survey of the dehydrogenative coupling reaction, to demonstrate the range of catalysts that have been employed for the process, and to summarize the mechanisms that have been proposed. The intent is to illustrate the range of the process as well as the current deficiencies. Future success in the use of hydrosilanes for coupling reactions will require selection of an appropriate catalyst as well as design of catalysts that will target specific processes. The fundamental requirements for the appropriate catalyst are not presently understood and this may be due to the somewhat primitive state of our understanding of the chemistry of the silicon-transition metal bond. Some basic reactions of hydrosilanes with low valent transition metal derivatives will be discussed since such chemistry is necessary to understand how the catalyzed condensation processes could occur. The survey focuses primarily on work that has been published in the last ten years. When required for general development or discussion earlier work will be quoted.

It is important to point out that most of the work that will be cited is of recent origin. In most reports conversions have not been maximized nor have a range of hydrosilanes and substrates been explored. Few systematic studies have been



Scheme 1.

published on any of the dehydrogenative coupling reactions, thus the conclusions that are drawn should be considered preliminary and certainly the responsibility of this author. It should also be understood that the actual catalyst species is unknown. The transition metal compound that is used is most likely converted to some other species which is the actual "active ingredient" and thus what is used is actually the catalyst precursor. In the following discussion the term catalyst will be used to infer catalyst/catalyst precursor.

2. COUPLING OF SiH/HC

Probably the first examples of dehydrogenative coupling of hydrosilanes with olefins appeared as byproducts in hydrosilation studies and may not have been recognized or characterized.[1] The first claim to successful coupling was for the rather unusual stereoselective cis double silylation of internal alkynes with $HSiCl_3$ in the presence of $Et_2Ni(bipy)$ which appeared in 1975.[3] However, the majority of the examples have appeared since 1983 and these are collected together in Table I. The effective transition metal catalysts are in the electron-rich category and include Ru(0), Rh(I), Rh(III), Rh(V), Pt(II), and Pt(VI). As can be seen from the table several of the catalysts are also effective in promoting hydrosilation of olefins. The most common product from the hydrosilation of a general olefin, $R'CH=CH_2$, is $R'CH_2CH_2SiR_3$ where the silicon substituent is bound to the terminal carbon atom (referred to as the β-product). When dehydrogenative coupling occurs the exclusive product is *trans*-$R'CH=CHSiR_3$ with the silicon bound to the terminal carbon. The exception appears to be the reaction of $HSiMe_3$ and $EtCH=CH_2$ in the presence of $Fe(CO)_5$.[5] This may imply a common intermediate for both hydrosilation and dehydrogenative coupling when the reactant is an olefin.

In those cases where the TM/Si ratio has been varied [$ClRhL_3$,[14] $HRh(CO)(PMe_3)_2$],[14] dehydrogenative coupling products increase with increasing ratio. In general, excess olefin also favors the formation of the coupling product [$Ru_3(CO)_{12}$;[7] $Cp^*{}_2Rh_2Cl_4$[15,18]]. Often, hydrosilation reactions are performed with low catalyst to silane ratios and with an excess of silane. This may account for the lack of observation of dehydrogenative coupling products in earlier hydrosilation studies. Hydrogen, the other coupling product, is not always observed (or reported). In some cases the reduction of the olefin to the saturated product, RCH_2CH_3, accounts for the formal consumption of H_2. In the case of $Cl_2Pt(sty)_2$[25] and $Ru_3(CO)_{12}$[7] the yields of silylstyrene (olefin coupling product) and ethylbenzene (reduction product) are approximately the same, whereas for $ClRh(PPh_3)_3$[16] the ratio of silylstyrene to ethylbenzene varied from 1.0–1.5. For $(Cp^*Rh)_2Cl_4$[15] the addition of Et_3SiH to 1-hexene provides hexane in amounts that are proportional to the vinylsilane and allylsilanes produced.[18] When styrene and $HSiEt_3$ are reacted in a 1 : 1 ratio, *trans*-$Et_3SiCH=CHPh$ is formed in 50% yield.[7] A method to improve the yields of the vinylsilane when using an expensive olefin is to add a "hydrogen acceptor". When the reaction of styrene and $HSiEt_3$ was run in the presence of hex-1-ene the yield of the silylstyrene product increased to 75 %. The best ratio for conversion of the styrene to vinylsilane was found to be hexene/styrene/silane = 3/2/3.

The effectiveness of the transition metal-catalyzed hydrosilation of olefins can be a function of the substituents on silicon. This is also observed in the dehydrogenative coupling reaction. Although the number of examples is not extensive, coupling of $RCH=CH_2$ and $HSi(OEt)_3$ either does not occur [R = CF_3, $Ru_3(CO)_{12}$[9], $ClRhL_3$[9a]] or occurs with low conversion and usually requires more drastic conditions (R = Ph, $ClRhL_3$[14]). An interesting exception appears to be the reaction of ethylene and $HSi(OEt)_3$ [$Ru_3(CO)_{12}$ catalyst] where 41% of triethoxyvinylsilane was produced but the conditions were not specified.[9a] Vinylsilanes are thus possible in one step from $HSi(OEt)_3$, which itself is the major product from reaction of elemental silicon with ethanol.[29]

As can be seen from Table I the most common hydrosilane used in the examples of dehydrogenative coupling is triethylsilane. The presence of a chlorine substituent on silicon tends to suppress the coupling reaction in favor of hydrosilation

Table I. Catalytic Dehydrogenative Coupling

Catalyst[•]	*Silane/Substrate*	*SiH/HC* *TM/Si*[a]	*Product (%)*[b,c]	*Comments*	*Reference*
Mn Triad					
$Ph_3SiMn(CO)_5$	$D_4H/PrCH=CH_2$	10^{-3}	$D_4CH=CHPr$(25)	$D_4CH_2CH_2Pr$(55); D_4-D_4(20).	4
Fe Triad					
$Fe(CO)_5$	$HSiMe_3/EtCH=CH_2$	10^{-3}	$^nC_4H_7SiMe_3$(40)	3 isomers; 90% conversion;[c] best case.	5
$Ru_3(CO)_{12}$	$HSiEt_3/HexCH=CH_2$	10^{-4}	$HexCH=CHSiEt_3$(47)	100% conversion.[c] Not an effective hydrosilylation catalyst.	6,7,8
	$HSiEt_3/PhCH=CH_2$	10^{-3}	$PhCH=CHSiEt_3$(93)	PhEt(96%); excess Sty. Inactive for $Ph_2C=CH_2$, $^cC_6H_{10}$.	7
	$HSiEt_3/CF_3CH=CH_2$	10^{-2}	$CF_3CH=CHSiEt_3$(100)	78% Conversion.[c]	9a
	$HSiEt_3/Me_3SiCH=CH_2$	10^{-3}	$Me_3SiCH=CHSiEt_3$(79)	$Me_3SiCH=CHSiMe_3$(19)	9b
	$HSiEt_3/PhCH_2CH=CH_2$	10^{-3}	$PhCH_2CH=CHSiEt_3$(77)	*t*-$PhCH=CHCH_2SiEt_3$(15).Yield of allylsilane rises to 86% at 140°C.	7
	$HSi(OEt)_3/CF_3CH=CH_2$	10^{-3}	$CF_3CH=CHSi(OEt)_3$(0)	$R_fCH_2CH_2Si(OEt)_3$(100).	9
	$HSi(OEt)_3/CH_2=CH_2$	*d*	$CH_2=CHSi(OEt)_3$(40)	$EtSi(OEt)_3$(19).	7
$HRu_3(CO)_{11}^{-e}$	$HSiEt_3/CH_2=CH_2$	10^{-3}	$CH_2=CHSiEt_3$(52)	$CH_3CH_2SiEt_3$(22).	10
Ru(COD)(COT)	$HSiEt_3/CH_2=CMeEt$	10^{-2}	$Me_2C=CHCH_2SiEt_3$(56)		11
	$HSiEt_3$/*n*-$BuCH=CH_2$	10^{-2}	$BuCH=CHSiEt_3$(15)	$PrCH=CHCH_2SiEt_3$(67) E/Z = 65/35.	11
$H_2OsCl_6.2H_2O$	$HSiR_2Me/PhCH=CH_2$ R = $OSiMe_3$	10^{-4}	$PhCH=CHSiMeR_2$(97)	PhEt. Highest yields occur only when the temperatures exceed 140°C.	1c
Co Triad					
$Co_2(CO)_8$	$HSiEt_2Me/CH_2=CHCO_2Me$	10^{-2}	$MeO_2CCH=CHSiEt_2Me$(86)	Fails with methylmethyacrylate and methyl crotonate. 2.5 molar excess of olefin gives 99% conversion and 95% coupling product.	12

Table I. (Continued)

Catalyst[•]	*Silane/Substrate*	*SiH/HC*		*Comments*	*Reference*
		TM/Si[a]	*Product (%)*[b,c]		
$Et_2MeSiCo(CO)_4$	$HSiEt_2Me/CH_2{=}CHCO_2Me$	10^{-2}	$MeO_2CCH{=}CHSiEt_2Me$(96)	100% conversion.	12b
$ClRh(PPh_3)_3$[e]	$HSiMe_2R/Me_3Si\ C{\equiv}CH$ R = 2-thienyl	[d]	$Me_3SiC{\equiv}CSiMe_2R$(16)	93% conversion.	13
	$HSiEt_3/PhCH{=}CH_2$	10^{-3}	$PhCH{=}CHSiEt_3$(43)	80% conversion;[c] 54% selectivity.	14
		10^{-4}	$PhCH{=}CHSiEt_3$(2)	74% conversion.[c]	14
	$HSiEt_3/BuCH{=}CH_2$	10^{-3}	$BuCH{=}CHSiEt_3$(50)	90% conversion.[c]	15
	$HSiEt_3/OctCH{=}CH_2$	10^{-3}	$OctCH{=}CHSiEt_3$(32)	$Et_3SiC_8H_{17}$(60).	6
	$HSiEt_3/CF_3CH{=}CH_2$	10^{-2}	$CF_3CH{=}CHSiEt_3$(87)	$CF_3CH_2CH_2SiEt_3$(13); 77% yield; $HSi(OEt)_3$ and $HSiMe_2Cl$ give only hydrosilation products.	9
	$HSiMe(i\text{-}Pr)_2/PhCH{=}CH_2$	10^{-4}	$PhCH{=}CHSiMe(i\text{-}Pr)_2$(72)	PhEt(72); 22% conversion (THF).	16
	$HSiMe(i\text{-}Bu)_2/PhCH{=}CH_2$	10^{-4}	$PhCH{=}CHSiMe(i\text{-}Bu)_2$(38)	29% conversion.	16
	$HSi(i\text{-}Pr)_3/PhCH{=}CH_2$	10^{-3}	$PhCH{=}CHSi(i\text{-}Pr)_3$	94% selectivity.	14
	$HSiPh_3/PhCH{=}CH_2$	10^{-3}	$PhCH{=}CHSiPh_3$(75)	88% conversion;[c] 85% selectivity.	14
	$HSi(OEt)_3/PhCH{=}CH_2$	10^{-3}	$PhCH{=}CHSi(OEt)_3$(7)	48% conversion.	14
$ClRh(CO)(PMe_3)_2$[e]	$HSiEt_3/C_6H_6$	10^{-3}	$PhSiEt_3$	376% Rh.	17
$HRh(CO)(PPh_3)_3$[e]	$HSiEt_3/PhCH{=}CH_2$	10^{-3}	$PhCH{=}CHSiEt_3$(44)	53% conversion[c,f]; 85% selectivity.	14
	$HSiEt_2Me/RCH{=}CH_2$ R = CO_2Me	10^{-3}	$RCH{=}CHSiEt_2Me$(67)	99% conversion.	12b
$(acac)_3Rh$[e]	$HSiEt_3/BuCH{=}CH_2$	10^{-3}	$BuCH{=}CHSiEt_3$(31)	93% conversion.[c]	18
	$HSiEt_3/PhCH{=}CH_2$	10^{-2}	$PhCH{=}CHSiEt_3$(75)	$PhCH_2CH_2SiEt_3$(24). With $HSi(OEt)_3$, only 15% vinylsilane formed.	19
$Cl_4(Cp^*Rh)_2$[e]	$HSiEt_3/BuCH{=}CH_2$	10^{-3}	$BuCH{=}CHSiEt_3$(58)	95% conversion. Excess olefin favors vinylsilane.	15

Table I. (Continued)

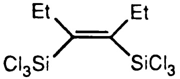
		SiH/HC			
Catalyst[*]	*Silane/Substrate*	*TM/Si*[a]	*Product (%)*[b,c]	*Comments*	*Reference*
	$HSiEt_3/PhCH{=}CH_2$	10^{-3}	$PhCH{=}CHSiEt_3$(55)	90% conversion; as silicon/olefin ratio decreases, yields of vinylsilane increase.	18
$Cp^*Rh(H)_2(SiR_3)_2$	$HSiEt_3/CH_2{=}CH_2$	[d]	$CH_2{=}CHSiEt_3$(75)	Et_4Si(25). Percent conversion not specified.	20
$[MeOIr(COD)]_2$[g]	$HSiEt_3/CH_2{=}CH_2$	10^{-2}	$CH_2{=}CHSiEt_3$(38)	$C_2H_5SiEt_3$(62).	21
	$HSiEt_3/BuC{\equiv}CH$	10^{-2}	$BuC{\equiv}CSiEt_3$(24)	100% conversion. $BuCH{=}CHSiEt_3$, t/c=13/63.	22
	$HSiEt_3/BuCH{=}CH_2$	10^{-3}	$C_6H_{11}SiEt_3$(81)	3 isomers.	21
$ClIr(CO)(PPh_3)_2$	$HSiMe_2R/C_6H_6$ ($R = Me_3SiO$)	10^{-2}	RMe_2SiPh(2)	Main products are from redistribution, $RSi(H)MeR$(75%).	23
$H_2Ir(SiEt_3)(COD)$	$HSiEt_3/BuCH{=}CH_2$	10^{-2}	$C_6H_{11}SiEt_3$(46)	95% conversion; C_6H_{14}(46); $C_6H_{13}SiEt_3$.	24
Ni Triad					
$Et_2Ni(bipy)$	$HSiCl_3/EtC{\equiv}CEt$	10^{-2}		Hydrosilation with the first mole of HSi and dehydrogenative coupling of second mole of HSi.	3
$Cl_2Pd(PhCN)_2$ + $AsPh_3$	$HSiCl_2Me/CF_3CH{=}CH_2$	10^{-3}		$CF_3CH(Me)SiMeCl_2$(88).	9
$Cl_2Pt(sty)_2$[e,i]	$HSiEt_3/PhCH{=}CH_2$	10^{-4}	$PhCH{=}CHSiEt_3$ (11-13)[j]	$PhCH_2CH_2SiEt_3$(73-75); $PhCH_2CH_3$(11-13%).	25
	$HSi(CH_2Ph)_3/PhCH{=}CH_2$	10^{-4}	$PhCH{=}CHSi(CH_2Ph)_3$(41)		26
	$HSiPh_3/PhCH{=}CH_2$	10^{-4}	No Reaction		26

Table I. (Continued)

Catalyst[*]	Silane/Substrate	SiH/HC		Comments	Reference
		TM/Si[a]	Product (%)[b,c]		
H_2PtCl_6[e]/I_2	$HSiEt_3/HC{\equiv}CPh$	10^{-5}	$PhC{\equiv}CSiEt_3$(90)	Polar solvents lower yields. Electronegative substituents on Si suppress reaction.	27
	$HSiEt_3/HC{\equiv}CH$	10^{-4}	$Et_3SiC{\equiv}CSiEt_3$(40)	$Et_3SiCH_2CH_2SiEt_3$.	27
Zn Triad					
Hg/hν	$HSiEt_3/CH_3CH_2OH$		$Et_3SiCH(Me)OH$(5)[k]		28

[*] Catalyst precursor.

Symbols: $D_4H = HSiMeO(SiMe_2O)_3$; hex, hexyl; oct, ^{n}octyl; COD, cyclooctadiene; COT, cyclooctatriene; Cp*, C_5Me_5; sty, $PhCH{=}CH_2$.

[a] Approximate ratios.

[b] Unless specified otherwise, product is the trans-olefin.

[c] Conversion to silicon containing products at time of reaction workup; in most cases reactions were not maximized.

[d] Not specified.

[e] Also a hydrosilylation catalyst.

[f] As TM/Si decreases, yield of $PhCH{=}CHSiEt_3$ decreases.

[g] Added $AsPh_3$.

[h] $R' = Me_nCl_{3-n}Si$.

[i] cis-isomer.

[j] Series of Pt catalysts give similar results.

[k] wt% of isolated products.

[$Ru_3(CO)_{12}$[9a] and $Cl_2Pd(PhCN)_2$[9a]]. This could possibly be due to the chlorination of a TM–H bond formed in a reactive catalyst species by SiCl (see Section 6).

The majority of the reported cases of dehydrogenative coupling involve olefin substrates. However, terminal alkynes also condense with $HSiEt^3$ in the presence of $[MeOIr(COD)]_2$[22] or the combination of H_2PtCl_6/I_2[27]. In the latter case the presence of electronegative substituents on silicon also suppresses the coupling reaction.

It appears that benzene will also couple with hydrosilanes[17,23] although this is probably not a practical method for forming silylbenzenes. The same catalyst that couples C_6H_6 and $HSiEt_3$ is also effective for coupling C_6H_6 and $CH_2{=}CHCO_2Me$.[30b] No examples of the coupling of an sp^3-CH and HSi were found.

The best catalysts for dehydrogenative coupling of CH/HSi appear to be $Ru_3(CO)_{12}$ and $[MeOIr(COD)]_2$ both of which are not particularly effective in promoting hydrosilation. Wilkinson's catalyst, $ClRh(PPh_3)_3$, which also promotes hydrosilation, appears to be useful but only when the concentration of the catalyst is high do the dehydrogenative coupling products fall in the useful 30–50% range. Allylsilanes are sometimes formed as minor by-products in the reaction of olefins and hydrosilanes. There are no reports of the dehydrogenative coupling of secondary silanes with olefins.

The temperature dependence of the coupling reaction has not usually been investigated. In the case of $(Cp^*Rh)_2Cl_4$ the yield of vinylsilane from Et_3SiH/hex-1-ene (ratio of 1/3) is 63% at 0°C and falls to 24% at 80°C.[18] In contrast, raising the temperature with the catalyst combination [$Rh(acac)_3$-$AlEt_3$] maximizes the formation of vinylsilanes vs. the saturated product.[19]

There is at least one case where CH/HSi coupling occurs without added transition metal catalyst but the substrate, $HCCo_3(CO)_9$, essentially contains its own catalyst. The reaction of Et_3SiH with the cobalt complex in refluxing toluene provides a 76% yield of $Et_3SiCCo_3(CO)_9$ with hydrogen evolution within one-half hour.[30a]

The development of new dehydrogenative coupling catalysts could occur from reagents that are known to promote hydrosilation of olefins, but with reactions run under conditions that involve higher concentrations of catalyst and excess olefin. Alternatively, if the reaction requires insertion of the olefin into TM–Si bonds (see Section 6), then the catalyst range could possibly be extended to silyl-transition metal derivatives that are electron deficient.

3. COUPLING OF SiH/HEl

3.1. SiH/HOR

The coupling of alcohols with hydrosilanes in the presence of transition metals, including transition metal complexes, has been reviewed recently.[31] Table II includes examples that have been published primarily in the past ten years. The transition metal complexes that promote the coupling of hydrosilanes and alcohols are mainly those that are electron rich and include Fe(O), Fe(II), Ru(II), Rh(I), Ir(I), Ir(III), Pt(II), and Pt(IV). In addition to the derivatives listed in Table II, $Co_2(CO)_8$ was one of the earliest catalysts used for the coupling reaction.[31] An interesting feature of the complexes listed in Table II is the preponderance of H–TM and Cl–TM derivatives [the exceptions are Fe(0) and Co(0)].

Iron and cobalt complexes have been used to couple $HSi(OEt)_3$ with alcohols but were not effective for other tertiary silanes. The iron complexes did, however, promote the coupling of alcohols with the secondary silane, Ph_2SiH_2. In the cases where variations of alcohols have been studied, reaction rates decrease as the chain length of R in ROH increases and also with branching of the alcohol. As an example of the effect of branching, *n*-BuOH and Ph_3SiH provide 83% of Ph_3SiOBu-*n* after 12 h at 80°C but *t*-BuOH requires 96 h to give only 35% Ph_3SiOBu-*t* [$ClRh(PPh_3)_3$ catalyst[33]]. The single exception to this generalization is the recently reported system, $[IrH_2(THF)_2L_2]^+ SbF_6^-$ for which reactions of the secondary alcohol, *i*-PrOH are considerably faster than either that of MeOH or EtOH.[35] There is no obvious explanation for this reversal in order. The differences in reaction of primary vs. tertiary alcohols are not always significant. Towards Et_3SiH, the order observed for $ClRh(PPh_3)_3$ is MeOH(100) > EtOH(64) > *t*-BuOH(0.8), whereas for $ClIr(CO)L_2$ the order is MeOH(3.5) > EtOH(1.0) > *t*-BuOH(0.5).[40]

The rates of alcoholysis probably follow the order observed with the catalyst $ClRh(PPh_3)_3$: $RSiH_3 > R_2SiH_2 > R_3SiH$. Partial substitution of primary and secondary silanes can be achieved. A comparison of the effectiveness (rate) of catalysts for the methanolysis of Ph_2SiH_2 showed the following order: $ClRhL_3 > L_3RuCl_2 > Co_2(CO)_8 >$ Raney Ni.[33] The cobalt complex gave substantial quantities of $Ph_2Si(OMe)_2$, whereas the remainder gave only $Ph_2SiH(OMe)$. Although the effect of the size of the substituent on the silicon center on the rate of the transition metal-catalyzed alcoholysis has not been studied, the results from Ph_2SiH_2 and 9,10-dihydrosilaanthracene (a less sterically hindered version of diphenylsilane) suggest that there probably is an effect. Under conditions where Ph_2SiH_2 gives monosubstitution, the alcoholysis of the silaanthracene could not be controlled to give only the mono-substituted product.[38] The primary silane, $ArSiH_3$, gives mixtures of monoalkoxysilane and dialkoxysilane products when the ratio of silane to alcohol is 1 : 1. Only when bulky alcohols are used can $ArSiH_3$ be converted successfully, stepwise to ArSiH(OR)(OR').[37]

The iridium catalyst, $[IrH_2(THF)_2(PPh_3)_2]^+SbF_6^-$, causes very rapid reaction of tertiary silanes with ROH: complete conversion occurs in less than 1 min at room temperature in CH_2Cl_2.[35] The alcoholysis of tertiary silanes catalyzed by $Cl_2Pt(sty)_2$ is exothermic at room temperature.[41] It is unlikely that stepwise substitution of secondary silanes with these two catalysts can be controlled to give isolable quantities of monoalkoxysilanes from a secondary silane.

The availability of several methods for the formation of alkoxysilanes probably accounts for the lack of development of catalysts for alcoholysis of hydrosilanes.

Table II. Catalytic Dehydrogenative Coupling

		SiH/ROH			
*Catalyst**	*Silane/alcohol*	*TM/Si*[a]	*Product*	*Comments*	*Reference*
Fe Triad					
$Fe(CH_2{=}CH_2)(dppe)_2$	$HSi(OEt)_3/EtOH^b$	10^{-2}	$Si(OEt)_4$	Alcohol in excess.	32
	$H_2SiPh_2/EtOH^b$	10^{-2}	$Ph_2Si(OEt)_2$	Not for R_3SiH, Ph_2MeSiH or Ph_3SiH.	
$FeH_2(PMePh_2)_4$	$HSi(OEt)_3/EtOH^b$	10^{-2}	$Si(OEt)_4$	Reactions complete in 1–4 h. Catalyst still active after consumption of the silane. Induction period. Not for R_3SiH(R = alkyl, aryl).	32
$FeH_2(N_2)(PEtPh_2)_3$	$HSi(OEt)_3/EtOH$	10^{-2}	$Si(OEt)_4$	Reactions complete in 1–5 h. Induction period.	32
	$H_2SiPh_2/EtOH$	10^{-2}	$Ph_2Si(OEt)_2$		32
$Cl_2Ru(PPh_3)_3^c$	$H_2SiPh_2/MeOH^d$	10^{-3}	$Ph_2SiH(OMe)$	Only example. Reaction time, 0.5 h.	33
$[Cl_2Ru(CO)_2L]_2^{c,e}$ L = PMe_3	$HSiEt_3/MeOH^d$	10^{-2}	Et_3SiOMe	0.1h/THF/18°C for MeOH. Inactive: $Cl_2Ru(CO)_2(L)_2$;[f] $Cl_2Ru(PMe_3)_4$. Turnover/h/mol.cat. = 2500.	34, 35
	$HSiEt_3/PhOH$	10^{-2}	No reaction		35
Co Triad					
CoH_3L_3 and $CoH(N_2)L_3$	$HSi(OEt)_3/ROH$	[i]	$(EtO)_3SiOR$	$Co(H)(CO)L_3$ not effective. MeOH reacts 3 times faster than EtOH. No reaction for R_3SiH.	36
$ClRh(PPh_3)_3^c$	$H_3Si(\alpha Np)/MeOH^d$	10^{-3}	$\alpha NpSiH_2(OMe)$ $\alpha NpSiH(OMe)_2$	Ratio,methoxy/dimethoxy = 0.19	37
	$H_3Si(\alpha Np)/MeOH^g$	10^{-3}	$\alpha NpSiH_2(OMe)$	100% yield.	37
	$H_3Si(\alpha Np)/i\text{-}PrOH^d$	10^{-3}	$\alpha NpSiH_2(Oi\text{-}Pr)$ $\alpha NpSiH(Oi\text{-}Pr)_2$	Ratio of monoalkoxy/dialkoxy = 0.85.	37
	$H_3Si(\alpha Np)/i\text{-}PrOH^g$	10^{-3}	$\alpha NpSiH(Oi\text{-}Pr)_2$	100% yield.	37

Table II. (Continued)

		SiH/ROH			
*Catalyst**	*Silane/alcohol*	*TM/Si*[a]	*Product*	*Comments*	*Reference*
	H_2SiPh_2/EtOH[d]	10^{-3}	$Ph_2SiH(OEt)$	3 min/RT/C_6H_6. Only product.	33
	H_2SiPh_2/EtOH[g]	10^{-3}	$Ph_2Si(OEt)_2$	Requires heating.	38
	H_2SiPh_2/*i*-PrOH[d]	10^{-4}	Ph_2SiH(O*i*-Pr)	5 min/RT/C_6H_6.	33
	H_2SiPh_2/*t*-BuOH[d]	10^{-4}	Ph_2SiH(O*t*-Bu)	20 min/RT/C_6H_6.	
	H_2SiAr_2/EtOH[g,h]	10^{-2}	$Ar_2Si(OEt)_2$	3h/RT/C_7H_8; with 1 equivalent EtOH mono- and dialkoxy substitution occurs.	38
	H_2Si(*t*-Bu)$_2$/MeOH		(*t*-Bu)$_2$SiH(OMe)		39
	$HSiEt_3$/n-BuOH[d]	10^{-3}	Et_3SiOBu^n	12 h/80°C/C_6H_6.	33
$ClIr(CO)(PPh_3)_2$	$HSiEt_3$/EtOH[d]	10^{-3}	Et_3SiOEt	Rate of reaction increased by changing PPh_3 to $PMePh_2$ or $AsPh_3$.	40
	$HSi(OEt)_3$/EtOH[d]	10^{-3}	$Si(OEt)_4$	Reaction slower if PPh_3 is replaced by $PMePh_2$.	40
$[ClIr(COE)_2]_2$	$HSiEt_3$/ROH	[i]	Et_3SiOR	Rates are faster than with $ClIr(CO)(PPh_3)_2$. Very exothermic.	40
	$HSi(OEt)_3$/ROH	[i]	$(EtO)_3SiOR$		40
$ClIr(N_2)(PPh_3)_2$	$HSiEt_3$/EtOH	[i]	Et_3SiOEt		40
	$HSiPh_3$/EtOH	[i]	Ph_3SiOEt		40
$[IrH_2(THF)_2(PPh_3)_2]^+$ SbF_6^-	$HSiEt_3$/EtOH	10^{-3}	$Et_3Si(OEt)$	Turnover/h/mol. cat.=47,000.	35
	$HSiEt_3$/*i*-PrOH	10^{-3}	Et_3SiO*i*-Pr	Turnover/h/mol. cat.=130,000. Catalyst is *not* effective for hydrosilylation of C=C.	35

Table II. (Continued)

		SiH/ROH			
*Catalyst**	*Silane/alcohol*	*TM/Si*[a]	*Product*	*Comments*	*Reference*
Ni Triad					
cis-$Cl_2Pt(sty)_2$[c]	$HSiEt_3$/MeOH	10^{-4}	Et_3SiOMe	Methanolysis may be conducted at −18°C.	41
	$HSiMePh_2$/EtOH	10^{-3}	$Ph_2MeSi(OEt)$		41
$H_2PtCl_6{\cdot}6H_2O$[c]	H_2SiAr_2/EtOH	10^{-2}	$Ar_2Si(OEt)_2$		38

*Or Catalyst precursor.

Symbols: dppe, $Ph_2CH_2CH_2PPh_2$; COE, cyclooctene; THF, tetrahydrofuran; sty, styrene.

[a] Approximate ratio.

[b] Ratio varies.

[c] Also a hydrosilylation catalyst.

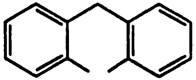
[d] Ratio Si/ROH = 1.

[e] Originally formulated as the monomer, $Cl_2Ru(CO)_2(PMe_3)_2$, which is essentially inactive.

[f] L = PPh_3, $P(C_6H_{11})_3$.

[g] Ratio Si/ROH = 0.5.

[h] Ar_2 =



[i] Data not provided.

The advantages of the dehydrogenative coupling could come from the control of successive substitution mentioned previously. Control of the alcoholysis of dichlorosilanes and trichlorosilanes is seldom realized. Selective reaction of primary, secondary, or tertiary silanes should be achievable since some catalysts appear to effect significantly different alcoholysis rates for secondary and tertiary silanes. Although the temperature variations where coupling can be effective have not been well-documented, it is noteworthy that *cis*-$Cl_2Pt(sty)_2$ catalyzed reactions can be run at low temperatures for tertiary silanes.[41] The secondary alcohol, *i*-PrOH, reacts with $MeSiH_3$ in the presence of Wilkinson's catalyst even at -56°C.[31]

A silica-supported catalyst suitable for aloholysis of hydrosilanes has been prepared by anchoring $Ph_2P(CH_2)_2Si(OEt)_3$ on silica followed by reaction with $[IrCl(COD)]_2$.[42a]

The majority of the catalysts that are effective appear to have TM–Cl or TM–H bonds. It is possible that the TM–Cl bonds are reduced to TM–H during the reaction with the hydrosilane (see Section 6). In some cases the original transition metal complex is converted to an inactive (or less active) form. The Fe(0) complex, $[Fe(CH_2{=}CH_2)(dppe)_2]$ forms $FeH_2(dppe)_2$ which is a poor catalyst for alcoholysis (although $FeH_2(PMePh_2)_4$ is effective).[32] Deactivation of $[IrH_2(S)_2L_2]SbF_6$ occurs in the absence of alcohol and the catalyst residue contains $[Ir_2(\mu\text{-}H)_3H_2L_4]SbF_6$ which is not effective for tertiary silanes but will promote the alcoholysis of secondary silanes.[35]

3.2. SiH/HN, SiH/HS, SiH/HCl

The coupling of amines, hydrogen halides, and hydrogen sulfide to hydrosilanes with heterogeneous Group VIII catalysts was demonstrated in 1967.[42b] The most effective catalyst for the tertiary silane, napthylphenylmethylsilane, was Pd (on carbon or alumina). There are only a few reports of homogeneous catalyzed reactions and these are summarized in Table III. The availablily of several SiN bond forming methods from chlorosilanes as well as SiN/HN′ exchange reactions of silylamines is probably responsible for the lack of development of dehydrogenative coupling as a useful synthetic route to silylamines. As in the alcoholysis reactions described peviously, aminolysis of a primary silane may be controlled to give monosubstituted products in high yield $[ClRh(PPh_3)_3]$.[47] One of the more unusual condensation reactions is the formation of polymers from Et_2SiH_2/NH_3 as well as oligomerization of $(HMe_2Si)_2NH/NH_3$ $[Ru_3(CO)_{12}]$.[45,46] These latter two reactions produce materials that are precursors for the pyrolytic generation of silicon nitride.

Only two attempts to survey a variety of catalysts that could be suitable for the dehydrogenative coupling of SiH/HN have been reported.[44,45b] Of the homogeneous catalysts (presumed) that were screened only $Ru_3(CO)_{12}$ exhibited any significant promise in the model reaction between Et_3SiH and HNMeBu in refluxing benzene or with Et_3SiH and H_2NR' in THF (70°C).

Table III. Dehydrogenative Coupling[a]

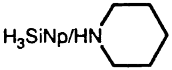
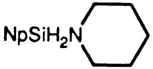
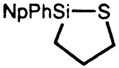
Catalyst[•]	*HSi/HN, HSi/HCl, HSi/HS* Silane/substrate	 TM/Si[b]	 Product	Comments	Reference
$WOCl_4$	$HSiEt_3/HNPh(CH_2Ph)$	10^{-1}	$PhCH_2N(Ph)SiEt_3$	97% conversion. Best case.	43
$Ru_3(CO)_{12}$	$H_2SiEt_2/HNMeBu$	10^{-2}	$Et_2Si(NMeBu)_2(15)$		44
	H_2SiEt_2/H_3N	10^{-3}	Polymer		45a
	$HSiEt_3/H_2NR'$[c]	10-3	Et_3SiNHR'	Primarily rate studies.	45b
	$HSiEt_3/HNMeBu$	10^{-2}	$Et_3SiNMeBu(95)$		44
	$HSiMe_2)_2NH/H_3N$[d]	10^{-4}	$[Me_2SiNH]_x$	x=3 is main cyclooligomer. Nonvolatile oligomers (5–21%).	46
	$HSiMe_2)_2NH/H_3N$[e]	10^{-3}		68% yield of nonvolatile product with M_n = 1200 Daltons.	46
$ClRh(PPh_3)_3$		10^{-4}	 (90)		47
	$HSiEt_3/HNMeBu$	10^{-2}	$Et_3SiNMeBu(0)$		44
	$HSiNpPh(CH_2CH_2CH_2SH)$				48
$NiCl_2/HSiMe_2Ph$	$HSiMe_2Ph/H_2NCH_2CO_2H$	10^{-2}	$RNHCH_2CO_2R(82)$ $R = SiMe_2Ph$		49
$PdCl_2$	$H_2SiEt_2/HNMeBu$	10^{-2}	$Et_2Si(NMeBu)_2(56)$		44
	$HSiEt_3/HNMeBu$	10^{-2}	$Et_3SiNMeBu(84)$	Highest yields in C_6H_6 solvent. Yds <30% in THF, CH_2Cl_2, and C_6H_{14}.	44

Table III. (Continued)

	HSi/HN, HSi/HCl, HSi/HS				
Catalyst[*]	*Silane/substrate*	*TM/Si*[b]	*Product*	*Comments*	*Reference*
	$HSiEt_3/H_2NBu$	10^{-2}	$Et_3SiNHBu$		44
	$HSiEt_3/H_2NNH_2$	10^{-2}	$Et_3SiNHNHSiEt_3$(39)		44
$PtCl_2$	$HSiEt_3/HNMeBu$	10^{-2}	$Et_3SiNMeBu$(14)		44
H_2PtCl_6	$HSiEt_3/HCl$	10^{-2}		No reaction.	50

[*] or catalyst precursor.

[a] Presumed heterogeneous catalysts.

[b] Approximate ratio.

[c] R' = *n*-Pr, *n*-Bu, *s*-Bu, *t*-Bu.

[d] Reactions run at 60 and at 90°C.

[e] Reaction run at 135°C.

The remainder of the catalysts studied by Barton,[44] $NiCl_2$, $H_2PtCl_6{\cdot}H_2O$, $ClRh(PPh_3)_3$, $Pd(OAc)_2$, $[RhCl(COD)]_2$, $Rh(acac)(CO)_2$, $PdCl_2(PPh_3)_2$, $[Ru(OAc)_2]_2$, $CrCl_3$, and $Ru(acac)_3$ gave no coupling products and $PtCl_2$ gave low yields of $Et_3SiNMeBu$. In Laine's study of the condensation of Et_3SiH with primary amines $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$ and $H_4Ru_4(CO)_{12}$ exhibited a moderate activity under conditions used with $Ru_3(CO)_{12}$ and $M_3(CO)_{12}$ (M = Fe, Os) and $H_2Os_3(CO)_{12}$ exhibited low activity even under more rigorous reaction conditions.[45b] The catalysts with the highest activity are formed from $(PhCN)_2PdCl_2$, $Pd(OAc)_2$, and $PdCl_2$ but the catalytic species is probably Pd metal produced from the reduction of the Pd(II) precursor by the hydrosilane.[45b]

The number of examples is too few to generalize but it appears that there is steric hindrance to the catalyzed condensation processes. The reaction of Et_3SiH and the primary amine, H_2NBu, gives only the silylamine, $Et_3SiNHBu$, and no evidence for the disilazane, $(Et_3Si)_2NBu$ [$PdCl_2$ or $Ru_3(CO)_{12}$ catalysts].[44] Reaction of Et_3SiH and hydrazine provided only 1,2-disubstituted hydrazine [$PdCl_2$].[44] The reaction of Et_3SiH and *t*-$BuNH_2$ is very slow relative to other primary amines.[45b]

Although $NiCl_2$ did not catalyze the reaction of Et_3SiH with HNMeBu, the combination of $NiCl_2/HSiMe_2Ph$ when heated to 100–120°C produced a catalyst suitable for the condensation of $HSiMe_2Ph$ with the amino group of glycine.[49]

The condensation of HSi/HS will probably be affected by catalyst poisoning. Very few examples have been published but hindered silanes gave very poor yields of silylthiols (heterogeneous catalysis) on reaction with H_2S and did not react at all with MeSH. Triethylsilane reacts with H_2S but not with MeSH ($Pd\text{-}Al_2O_3$).[42b] One example of $ClRh(PPh_3)_3$ catalyzed intramolecular coupling of a mercaptopropylsilane has been published.[48]

3.3. SiH/D_2

The reaction of hydrosilanes with D_2 can lead to an incorporation of deuterium. The reaction of $HSi(OEt)_3/D_2$ gives 40% $DSi(OEt)_3$ after 5 h in the presence of $[CoH(N_2)L_3]$[36] and 55% after 18 h with $IrCl(CO)(PPh_3)_3$[40]. Triethylsilane gave 62% incorporation after 5 h in the presence of $[CoH(N_2)L_3]$[36] and Et_3SiD is formed catalytically under a D_2 atmosphere in the presence of *trans*-$H_2Pt(PEt_3)_2$.[51]

4. COUPLING OF HYDROSILANES

The fact that a hydrosilane could couple with itself in the presence of Wilkinson's catalyst was reported in a brief communication in 1973;[2] however, there was essentially no follow-through of this interesting observation until the mid 1980's. Presently, work in this area is motivated by the possiblity that transition metal coupling of hydrosilanes could provide an alternative to Wurtz coupling for formation of polysilanes. The examples that have been reported for condensation of primary, secondary, and tertiary silanes are summarized in Table IV. Because this represents a new area of investigation, many details are missing and some early statements concerning lack of catalytic activity of certain transition metal complexes have been reversed when conditions have been changed. However, some generalizations are possible. The order of reactivity of silanes appears to be: primary > secondary > tertiary. Therefore catalysts that are active for primary silanes may not be effective for the conversion of secondary (or tertiary) silanes and the extent of oligomerization is likely to be different for $RSiH_3$ than for R_2SiH_2.

There appear to be two classes of transition metal complexes that promote silicon–silicon bond formation. The first grouping have the general formula Cp_xMR_y, where M is an electron-poor element such as Ti, Zr, V, and Cr and R is usually methyl but can also be a hydride. The highest molecular weight oligomers (from primary silanes) are formed from Cp_2MMe_2 (M = Ti[53], Zr[58]), whereas $Cp_2VMe_2$52 (and Cp_2V) forms only dimer and trimer from $PhSiH_3$. The hydride, Cp_2ZrH_2,[61] provides disilane only and $Cp_2MoH_2$52 and $Cp_2NbH_3$52 produce the dehydrogenative coupling product between the metal complex and the starting silane. The third row complexes, Cp_2HfMe_2 and Cp_2WH_2, exhibited no reaction with primary silanes and Cp_2TaH_3 may give the silyltantalum complex only after prolonged heating.[52] The monocyclopentadienyl complexes, $CpMMe_3$ (M = Ti, Zr), gave only traces of oligomers as did $(Cp^*)_2MMe_2$ (Cp^* = Me_5C_5; M = Ti, Zr), which should provide some clues concerning the structural requirements of the Ti Triad catalysts (see Section 6). The cyclopentadienylmetal catalysts are most successful in the coupling of primary silanes, although it is possible to promote the coupling of secondary silanes as will be described later in this section.

The second grouping of catalysts exhibit the general formula, Cl_xML_y, where M is an electron-rich metal. The best results occur for systems where M is Rh or Pt. The metal halide is most likely reduced by the hydrosilane to either an H_aML_b or "M^o" species as will be argued in the section describing the mechanistic suggestions for dehydrogenative coupling. There are several complications in the use of these metal halide catalysts. An important side reaction for both primary and secondary silanes is disproportionation [$ClRh(PPh_3)_3$].[2] As an example, $H_2SiMePh$ gives disilane and trisilane (44% combined yield) as well as 30% Ph_2MeSiH.[2] The platinum catalysts [both Pt(II) and Pt(0)] also give significant disproportionation, especially $Pt(CH_2{=}CH_2)(PPh_3)_2$.[66] A second difficulty is the fact that silicon–silicon bonds are readily oxygenated in the presence of the heavy metal halides.[57,66] It is probably this fact that accounts for the slow development of dehydrogenative coupling as an approach to silicon–silicon bond formation because the first catalyst used was $ClRh(PPh_3)_3$.[2] An exception seems to be in the use of Speier's catalyst, H_2PtCl_6, where formation of oligomers of $H(HexSiH)_xH$ (x = 2–5) is claimed from H_3SiHex when O_2 is bubbled into the reaction mixtures.[64] Considering the experimentally rigorous conditions that were used by Brown-Wensley to avoid oxygen in her studies using platinum catalysts,[66] the aforementioned results with H_2PtCl_6 should be considered suspect until a follow-up study shows that polysilanes and not polysiloxanes were actually obtained. With the exception of

Table IV. Dehydrogenative Coupling

	SiH/HSi							
				H-(SiRR')$_x$H				
Catalyst*	*Silane*	*TM/Si*^{a}	*S/T(C)/t(h)*	*R*	*R'*	*x(%)*^{b}	*Comments*	*Reference*
Ti Triad								
$\mathrm{CpTiMe_3}^c$	$\mathrm{H_3SiPh}$	10^{-1}	$\mathrm{C_7H_8}/^d/6$	H	Ph	^{e}(tr)		52a
$\mathrm{Cp_2TiMe_2}$	$\mathrm{H_3SiPh}$	10^{-2}	$\mathrm{C_7H_8}$/RT/168	H	Ph	~10(88)^f	Bimodal distribution. Light fraction, x = 9. Heavier fraction, x = 14–16.	53
			$\mathrm{C_7H_8}$/0/168	H	Ph	~8(55)		53
	$\mathrm{H_2SiMePh}$	10^{-2}	$\mathrm{C_7H_8}$/RT/336	Me	Ph	~4	50% conversion.	54
			$\mathrm{C_7D_8}/30/^{g,h}$	Me	Ph	2^i		
	$\mathrm{H_2SiPh_2}$	^{h}	^{h}	Ph	Ph	2^i		55
	$\mathrm{H_2SiAr_2}^j$	10^{-2}	$\mathrm{C_7H_8}$/25/168				No reaction.	56
$\mathrm{(MeCp)_2TiMe_2}$	$\mathrm{H_3SiPh}$	10^{-2}	$\mathrm{C_7H_8}$/RT/6	H	Ph	^{e}(85)		52
$\mathrm{CpCp^*TiMe_2}$	$\mathrm{H_3SiPh}$	10^{-1}	$\mathrm{C_7H_8}$/RT/40	H	Ph	^{e}(80)		52
$\mathrm{Cp^*_2TiMe_2}$	$\mathrm{H_3SiPh}$	0.5	$\mathrm{C_7H_8}/^k/12$	H	Ph	^{e}(0)		52
$\mathrm{Cp_2TiPh_2}$	$\mathrm{H_3SiPh}$	10^{-2}	neat/110/1	H	Ph	~7(83)^l	Highest degree of polymerization is 160; bimodal distribution.	57
			decene/110/24	H	Ph	~6(99)^l	Highest degree of polymerization is 30.	57
	$\mathrm{H_2SiPhMe}$	10^{-2}	neat/110/24	Me	Ph	2(14)	68% conversion. No reaction at RT.	57
			^{m}/110/24	Me	Ph	2(7) 3(88)	80% conversion.	57
	$\mathrm{H_2SiPh_2}$	10^{-2}	neat/110/24	Ph	Ph	2(72)	$\mathrm{Ph_3SiH}$(3%); 66% conversion.	57
			decene/110/24	Ph	Ph	2(66)	$\mathrm{Ph_3SiH}$(3%); 83% conversion.	57
	$\mathrm{HSiEt_3}$	10^{-2}	neat/110/1				$\mathrm{Et_3SiSiEt_3}$(0.6%).	57
$\mathrm{CpZrMe_3}^n$	$\mathrm{H_3SiPh}$	10^{-1}	$\mathrm{C_7H_8}/^d/6$	H	Ph	^{e}(tr)		52
$\mathrm{Cp_2ZrMe_2}$	$\mathrm{H_3SiPh}$	^{h}	^{h}	H	Ph	~20(^{i})		58

Table IV. (Continued)

	SiH/HSi							
				H-(SiRR')$_x$H				
Catalyst*	Silane	TM/Si[a]	S/T(C)/t(h)	R	R'	x(%)[b]	Comments	Reference
	H_3SiBu	10^{-3}	C_7H_8/RT/24	H	Bu	$2–7^{o}(^{i})$	55% by weight of product mixture is nonvolatile at reduced pressure. For x = 5–7, cyclic products were observed.	59,60
	H_2SiPh_2	^{h}	^{h}/65/^{h}	H	Ph	$2(^{i})$		61
	$H_2SiAr_2^{j}$	10^{-2}	C_7H_8/90/10	$–Ar_2–$		2(12), 3(87)	100% conversion.	56
	$H_2SiAr'_2{}^{p}$	10–2	C_7H_8/90/100	$–Ar'_2–$			No reaction.	56
$(MeCp)_2ZrMe_2$	H_3SiPh	10^{-2}	C_7H_8/RT/6	H	Ph	$^{e}(100)$		52
$CpCp^{*}ZrMe_2$	H_3SiPh	10^{-1}	C_7H_8/RT/40	H	Ph	$^{e}(100)$		52
$Cp^{*}{}_2ZrMe_2$	H_3SiPh	0.5	C_7H_8/^{k}/12	H	Ph	^{e}(tr)		52
Cp_2ZrH_2	H_2SiR_2	^{h}	^{h}			$2(^{i})$		61
Cp_2ZrCl_2/n-BuLi	H_3SiPh	10^{-2}	C_7H_8/0/1h	H	Ph		100% conversion. Chain length unknown.	62
	H_3SiHex	10^{-2}	C_7H_8/25/26	H	Hex	2,3(2) ≥4 (98)	59% conversion.	62
	$H_2SiMePh$	10^{-2}	C_7H_8/90/24	Me	Ph	2,3(87)	48% conversion.	62
		10^{-2}	C_7H_8/90/48	Me	Ph	2(24) 3(42) 4(17) 5(14)	76% conversion.	62
	$H_2SiEtPh$	10^{-2}	C_7H_8/90/120	Et	Ph	2(60) 3(16)	44% conversion.	62
	H_2SiPr_2	10^{-2}	C_7H_8/90/	Pr	Pr	2,3		62
	H_2SiPh_2	10^{-2}	C_7H_8/90/96	Ph	Ph	2(100)	47% conversion.	62
Cp_2HfMe_2	H_3SiPh	0.5	C_7H_8/^{q}/12	H	Ph		No reaction.	52

Table IV. (Continued)

	SiH/HSi							
				H-(SiRR')$_x$H				
Catalyst[*]	*Silane*	*TM/Si*[a]	*S/T(C)/t(h)*	*R*	*R'*	*x(%)*[b]	*Comments*	*Reference*
V Triad								
Cp_2V	H_3SiPh	10^{-2}	C_7H_8/100/160	H	Ph	2(25)[r] 3(75)[r]	After 100 h: Disilane (50%); SM(40%); trisilane(10%).[r]	52
Cp_2VMe_2	H_3SiPh	10^{-2}	C_7H_8[s]/40	H	Ph	2(40) 3(20)		52
Cp_2NbH_3[t]	H_3SiPh	10^{-1}	C_7H_8[s]/12				No isolated silicon product.	52
Cr Triad								
Cp_2Cr	H_3SiPh	10^{-1}	C_7H_8/RT/12				No reaction.	52
Cp_2MoH_2	H_3SiPh	0.5	hex/hv/4				$Cp_2Mo(H)(SiH_2Ph)$; secondary and tertiary silanes react similarly.	52
Cp_2WH_2	H_3SiPh	0.5	hex/hv/12				No reaction.	52
Mn Triad								
$Ph_3SiMn(CO)_5$	HD_4	10^{-3}	neat/180/1				D_4–D_4(20).	43
Fe Triad								
$Fe_2(CO)_9$	$HSiMe_2Ph$	10^{-2}	–/150/12				No reaction.	65b
$Fe(dppe)_2L$ $L = CH_2{=}CH_2$	$HSi(OEt)_3$	[h]	tol/80/[h]				$(EtO)_3SiSi(OEt)_3$.	63
$Ru_3(CO)_{12}$	$HSiMe_2Ph$	10^{-2}	–/150/12				Redistribution.	65b

Table IV. (Continued)

	SiH/HSi							
				H-(SiRR')$_x$H				
Catalyst[•]	Silane	TM/Si[a]	S/T(C)/t(h)	R	R'	x(%)[b]	Comments	Reference
Co Triad								
$Co_2(CO)_8$	$HSiMe_2Ph$	10^{-2}	–/150/12				No reaction.	65
$ClRh(PPh_3)_3$	H_3SiPh	10^{-3}	neat/80/1	H	Ph	2(i) 3(i)	$HPh_2SiSiPhH_2$(i).	2
	H_3SiHex		neat/20/[h]	H	Hex		Products not well-characterized.	64
	H_2SiPh_2		neat/80/1	Ph	Ph	2(38)	Ph_3SiH(8%); 55% conversion.	2
	H_2SiAr_2[j]		C_7H_8/25/10	–Ar_2–		2(38) 3(42)	83% conversion.	56
			C_7H_8/82/1.5	–Ar_2–		2(17) 3(66)	93% conversion.	56
			neat/80/3	–Ar_2–		2(21) 3(58)	81% conversion.	56
	$H_2SiAr'_2$[p]		C_7H_8/85/3	–Ar'_2–		2(48) 3(17)	77% conversion.	56
	$H_2SiMePh$		neat/70/1	Me	Ph	2(14) 3(30)	Ph_2MeSiH(30).	2
		10^{-2}	C_6H_6/80/0.5	Me	Ph	2(6.4)	Redistribution.	65a
	H_2SiEt_2		[h]	Et	Et	2,3(i)		2
	$HSiMe_2Ph$		–/150/12				No reaction.	65b
		10^{-2}	C_6H_6/70/168				$PhMe_2SiSiMe_2Ph$(2.9).	65a
	$HSiEt_3$	10^{-3}	C_6H_6/60/120				$Et_3SiSiEt_3$(11) (aniline present).	43
(acac)RhL_2 L = CH_2=CH_2	$HMePhSi)_2O$	10^{-2}	C_6H_6/1/40				$MePh_2SiSiPhMeH$(33); 20% conversion.	65a
$ClIr(CO)L_2$ L=PPh_3	$HMeBzSi)_2O$	10^{-3}	C_6H_6/45/40				$HBzMeSiSiBzH_2$(3.7); HBzMeSiSiBz-MeH(11); 70% conversion.	65a

Table IV. (Continued)

	SiH/HSi			*H-(SiRR')$_x$H*				
Catalyst*	*Silane*	*TM/Si*^{a}	*S/T(C)/t(h)*	*R*	*R'*	*x(%)*^{b}	*Comments*	*Reference*
	$HSiMe_2Ph$	10^{-2}	C_6H_6/70/168				Redistribution.	65b
Ni Triad								
$Cl_2Ni(PPh_3)_2$	$HSiMe_2Ph$	10^{-2}	neat/150/12				No reaction.	65
$[ClPd(allyl)]_2$	$HSiEt_3$	10^{-2}	neat/18/				Et_6Si_2.	66
	H_2SiEt_2	10^{-2}	neat/18/	Et	Et	2		
$[R_3NH]_2PdCl_4$ R = C_8H_{17}	$HSiEt_3$ + H_2NPh	10^{-2}	neat/19/RT				Et_6Si_2(38); 95% conversion. $Et_3SiNHPh$(8).	43
$Pt(PMe_2Ph)_4$	$HSiMe_2Ph$	10^{-3}	neat/150/12				$Me_2PhSiSiMe_2Ph$(6.8%); (48% based on conversion of SM. Yields are lower with PtL_4(L = PPh_3).	65b
$Pt(L)(PPh_3)_2$ L = CH_2=CH_2	$H_2SiMePh$	10^{-3}	neat/18/75	Me	Ph	2(27)^{u}	Ph_2MeSiH(52%).	66
	H_2SiEt_2	10^{-3}	neat/18/75	Et	Et	2(95)	No reaction of $PhMe_2SiH$, Et_3SiH.	66
	H_2SiEt_2 + Et_3SiH	10^{-3}	neat/18/75	Et	Et	2(58)	Et_5Si_2H(8).	66
	$HSi(OEt)_3$	10^{-3}	neat/18/75	OEt	OEt	2(0)	$(EtO)_4Si$(61).	66
$Cl_2Pt(PEt_3)_2$	H_3SiPh	^{h}	^{h}	H	Ph	2(^{i}) 3(^{i})	Oligomers probably also formed in reaction of $CySiH_3$.	67
$Cl_2Pt(PMe_3)_2$	$HSiMe_2Ph$	10^{-3}	neat/150/12				$Me_2PhSiSiPhMe_2$(7%); 30% based on consumed starting material. Yields decrease with larger phosphine ligands. $PtCl_2L_2$ (L = PhCN) ineffective.	65b

Table IV. (Continued)

	SiH/HSi							
				H-(SiRR')$_x$H				
Catalyst$^{\bullet}$	*Silane*	*TM/Si*^{a}	*S/T(C)/t(h)*	*R*	*R'*	*x(%)*^{b}	*Comments*	*Reference*
$L_2Pt\genfrac{}{}{0pt}{}{(SiPhX)}{(SiPhY)}PtL_2$ L = PEt_3	H_3SiPh	^{h}	^{h}	H	Ph	2(^{i}) 2(^{i})	Disproportionation products also formed.	67
Pt(II)Phosphite Complex	H_2SiRR'		hν/^{h} /^{h}	R	R'		68	
$H_2PtCl_6·6H_2O$	H_3SiHex	^{h}	neat/20/^{h,v}	Me	Ph	2,3(^{i})		64
			neat/20/^{h,w}	Me	Ph	2(27) 3(32) 4(24) 5(17)		
$[R_4P]_2PtCl_6$ R = $C_{10}H_{21}$	$HSiEt_3$ + $PhCH_2$-NHMe	10^{-2}	neat/120/16				Et_6Si_2(27); 41% conversion.	43
Zn Triad								
$ZnCl_2$	$HSiEt_3$ + $PhCH_2$-NHMe	10^{-2}	neat/120/16				Et_6Si_2(8); 72% conversion.	43
Hg/hν	$HSiEt_3$		^{h}				$Et_3SiSiEt_3$(95%).	69
	H_2SiEt_2		h /80/20	Et	Et	2(37)^{x} 4(21) >4(42)	Product distribution may be a function of the period of photolysis (not explored).	69
Lanthanides/ actinides								
$Cp^*{}_2UMe_2$	H_3SiPh	10^{-1}	C_7D_8/RT/^{h}				$PhMeSiH_2$. With large excess of silane, small amounts of low MW oligomers obs.	52

Table IV. (Continued)

	SiH/HSi							
				H-(SiRR')$_x$H				
Catalyst*	Silane	TM/Si[a]	S/T(C)/t(h)	R	R'	x(%)[b]	Comments	Reference
	H_3SiPh	10^{-1}	Et_2O/RT/6	H	Ph	[e](30)	Rapid formation of oligomers.	
Cp*$_2$ThMe$_2$	H_3SiPh	10^{-1}	Et_2O/RT/6	H	Ph	2(70)	Complex reactions occur in toluene.	52

* or catalyst precursor

Symbols: dppe, $Ph_2PCH_2CH_2PPh_2$; Cp*, C_5Me_5; Bz, $C_6H_5CH_2$; RT, room temperature.

[a] Approximate ratio.

[b] Weight percent of products unless specified otherwise.

[c] Similar results for Cp*TiMe$_3$.

[d] –80 to 20°C.

[e] x is undefined.

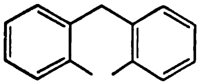
[f] Average degree of polymerization (% yield calculated on the basis of this oligomer from data given in the reference).

[g] Olefin must be present for reaction to occur.

[h] Condition or conditions not specified.

[i] Yield not specified.

[j] Ar_2=



[k] –60 to 20°C.

[l] Crude yield.

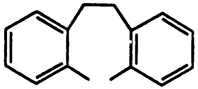
[m] Cyclooctene present.

[n] Similar results for Cp*ZrMe$_3$.

[o] Products determined by gc-ms.

Table IV. (Continued)

[p] Ar'_2 =



[q] 20–90°C.

[r] Estimated from graphical data given in Ref. 52.

[s] 100–120°C.

[t] Similar results for Cp_2TaH_3.

[u] Yields reported as percentage of total products.

[v] N_2 atmosphere.

[w] $N_2 + O_2$.

[x] 88% purity.

Speier's catalyst, which was reported for reaction of a primary silane, these heavy metal halides promote primarily the formation of disilanes and trisilanes. The relative rates of disilane formation from H_2SiEt_2 for a series of metal halides was determined by Brown-Wensley.[66] The observed order was $ClRh(PPh_3)_3$ > $[ClPd(allyl)]_2$ > $[ClRh(CO)_2]_2$ > $[ClRh(COD)]_2$ > $Cl_2Pt(COD)$ > Cl_3Rh > $[ClIr(COD)]_2$ > $Cl_2Pt(PPh_3)_2$ ~ H_2PtCl_6. All of these catalysts are also hydrosilation catalysts with rates that are faster than the coupling reaction in all cases except $Cl_2Pt(PPh_3)_2$, where the two processes occur at about the same rate.

The variations for the cyclopentadienyl catalysts of titanium and zirconium which have met with such success in oligomerization of primary silanes do not appear to be extensive. Substitution at the Cp ring has been explored somewhat. The rate of oligomerization of $PhSiH_3$ follows the order: Cp_2TiMe_2~$(MeCp)_2TiMe_2$ > $CpCp^*TiMe_2$ >>> $Cp^*{}_2TiMe_2$ (all reactions performed no higher than room temperature).[52] Harrod and co-workers attempted to vary the other substituents at titanium or zirconium but met with limited success. The benzyl derivative, $Cp_2Ti(CH_2Ph)_2$, was found to be an effective catalyst for the condensation of primary silanes but Cp_2TiPh_2 was not,[54,55] although the reaction was probably run at room temperature. Later, it was shown by Nagai[57] that Cp_2TiPh_2 is an effective catalyst for the condensation of both primary and secondary silanes at 110°C, temperatures that are higher than the decomposition of diphenyltitanocene.

Most of the reactions reported by Harrod and co-workers were conducted at room temperature. Under these conditions, sterically hindered primary silanes as well as secondary silanes did not couple unless an olefin was present as a dihydrogen acceptor. Only disilanes were reported as products. Under the higher temperature conditions used by Nagai, the presence of olefin acceptors (1-decene or cyclooctene) not only increased conversion of starting secondary silane but gave, as well, excellent yields of trisilane from $PhMeSiH_2$ (but not from Ph_2SiH_2).[57] The highest degree of oligomerization observed from a secondary silane using a preformed catalyst is three.

We have taken a different approach to the generation of an active catalytic species based on zirconium but formed from commercially available materials. A possible intermediate in the use of the preformed Cp_2ZrR_2 catalysts could be zirconocene. Negishi et al.[70a] has provided evidence for the intermediacy of zirconocene from the reaction of Cp_2ZrCl_2 and *n*-BuLi at low temperatures followed by warming to room temperature. The original assignment was based on NMR evidence, but more recently the zirconocene equivalent has been isolated as the olefin complex (containing an additional phosphine ligand).[71] Although the original experiments were performed in tetrahydrofuran starting at –78°C, we used toluene at 0°C and heated mixtures to about 85–90°C in the presence of $PhMeSiH_2$. Under these conditions, disilane is formed initially and maximizes within 3 h. Detectable quantities of trisilane are present within 5 h and maximize at approximately 36 h. After 5 days tetrasilane through heptasilane and probably octasilane are also obtained although only disilane, trisilane, and tetrasilane have been individually separated and studied spectroscopically. This is the only catalyst system thus far that produces chains longer than tetrasilanes starting from a secondary silane. A tetrasilane has been produced with $(PPh_3)_3RhCl$.[66b] The disilane and trisilane that are formed from the catalyst system Cp_2ZrCl_2/*n*-BuLi are present as statistical mixtures of diastereomers (meso and d,l pair for the former and two meso and one d,l pair for the latter) as determined from ^1H, ^{13}C and ^{29}Si NMR spectroscopy measurements. The tetrasilane data are not consistent with a statistical mixture of two meso and four d,l pairs and suggest that there could be diastereomeric induction in the chain growth process. The maximum conversion of starting silane appears to be about 80% under these conditions. Just as was observed for Cp_2TiMe_2 and Cp_2TiPh_2 we obtained only disilane from Ph_2SiH_2. This limitation suggests that there are steric restrictions to the condensation process. The short-chain oligomeric products are stable in air. Samples that have been stored for a year under normal laboratory conditions exhibit no signs of oxidation. The oxidation products which can be produced on prolonged heating with traces of air are clearly discernible by GC-mass spectrometry.

The primary silane, $PhSiH_3$, reacts extremely rapidly with the species generated from Cp_2ZrCl_2/BuLi even at 0°C and starting material is consumed within 1 h at room temperature. Hexylsilane also reacts but more slowly and intermediate chain lengths are observable by gas chromatography in the first few hours at room temperature. The state of oligomerization of the polysilanes obtained from the primary silanes with this catalyst system has not yet been determined.

The oligomers produced from the reaction of $PhSiH_3$ in the presence of Cp_2TiMe_2 have been spectroscopically analyzed. A bimodal distribution was obtained and the lighter fraction seemed to contain a single component, which was assigned to $H(PhSiH)_9H$, whereas the heavier fraction was assigned to chains of 14–16 silicon atoms (probably at least two species).[53] The properties of the products were determined after 7 days of reaction at room temperature. Only straight-chain products were claimed although in a recent study it was stated that the all trans isomer of hexaphenylcyclohexasilane is produced after long polymerization times but is less than 1% of the products.[52a] The condensation of benzylsilane provided mainly cyclic products, $[BzSiH]_n$ with *n*-7 within 24 h.[52b] After several weeks, the all-trans isomer of hexabenzylcyclohexasilane, $[BzSiH]_6$, precipitates out in yields of up to 35%. The material is so insoluble that it was never detected in solution. Hilty has studied the reaction of $BuSiH_3$ in the presence of Cp_2ZrMe_2 and sampled the reaction products as a function of time. He observed that a large percentage of the higher oligomers (Si_5 products and higher) are cyclic.[59a] Running the reactions at higher temperatures increased the proportion of cyclics and cyclics appear to be the thermodynamic products in Wurtz Coupling reactions.[59b]

Although this chapter focuses on the catalytic formation of silicon–silicon bonds, there are some important results that have been produced from the study of stoichiometric processes investigated by Tilley and co-workers. The reaction of $Cp_2Ti(SiMe_3)Cl$ with $PhSiH_3$ produced the disilane, PhH_2SiSiH_2Ph.[69b] Similar results were obtained from the reaction of $Cp^*Ta(SiMe_3)Cl_3$.[69b] The silyltitanium complexes also function as catalysts for the oligomerization of hydrosilanes.

5. COUPLING OF SiH/HTM

Hydrosilanes are major silicon reactants leading to formation of silicon-transition metal bonds. One of the classes of reactions that occurs is dehydrogenative coupling of the silane and the transition metal hydride derivative. Earlier examples have been summarized[72] and more recent studies are given in Table V. As can be seen from the table, the cyclopentadienylmetal hydride derivatives of the titanium, vanadium, and chromium triads undergo coupling reactions with hydrosilanes. This grouping has also exhibited activity in the self-coupling of hydrosilanes as described in the previous section.

Probably one of the most interesting examples given in Table V is the observation that $HCo(CO)_4$ does not react with $HSiEt_3$.[77] In earlier studies the reaction of $Co_2(CO)_8$ with hydrosilanes was thought to produce $R_3SiCo(CO)_4$ and $HCo(CO)_4$. The latter species condensed with an additional mole of hydrosilane to give $R_3SiCo(CO)_4$ plus dihydrogen.[85] Recently, it has been shown that no $HCo(CO)_4$ is formed from the starting $Co_2(CO)_8/HSiR_3$ mixture unless a base is present.[77] Therefore, a more complex sequence was proposed for the formation of $R_3Si(CO)_4$ beginning with the dissociation of $Co_2(CO)_8$ to $Co(CO)_4$ followed by reaction with the silane. Because the key step in the Chalk-Harrod hydrosilation mechanism involves addition of $HCo(CO)_4$ to the olefin, a revised or expanded version of the mechanism for hydrosilation is in order. An alternative mechanism has been provided by Wrighton and co-workers based on insertion of olefin into the Co–Si bond of $[(CO)_3CoSiR_3]$ (produced from the photolysis of $(CO)_4CoSiR_3$). Subsequent reaction involves oxidative addition of a mole of hydrosilane to the cobalt center followed by reductive elimination of $CH_3CH_2SiR_3$ (the product of hydrosilation) from the intermediate species, $(H)(R_3Si)CoCH_2CH_2SiR_3$.[86] The $Co_2(CO)_8$ catalyzed condensation of $HSiEt_2Me$ with methyl acrylate also seems to require insertion of the olefin into a Co–Si bond in order to account for the product distribution.[12b]

The reactions of hydrosilanes with transition metal derivatives are, of course, much more varied and complicated than the formal coupling reactions shown in Table V. Some additional variations will be discussed in Section 6.

6. MECHANISTIC CONSIDERATIONS

6.1. Basic Reaction Chemistry

In order to understand how dehydrogenative coupling processes could occur, it is useful to know the variations in the stoichiometric reactions that hydrosilanes

Table V. Dehydrogenative Coupling: Stoichiometric

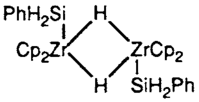
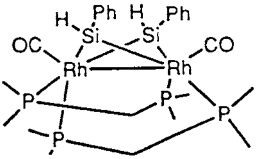
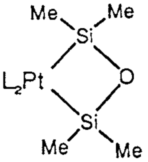
	TM-H/HSi			
Catalyst	*Silane*	*Product*	*Comments*	*Reference*
Ti Triad				
Cp_2ZrH_2	H_3SiPh		Not isolated.	60
V Triad				
$[Cp_2V(H)SiCl_3]$	$HSiCl_3$	$Cp_2V(SiCl_3)_2$	Formed stepwise from Cp_2V.	73
Cp_2MH_3 (M = Nb, Ta)	$HSiMe_2Ph$	$Cp_2M(SiMe_2Ph)H_2$	No Nb–Si products when $HSiEt_3$ employed.	74
Cr Triad				
Cp_2MoH_2	$HSiCl_3$		Product not characterized.	73
	H_3SiPh	$Cp_2Mo(H)(SiH_2Ph)$	Secondary and tertiary silanes react similarly.	52
Cp_2WH_2	$HSiCl_3$	$Cp_2W(H)(SiCl_3)$		73
Fe Triad				
FeH_2L_4[a] L = PMe_2Ph	$HSiEt_3$	No reaction.	Chlorination occurs with $HSiCl_3$.	63
$Ru(CO)_4(SiCl_3)H$	$HSiCl_3$	*cis*-$Ru(CO)_4(SiCl_3)_2$		75
$[H\{Os(CO)_4\}_3SiCl_3]$	$HSiCl_3$	$Cl_3Si\{Os(CO)_4\}_3SiCl_3$	Formed stepwise from $Os_3(CO)_{12}$.	76
Co Triad				
$HCo(CO)_4$	$HSiEt_3$	No reaction.	Refutes Chalk/Harrod mechanism. (See text.)	77
$HCo(CO)_2L_2$ L = PPh_3	$HSiF_3$	$Co(SiF_3)(CO)_2L_2$	Tentative assignment. No reaction with other R_3SiH and SiCl chlorinates CoH.	78
$HCo(CO)_3L$ L = PPh_3	$HSiF_3$	$Co(SiF_3)(CO)_3L$	Tentative assignment.	78
	$HSiPh_3$	$Co(SiPh_3)(CO)_3L$	via $[CoH_2(SiPh_3)(CO)_2L]$.	78
H_3CoL_3[b] L = PPh_3	$HSiR_3$	$CoH_2(SiR_3)L_3$		36

Table V. (Continued)

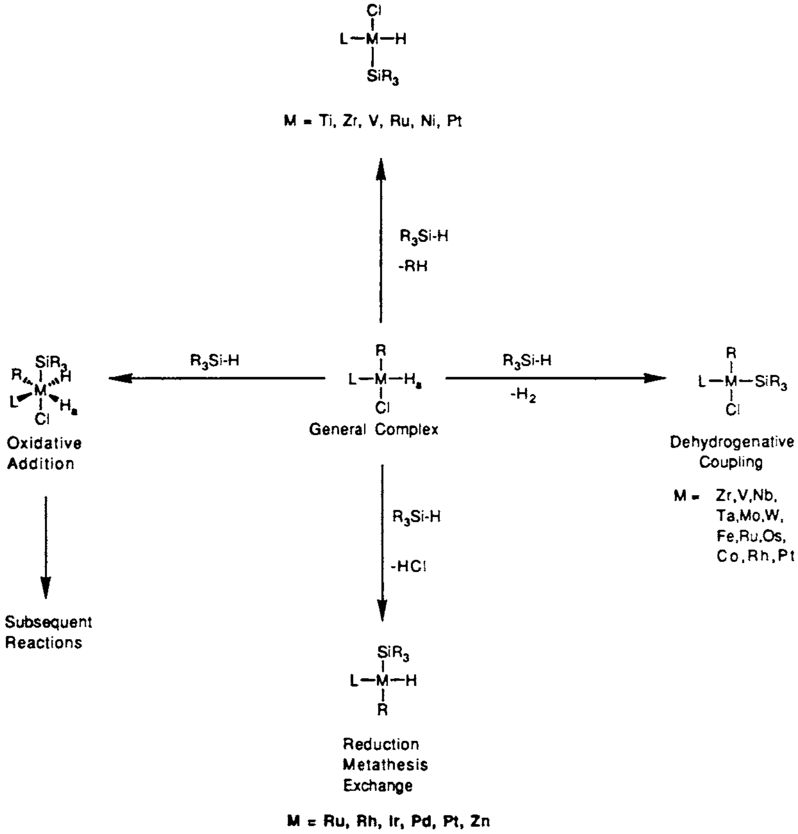
	TM-H/HSi			
Catalyst	*Silane*	*Product*	*Comments*	*Reference*
$HCo(CO)L_3$[c] $L = PPh_3$	$HSiF_3$	$CoH_2(SiF_3)(CO)L_2$	Tentative assignment.	78
$H_2Rh(CO)_2(dppm)_2$	H_3SiPh			79
Ni Triad				
trans-$H_2Pt[P(i\text{-}Pr)_3]_2$	$HSiPh_3$	*trans*-$PtH(SiPh_3)[P(i\text{-}Pr)_3]_2$		80,81
cis-$H_2Pt(PMe_3)_2$	$HSiPh_3$	*cis*-$PtH(SiPh_3)(PMe_3)_2$		82
cis-$H_2Pt(PEt_3)_2$	$HSiEt_3$	*cis*-$PtH(SiEt_3)(PEt_3)_2$		51
trans-$H(I)PtL_2$[d] $L = PEt_3$	$(H_3Si)_3N$	*trans*-$(H_3Si)_2NSiH_2PtL_2I$		83
$L_2Pt(H)SiMe_2OSiMe_2H$ $L = PPh_3$				84

Symbols: dppm, $Ph_2PCH_2CH_2PPh_2$.

undergo with transition metal complexes. A recent review surveys the reactions of both early and late transition metal complexes that contain silyl ligands and provides a good introduction to the basic chemistry of the silicon-transition metal bond.[115a] The stereochemistry of mechanisms of reactions with transition metal complexes has also been described in some detail particularly with the α-naphthylphenylmethylsilyl group.[115b]

The most common reaction of a hydrosilane is probably oxidative addition to the metal center which can be followed by secondary processes that lead to the observed products. If the reaction involves an 18 electron complex, loss of ligand is required and in the simplest case would give a 16-electron, coordinatively unsaturated metal center prior to the oxidative addition of the hydrosilane. This is illustrated for the general case in equation 1. The reverse of oxidative addition is referred to as reductive elimination. There are also more complex versions of the two processes but these are not required to understand the mechanistic proposals that will be summarized in subsequent sections.

$$\underset{\substack{18e\\(\text{or }16e)}}{L_nM} \xrightarrow{h\nu \text{ or } \Delta} \underset{\substack{16e\\(\text{or }14e)}}{L_{n-1}M^{0(I)}} \underset{\substack{\text{reductive elimination}\\ -HX}}{\overset{\substack{+HX\\ \text{oxidative addition}}}{\rightleftharpoons}} \underset{\substack{18e\\(\text{or }16e)}}{L_{n-1}M^{II(III)}(H)(X)} \tag{1}$$



Scheme 2.

Oxidative addition of hydrosilanes to metal centers may not be the only reaction pathway for hydrosilanes. The products that are obtained from MX/HSiR3 are often the equivalent of an HX elimination reaction. Examples of the overall processes exhibited in the reactions of hydrosilanes that are pertinent to this review are shown for a generic "complex" in Scheme 2.

The variations in the stoichiometric reactions of hydrosilanes with transition metal derivatives have been nicely summarized by Aylett.[72] Examples of the processes shown in Scheme 2 that involve the elimination of small molecules (H_2, HCl, RH) are included in this report. The current review emphasizes results from the past ten years therefore the elimination/coupling reactions have been updated in the appropriate tables including the dehydrogenative coupling of SiH/HTM that was presented in Table V. Because transition metal halides have been used to promote dehydrogenative coupling reactions, it is important to realize that reduc-

Table VI. Reduction of M–Cl by SiH

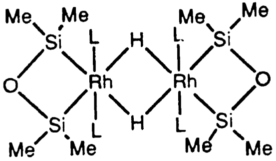
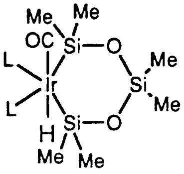
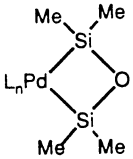
Metal halide	*Silane*	*Product*	*Comments*	*Reference*
Fe Triad				
Cl_2RuL_3 $ClHRuL_3$ L = PPh_3	$HSiR_3$	$RuH_3(SiR_3)L_3$	Combination of reduction and oxidative addition.	87
Co Triad				
$ClCoL_3$ L = PPh_3	$HSiR_3$	No reaction.		36
$ClRhL_3$ L = PPh_3	$HMe_2Si)_2O$		Tentative assignment; combination of reduction and oxidative addition.	88
$\{Cp^*RhCl_2\}_2$	$HSiEt_3$	$Cp^*Rh(H)_2(SiEt_3)_2$	Proceeds through $Cp^*RhH_2Cl(SiEt_3)$.	89
$\{Cp^*IrCl_2\}_2$	$HSiEt_3$	$Cp^*Ir(H)_2(SiEt_3)_2$	Proceeds through $\{Cp^*IrCl(H)\}_2$ and $Cp^*IrH_2(SiEt_3)Cl$	90
$ClIr(CO)L_2$ L = PPh_3	$HMe_2SiO)_2SiMe_2$			88

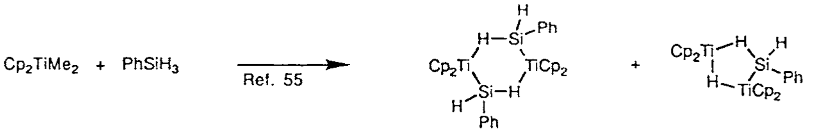
Table VI. (Continued)

Metal halide	Silane	Product	Comments	Reference
Ni Triad				
Cl_2PdL_2	$HMe_2Si)_2$			88
Cl_2Pd	$HSiEt_3$	"Pd"	$Et_3SiCl(100)$. Pd residues contain 2.6%C, 0.6%H.	44
$[ClPd(allyl)]_2$	H_2SiEt_2		Black solids.	66
$Cl_2Pt(sty)_2$	$HSiEt_3$	$Pt(sty)_3$	Two equivalents of silane are required. EtC_6H_5 also produced.	26
	$HSiPh_3$			
$Cl_2Pt(COD)$	$HSi(OEt)_3$	Pt	Colloid	91
H_2PtCl_6	$HSi(OEt)_3$	Pt	Colloid	91
Zn Triad				
Cl_2Zn	H_2SiPh_2	"ZnH"	Ph_2SiHCl detected; Et_2SiH_2 is inert.	92

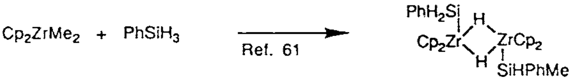
Symbols: Cp*, C_5Me_5; sty, styrene; COD, 1,5-cyclooctadiene.

tion to the metal hydride by hydrosilanes can occur. Illustrations of this type of process are shown in Table VI.

Elimination of alkanes on reaction with a hydrosilane is covered in Aylett's review,[72] but examples from the titanium triad where catalysts that are particularly effective in oligomerization of hydrosilanes originate had not yet been observed. The stoichiometric reactions of dimethyltitanocene and dimethylzirconocene reveal the formation of unusual hydride bridged dimers shown in equations 2 and 3. The titanium derivatives contain novel TiHSi bridges and the zirconium derivative shows transfer of a methyl group to silicon. An additional example from ruthenium chemistry is shown in equation 4 where the reaction produces its own internal NMR standard.



(2)



(3)

$$Cp^*L_2RuCH_2SiMe_3 + HSiR_3 \xrightarrow[\text{Ref. 116}]{} Cp^*L_2RuSiR_3 + SiMe_4 \qquad (4)$$

$L = PMe_3$

As has already been described, there are several variations of oxidative addition since other processes may also occur simultaneously or subsequent to those depicted in Scheme 2. Examples of addition to both 16- and 18-electron complexes are shown in Table VII. There are a few observations from Table VII that may be important in the mechanistic aspects of dehydrogenative coupling. The chromium and manganese triads provide isolated examples of 3c/2e HMSi interactions and there are variations that appear to be on the pathway to oxidative addition (HSi interaction with the metal) as well as full oxidative addition to produce H–M–Si, where the H and Si do not interact. In some cases, the M–H bond formed during oxidative addition reacts further and the final complex contains Si–M but not MH. The examples given in Table VII represent stable silyl-substituted complexes; however, in terms of the catalyzed formation of new silicon compounds the silicon transition metal bond must be cleaved to form the final product. Therefore the examples shown in this table could be expected to show little catalytic behavior although this actually turns out not to be the case. Examples from Table V include $Fe(CO)_5$ (HSi/HC coupling), $[MeOIr(COD)]_2$ (HSi/HC coupling), FeH_2L_4 (HSi/HOR coupling), $[Fe(dppe)_2(CH_2{=}CH_2)]$ (HSi/HOR and HSi/HSi coupling), $ClIr(CO)L_2$ (HSi/HOR coupling) and $Pt(CH_2{=}CH_2)(PPh_3)_2$ (HSi/HSi coupling). Because the entries in Table VII are only a partial listing of all reported reactions

Table VII. Oxidative Addition of SiH to Transition Metal Organometallics

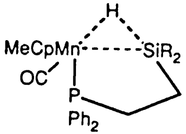
Organometallic (electron count)	*Silane*	*hv or heat*	*Product*	*Comments*	*Reference*
Ti Triad					
$Cp_2Ti(CO)_2$ (18)	$HSiCl_3$	110°C	$Cp_2Ti(H)SiCl_3$ $Cp_2Ti(H)(CO)SiCl_3$	Mixture of two products according to analysis. Supportive data are weak.	73
Cr Triad					
$C_6Me_6Cr(CO)_3$ (18)	H_2SiPh_2	hv/–15°C	$C_6Me_6Cr(H)(CO)_2SiHPh_2$	3c/2e bond	93
Mn Triad					
$Cp'Mn(CO)_3$ (18)	H_4Si	hv/10°C	$[Cp^*Mn(CO)_2H]_2SiH_2$	Attempt to eliminate H_2 was unsuccessful. Crystal structure.	94
	$HXSiRR'$	hv/RT	$MeCpMn(CO)_2H$-$SiXRR'$		95
	$HSiR_2CH_2CH_2$-PPh_2	hv/0°		Crystal structure supports 3c/2e bonding.	96
$Cp'Re(CO)_3$ (18)	H_2SiPh_2	hv	$CpReH(SiPh_2H)(CO)_2$	Loss of CO.	97
	H_2SiEt_2	hv/RT	$CpReH(SiEt_2H)(CO)_2$	Loss of CO.	98
	$HSiPh_3$	hv/RT	$CpReH(SiPh_3)(CO)_2$	Loss of CO.	98,99
Fe Triad					
$FeH_2(PMe_2Ph)_4$ (18)	$HSiR_3$		$R_3SiFeH_3L_3$	Loss of PMe_2Ph.	78
$Fe(CO)_4PMe_3$ (18)	$HSiPh_3$	hv/RT	$FeH(CO)_3(SiPh_3)PMe_3$	Loss of CO.	100
$Fe(CO)_5$ (18)	$HSiMe_3$	hv/RT	$(OC)_4Fe(H)SiMe_3$	Loss of CO.	5

Table VII. (Continued)

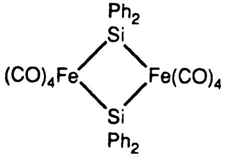
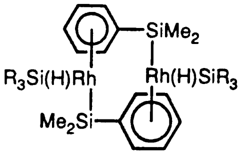
Organometallic (electron count)	*Silane*	*hv or heat*	*Product*	*Comments*	*Reference*
	H_2SiPh_2	hv/RT		Loss of CO.	101
$[Fe(dppe)_2(L)]$ (18) $L = CH_2{=}CH_2$	$HSi(OEt)_3$	RT	$Fe\{Si(OEt)_3\}_2(dppe)_2$	Elimination of H_2, loss of $CH_2{=}CH_2$.	63
$FeH_2(CO)_2(dppe)$ (18)	$HSiR_3$		$FeH_3(CO)(dppe)SiR_3$	Loss of CO.	102
η^4-$C_4H_4Fe(CO)_3$ (18)	$HSiEt_3$	hv/133K	η^4-$C_4H_4FeH(SiEt_3)(CO)_2$	Unstable above ~230K; Loss of CO.	103
Co Triad					
$(\eta^5$-indenyl$)Rh(L)_2^-$ $(CH_2{=}CH_2)$(18)	$HSiMe_2Ph$			Loss of ethylene and displacement of indenyl.	104
$CpRh(CH_2{=}CH_2)_2$ (18)	$HSiEt_3$	hv/RT	$CpRh(H)_2(SiEt_3)_2$		105
$[Rh(COD)Cl]_2$ (16)	$HSiR_3$[a]		[Rh(tripSi)H(Cl)]		106
$Ir(OR)(CO)L_2$[b] (16) $L = P(p\text{-}tol)_3$	$HSiMe_2Ph$		$H_2Ir(CO)(SiMe_2Ph)L_2$	Addition of HSi followed by elimination of ROSi to give $HIrL_2CO$. Addition of 2nd mole of HSi gives product. X-ray structure.	107

Table VII. (Continued)

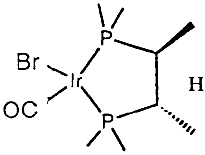
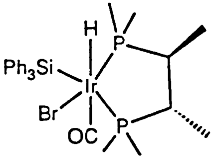
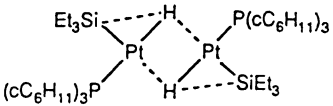
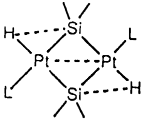
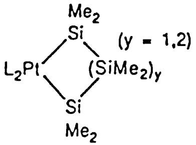
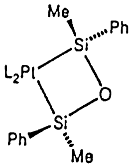
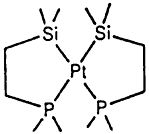
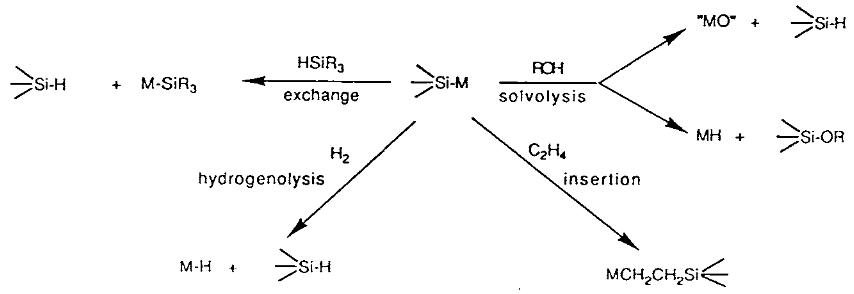
Organometallic (electron count)	*Silane*	*hν or heat*	*Product*	*Comments*	*Reference*
$IrCl(CO)L$ (16) $L = PPh_3$	$HSiR_3$		$R_3SiIrH(Cl)(CO)L_2$	With excess $HSiR_3$, R_3SiCl is eliminated. Addition of the 2nd mole of R_3SiH gives $R_3SiIrH_2(CO)L_2$.	108
$[Ir(OMe)(COD)]_2$ (16)	$HSiEt_3$	RT	$(COD)Ir(SiEt_3)(H)_2L$		24
	$HSiPh_3$			Kinetic product, >99.5% Thermodynamic isomer is trans-H,Br.	109
Ni Triad					
NiL_4 (18) $L = PPh_3$	$HSiPh_3$	60°C	$L_2Ni(SiPh_3)_2$	Elimination of H_2 is required.	110
$Pt(=)_2L$ (16) $L = P(c\text{-}C_6H_{11})_3$	$HSiEt_3$	RT		X-ray structure.	111
$L = PMe(t\text{-}Bu)_2$	H_2SiMe_2			X-ray structure for $L = P(^cC_6H_{11})_3$.	111

Table VII. (Continued)

Organometallic (electron count)	Silane	hv or heat	Product	Comments	Reference
$Pt(=)L_2$ (16) L = PPh_3	$H(SiPh_2)_xH$	35°C		Elimination of H_2.	112
	$HPhMeSi)_2O$	60°C			65a
$[Pt(COD)_2]$ (16)	HMe_2SiR			X-ray structure, elimination of H_2 required.	113
L_2PtCO_3 L = PMe_2Ph	$H_2SiMePh$		cis-$(HSiMePh)_2PtL_2$	Rapid reaction.	114

Symbols: Cp*, C_5Me_5; dppe, $Ph_2PCH_2CH_2PPh_2$; COD, 1,5-cycloctadiene.

a. R = $CH_2CH_2PPh_2$; tripSi = $Si(CH_2CH_2PPh_2)_3$.



Scheme 3.

of hydrosilanes with transition metal derivatives, it is likely that other cases in which the transition metal catalyst precursor forms a stable silyl complex exist.

In order to develop the mechanistic arguments that have been presented in the literature, it is also necessary to provide an overview of the possible reactions of the silicon-transition metal bond that can occur in the medium of the reactants previously described. In most cases dihydrogen is evolved which can cause hydrogenolysis of the Si–TM bond. Also there are coreactants such as olefins and alcohols. The additional reaction processes that may be of importance in developing mechanisms for the dehydrogenative coupling reactions are exchange, hydrogenolysis, insertion, and solvolysis. An outline of these reactions is given in Scheme 3 and specific examples that illustrate the general processes are given in Table VIII.

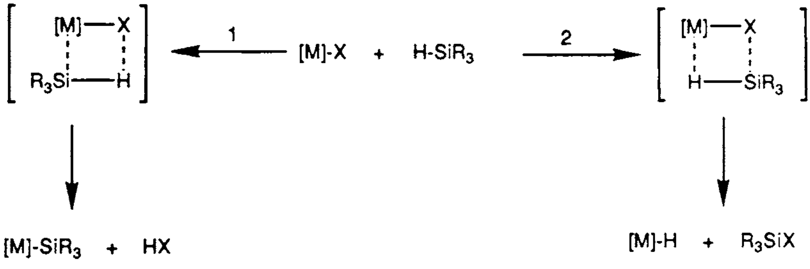
The examples shown in Table VIII are for reactions in which the products have been characterized. The results shown in the table demonstrate the possiblity of the reactions but the entire range of metals has not been studied. Certainly the problem of insertion of an olefin into an M–Si bond has received attention in the last few years since it has relevance to the hydrosilation mechanism. Several examples where the chemistry observed requires some alternative to the Chalk-Harrod mechanism have appeared and include $R_3SiCo(CO)_3$[12b,86] and $Ru_3(CO)_{12}$;[7,9] however, these appear as mechanistic rationales and thus are not included in the table.

Although the previous discussion has focused on the role of oxidative addition of the hydrosilane to the metal center another process that could occur, but has not received much popular support, is the possiblity of a sigma bond metathesis reaction. Such a process would occur via a four-center transition state and is depicted in general fashion in equation 5. Such a process would seem to be most consistent for explaining the observation that $CpCp^*Hf(Cl)[Si(SiMe_3)_3]$ reacts with $PhSiH_3$ to give the $HfSiH_2Ph$ complex and $HSi(SiMe_3)_3$.[124b] As will be seen in the discussion of the mechanisms for SiH/HSi coupling, sigma-bond metathesis may be the most important process for early transition metal catalysts.

Table VIII. Reactions of the Silicon-Transition Metal Bond

Complex	*Reactant*	*Products*	*Reaction type comments*	*Reference*
$Me_3SiMn(CO)_5$	MeOH	$Me_3SiOMe + (CO)_5MnH$	Solvolysis.	117
$(R^*{}_3Si)HMn(CO)_2Cp^+$	MeOH	$R^*{}_3SiOMe$	Solvolysis; inversion at silicon.	118, 95
$R^*{}_3SiCo(CO)_4$	H_2O	$R^*{}_3SiOH$	Solvolysis; inversion at silicon.	119
$R^*{}_3SiFe(CO)_2Cp$	H_2O	$R^*{}_3SiOH$	Solvolysis; retention at silicon.	120
$Me_3SiZr(Cl)Cp_2$	H_2O	$Me_3SiH + [Cp_2ZrCl]_2$	Solvolysis.	121
cis-$Me_3SiPt(H)dppe$	H_2	Me_3SiH + *cis*-$(dppe)PtH_2$	Hydrogenolysis.	122
$[(Me_3Si)_3Si]ZrCp_2(SiMe_3)$	H_2	$HSiMe_3 + HSi(SiMe_3)_3 + [Cp_2ZrH_2]_n$	Hydrogenolysis.	123
$[(Me_3Si)_3Si]ClZrCpCp^*$	H_3SiPh	$HSi(SiMe_3)_3 + CpCp^*Zr(SiH_2Ph)Cl$	Exchange; product complex. Decomposes to give $H\text{-}(PhSiH)_xH$ oligomers.	124b
$[(Me_3Si)_3Si]HfClCpCp^*$	H_3SiPh	$HSi(SiMe_3)_3CpCp^*Hf(SiH_2Ph)Cl$	Exchange; new method for silylhafnium complexes.	124b
$Et_3SiFeH(CO)_3L$	$HSiPh_3$	$HSiEt_3 + Ph_3SiFeH(CO)_3L$	Exchange.	124a
$R_3SiRuH_3(PR'_3)_3$	$HSiR''_3$	$HSiR'_3 + (R'_3P)_3RuH_3(SiR''_3)$	Exchange.	87
$R_3SiCo(CO)_4$	$HSiR'_3$	$HSiR_3 + R'_3SiCo(CO)_4$	Exchange	85a
$(Me_3Si)_3SiZrClCpCp^*$	C_2H_4	$(Me_3Si)_3SiCH_2CH_2ZrCpCp^*Cl$	Requires photochemical activation.	126
$[(Me_3Si)_3Si]ZrCl_2Cp^*$	C_2H_4	$(Me_3Si)_3SiCH_2CH_2ZrCl_2Cp^*$	Insertion; rapid with room light. Also thermal induced. Unreactive to styrene, propene and $Me_3SiCH{=}CH_2$.	
$[(Me_3Si)_3Si]HfCl_2Cp^*$	C_2H_4	$(Me_3Si)_3SiCH_2CH_2HfCl_2Cp^*$	Insertion. Inert to diphenylacetylene and 1-hexene.	126
$Me_3SiFe(CO)_2Cp^*$	C_2H_4	$Me_3SiCH_2CH_2Fe(CO)_2Cp^*$	Insertion; loss of CO followed by coordination of olefin to Fe.	125

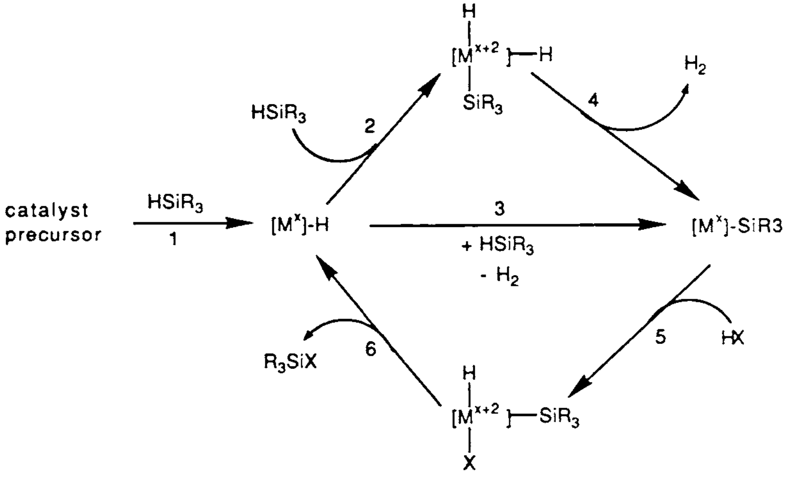
Symbols: R^*_3Si = αNaphPhMeSi; Cp^* = C_5Me_5.



(5)

Reactions that occur stoichiometrically can provide a guide for reconstructing the steps in a catalytic cycle. A simple cycle is shown in Scheme 4. The actual catalyst (step 1, Scheme 4) is probably produced by some reaction between the transition metal complex and the hydrosilane which could be any one of the processes shown in Scheme 2 (or 3) followed by a combination of basic processes such as oxidative addition (steps 2 and 5) reductive elimination (steps 4 and 6). Step 3 could be a σ-bond metathesis reaction. Scheme 4 is intended to illustrate the general features of a catalytic cycle and does not represent any particular reaction. Additional processes that are not shown in the general cycle include insertion into the metal-silicon bond, α- and β-hydride elimination. These processes will be included in the sections where such steps may be necessary to explain the overall chemistry observed.

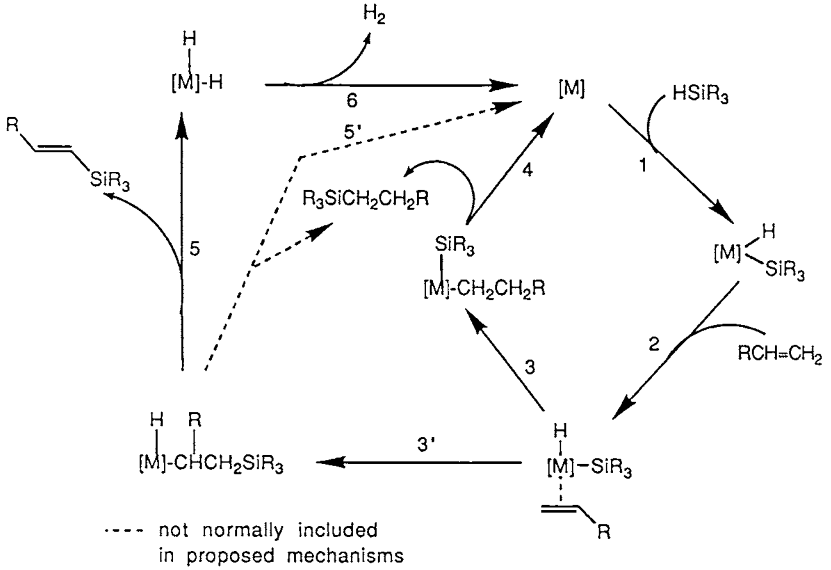
In the next sections, the mechanistic proposals that have been suggested for the dehydrogenative coupling reactions of hydrosilanes will be summarized.



Scheme 4.

6.2. SiH/HC

As summarized in Section 2, hydrosilanes couple with both sp- and sp^2-C centers. A broad range of catalysts has been observed to promote the reaction but to varying degrees. Many of the catalysts that promote SiH/HC coupling are also hydrosilation catalysts. The basic accepted mechanism for d^8 metals is the Chalk-Harrod proposal, which includes the following steps: (1) coordination of the olefin to the metal center (reversible); (2) oxidative addition of the hydrosilane (reversible); (3) olefin insertion into the M–H bond (reversible); and (4) reductive elimination of SiC (irreversible). There is some uncertainty as to whether the olefin coordinates to the metal prior to or after the oxidative addition of the hydrosilane therefore steps 1 and 2 may be reversed. It was believed that the olefin stabilized the lower oxidation state of the metal and therefore the first step in the sequence given above was favored. Scheme 5 illustrates the basic Chalk-Harrod mechanism (steps 1–4) with oxidative addition of the hydrosilane preceding the olefin coordination. The products shown in Scheme 5 are those from β-addition of $HSiR_3$ to the olefin. This is the major product and sometimes the exclusive product of hydrosilation reactions. There were no coupling products of the type $R(R'_3Si)C{=}CH_2$ or *cis*-$RCH{=}CH(SiR'_3)$ unless these are present in the unidentified mixture of isomers produced from the $Fe(CO)_5$ catalyzed reaction of $RCH{=}CH_2$ and R'_3SiH. The reductive elimination shown as step 5′ (Scheme 5) could account for the usual products of hydrosilation, but this sequence (insertion of the coordinated olefin into the M–Si bond followed by reductive elimination) has not received much consideration.



Scheme 5.

The observation of a M(olefin)(H)(SiR_3) containing intermediate, a key species in the catalytic cycle, is rare but does exist in the case of CpRh(CH_2=CH_2)(H)($SiEt_3$).[105] The mechanism illustrated in Scheme 5 has been extended to show a possible (but not required) relationship between hydrosilation and dehydrogenative coupling. The major product from hydrosilation is the β-addition product shown. This requires that a terminal olefin insert into the M–H bond so that C-1 is bound to the metal. Reductive elimination occurs presumably from cis positions on the metal to give the final product of hydrosilation, $RCH_2CH_2SiR_3$. The insertion of the olefin is essentially reversed in hydrosilation as compared to dehydrogenative coupling since the C-2 of the olefin must become bound to the metal in order to account for the observed products. The insertion of olefin into M–H requires coordination of olefin in the position cis to MH followed by a "slip" of the olefin such that the MCCH fragment becomes coplanar. If the same requirement is necessary for insertion into an M–Si bond, then Figure 1 shows a possible relationship between dehydrogenative coupling and hydrosilation. If the rate of the two insertion reactions is similar then the presence of both products could be expected and rationalized.

Insertion into the M–Si bond (step 3′, Scheme 5) would be followed by a β-hydride elimination (step 5) to give the observed silicon-substituted trans olefin. If the coplanarity restriction applies to the elimination reaction, then the formation of the trans product can be rationalized through the rotamers shown in Figure 2. The relative bond strengths of MSi vs. MH may play a role in the relative rates of insertion, but such data are not presently available.

Formation of the cis isomer requires a transition state in which the R group and the silyl substituent are in eclipsed positions (formed from B and C, Figure 2), which is probably higher in energy than that which precedes the formation of the trans olefin (formed from A and B, Figure 2). There is some evidence that substituents on silicon can influence the preference for β-hydride elimination from the H[M]$CHRCH_2SiR'_3$ species. If R′ is an electron-withdrawing group, β-hydride elimination is suppressed even at the higher M/Si ratios that seem to favor dehydrogenative coupling (Rh catalysis).[14] This would be expected if the carbon atom α to silicon (β to the metal) develops a positive charge during the transfer of "hydride" to the metal. It should be emphasized that this proposal is merely a suggestion since the olefin–metal bond rotation shown in Figure 1 can be quite facile and occurrence or preference for insertion into M–Si or M–H may be a result of combinations of factors that may include the specific orbitals on the metal and the electronic effect of substituents at the silicon, metal, or carbon centers (carbon bearing the R substituent). Cationic or radical species could also be involved.

An interesting corollary to the contrast in olefin insertion into M–H vs. M–Si also exists in reaction of carbonyl derivatives with hydrosilanes. The mechanism probably involves coordination of the carbonyl (step 2, Scheme 5) to Si[M]H. In this case insertion into the M–Si bond results in formation of a strong Si–O bond and can tip the balance of the reaction in this direction (L_3RhCl catalysis[115b]).

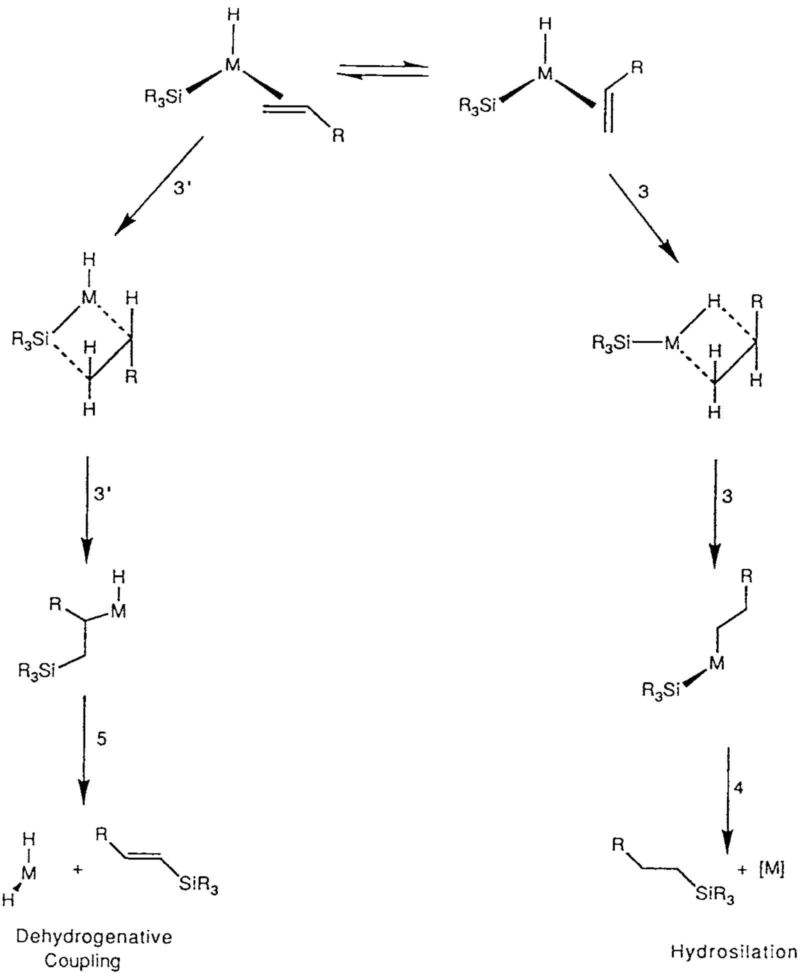


Figure 1.

Also illustrated in Figure 2 is the reverse of insertion into the M–Si bond, β-silyl group elimination. Such a step has been proposed to account for the $Ru_3(CO)_{12}$ catalyzed reaction of $Me_3SiCH{=}CH_2$ and $HSiEt_3$, which provides *trans*-$Me_3SiCH{=}CHSiEt_3$ (product of dehydrogenative coupling) as well as *trans*-$Me_3SiCH{=}CHSiMe_3$ (product of disproportionation).[9b] Formation of the disproportionation product is actually catalytic in hydrosilane although $HSiPh_3$ is a better catalyst than $HSiEt_3$. To account for the product of "disproportionation", step 3 (Scheme 5) produces the intermediate $Ph_3SiRuCH_2CH_2SiMe_3$, which then eliminates $CH_2{=}CH_2$ to give $Me_3Si[Ru]SiPh_3$. Subsequent coordination of

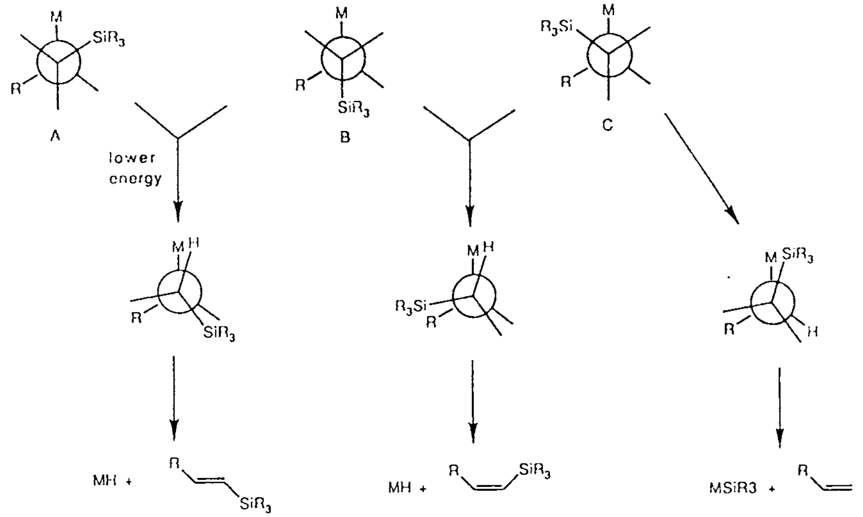


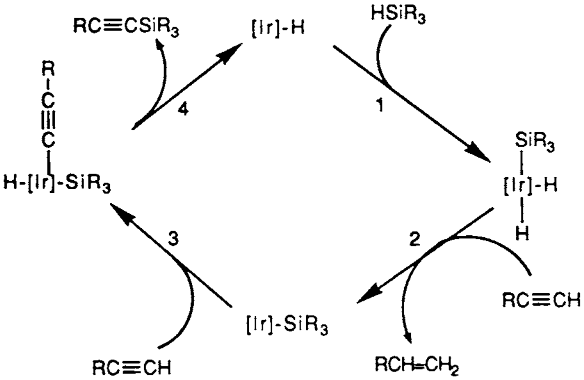
Figure 2.

$Me_3SiCH{=}CH_2$, insertion into the Me_3SiRu bond and β-hydride elimination (equivalent of steps 3′ and 5 of Scheme 5) produces the disproportionation product. The authors claimed that this could be a new method for forming Si–Ru bonds although this has yet to be proved practical.

There are various proposals that elaborate on Scheme 5. Insertion of olefin into both M–H and M–Si to give $RCH_2CH_2MCH_2CH_2Si$, β-hydride elimination from the silyl(alkyl)metal species and reductive elimination of RCH_2CH_3 accounts simultaneously for products of dehydrogenative coupling and hydrogenation of the olefin (Ru and Rh catalysis[9a]). Oxidative addition of the organic substrate to the metal center has also been proposed as illustrated in Scheme 6 starting from a metal hydride species.

The first step in the catalytic cycle in Schemes 5 and 6 is the same, but in the latter cycle the hydrogen is removed by the alkyne (step 2) and a second mole of alkyne oxidatively adds to the Ir–Si species followed by reductive elimination to give the silylated alkyne.[22] A similar proposal has been suggested for the coupling of hydrosilanes to arenes with $ClRh(CO)L_2$. In this case the Rh catalyst is reduced to RhH which is carried through a cycle similar to that in Scheme 6 except that reductive elimination of H_2 from the metal center was proposed to occur prior to the oxidative addition of ArH.[17a]

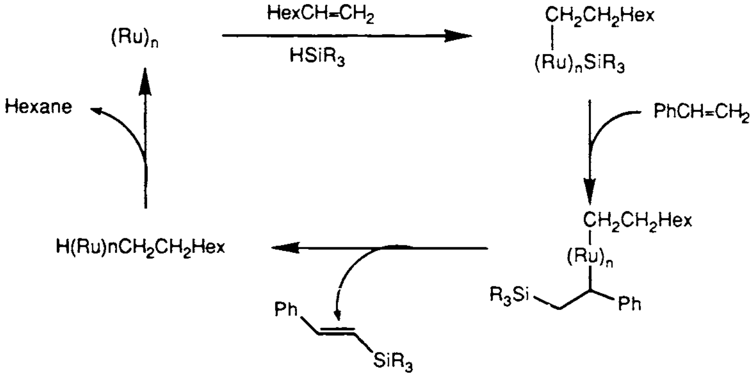
Oxidative addition of the olefin to the intermediate formed in step 2, Scheme 5, has also been proposed although this would result in a rather high oxidation state for the metal (Rh and Ir catalysis)[20]. Metal activation of a C–H bond is a known



Scheme 6.

process (although not common) and occurs more readily for sp^2 than sp^3 carbon centers.

If insertion of an olefin into a metal–silicon bond is the key step in the formation of vinylsilanes, then one way to improve the formation of this product over that of hydrosilation would be to create a catalyst in which the rate of insertion of the olefin into M–Si occurs more rapidly than insertion into M–H. Alternatively, it may be possible to separate the metal centers that contain M–H and M–Si. This may be why the cluster, $Ru_3(CO)_{12}$, is one of the better coupling catalysts and why the tactic of using an inexpensive olefin to promote the coupling of silicon to a desired olefin works as well as it does.[7] Scheme 7 illustrates the mechanism proposed for this approach. In the $(Ru)_n$ system, the lack of a Ru–H bond after addition of



Scheme 7.

olefin/silane may be the explanation for the fact that $Ru_3CO)_{12}$ is a good coupling catalyst but inactive as a hydrosilation catalyst.

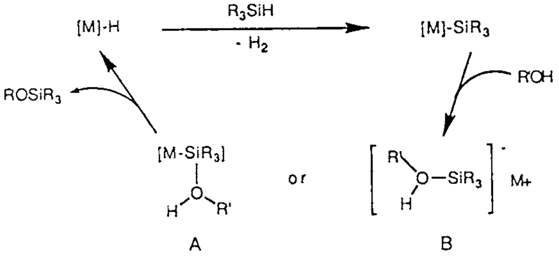
There are certainly examples of dehydrogenative coupling in Table I that may not be explained by this approach, but until studies provide more information for the actual catalytic species the competition for insertion of the organic substrate into M–H vs. M–Si provides about the only operating premise.

6.3. HSi/HO and HSi/HN

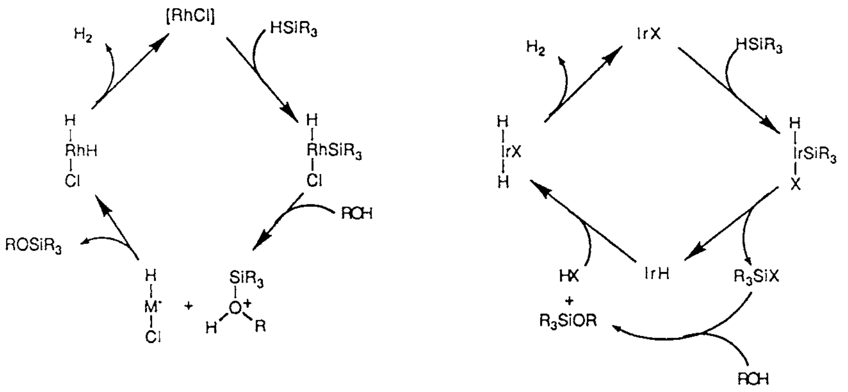
The silicon-transition metal bond is cleaved by alcohols in most cases (the exception(s) occur for the silicon–iron bond). Therefore, any of the processes already described that lead to the formation of a silicon-transition metal bond should provide a system that would be subject to alcoholysis. The earlier mechanistic proposals have been summarized in a recent review.[31] Most proposals for the alcoholysis reaction assume nucleophilic attack by the alcohol at silicon. The differences in detail involve the degree of M–Si separation after attack by the alcohol or the extent of formation of negative charge on the metal fragment. The basic mechanism is outlined in Scheme 8.

Corriu and co-workers argue that if the metal fragment $[M]^-$ is a weak nucleophile, it constitutes a good leaving group and therefore nucleophilic cleavage should occur with predominant inversion at silicon and with high stereoselectivity. If the reverse is true, then the metal fragment is a poorer-leaving group and substitution with retention can occur with loss of stereoselectivity. Consistent with this observation is substitution with inversion at Mn–Si and Co–Si but significant retention with similar reactions of Fe–Si (Table VIII).[115b] The effective electronegativity of the metal fragment, L_nM, can be determined by the ligands. With strong pi-acceptor ligands the fragment can approach the electronegativity of fluoride ion as is the case for $Mn(CO)_5$.[127] It therefore should follow that solvolyis of $(CO)_5MnSiR_3^*$ would provide MnH and SiOMe with retention (57%) which contrasts to that observed for solvolysis of $(Cp^*)(CO)_2Mn(H)SiR_3^*$ which gives R_3^*SiOMe with inversion (74%).

Additional variations have been proposed for metal-halide catalysts as shown for the specific systems L_2RhCl (formed from Wilkinson's catalyst[33]) and L_2IrX



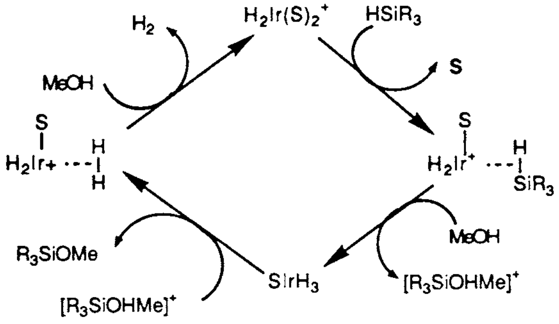
Scheme 8.



Scheme 9.

(formed from $IrX(CO)L_2$, where X = Cl, Br, I, and P = $PMePh_2$, PPh_3 and $AsPh_3$[40]). The rhodium system is similar to that shown in Scheme 8 and the iridium case involves reductive elimination of silyl chloride which is then solvolyzed by the alcohol. These proposals are outlined in Scheme 9.

The preceding mechanisms are based on oxidative addition. A recent study utilizing $[IrH_2S_2(PPh_3)_2]SbF_6$ argues persuasively for an alternative approach which essentially involves adduct formation with an η^2-bound silane[35] (without oxidative addition). The suggestion avoids the necessity of converting Ir(III) to Ir(V). The basic features of the mechanism are shown in Scheme 10. The starting complex, $[IrH_2(THF)_2(PPh_3)_2]SbF_6$, is converted to the methanol adduct, $[IrH_2(MeOH)_2(PPh_3)_2]SbF_6$ $(IrH_2S_2L_2)$,$^+$ which is the starting point for the



S = methanol

Scheme 10.

catalytic cycle. The catalyst is simplified as $H_2IrS_2^+$ (S = MeOH) to show the relationship with the previous cycles.

The major advantage of Scheme 10 is the location of both the alcohol and the hydrosilane in cis positions within the coordination sphere of the metal. This should lead to an intramolecular nucleophilic attack. The reason why secondary alcohols appear to react so rapidly with this catalyst system may be attributed to the first step in the cycle. In this case the secondary alcohol is displaced more readily by the incoming silane. The slow step in the process is believed to be step 3 (reprotonation of the Ir complex, Scheme 10).

The dehydrocoupling of hydrosilanes and amines appears to involve a more complex set of equilibria which depend on the steric requirements of the amine when $Ru_3(CO)_{12}$ is the catalyst.[45b] As R in RNH_2 is changed from *n*-Bu to *s*-Bu to *t*-Bu, the rate dependence of the coupling reaction changes from a nonlinear inverse relationship (R = *n*-Bu) to a positive nonlinear dependence (R = *s*-Bu) to a slight positive linear dependence (R = *t*-Bu). The results certainly support the hypothesis that the steric environment of the amine influences the exact mechanism for the dehydrocoupling. The authors favored three different rate-determining steps in the catalytic cycle. In the cases where an inverse dependence on $[RNH_2]$ is observed, the rate-determining step was believed to be oxidative addition of the hydrosilane to the active catalyst. For the secondary amine a rate-determining step with Si–N formation was favored. The Si–N bond is presumably formed by nucleophilic attack of the amine at the metal-bound silicon center. Thus, features of the alcoholysis shown in Scheme 9 and aminolysis reactions may be similar.

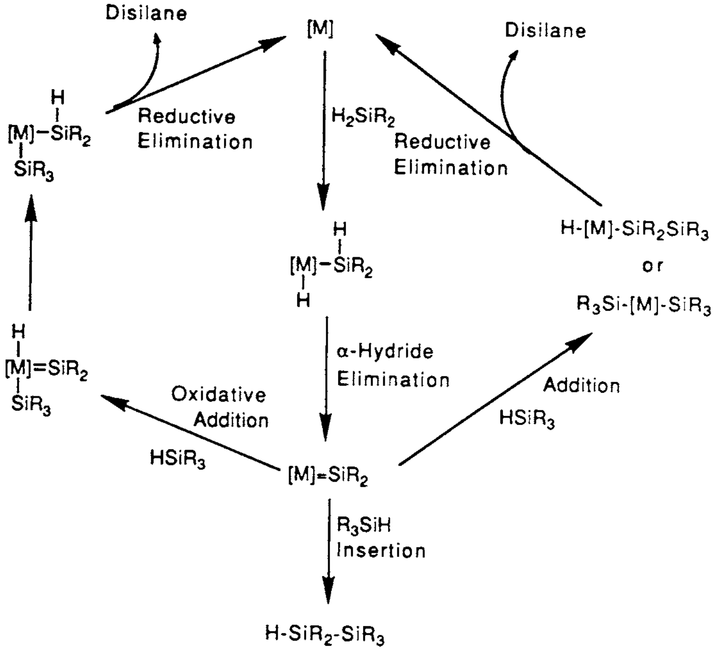
The mechanisms of reactions with other HEl (El = main group element from Groups XV–XVII) have not been proposed.

6.4. SiH/HSi

The coupling of two or more hydrosilanes represents the only alternative to Wurtz coupling for the formation of silicon–silicon bonds. Of all of the dehydrocondensation reactions described in this chapter, this particular coupling provides an important alternative to the only other synthetic route to silicon oligomers/polymers. In all of the other dehyrocondensation reactions, there are several other routes for the specific bond formed (i.e., CSi, SiO, SiN, SiTM). The technological potential of polysilanes provides the impetus behind the effort to understand the role of catalysis for SiH/HSi coupling.

The early ideas in this area all invoked the possibility of a metal silylene as the important catalyst intermediate. The fate of the metal silylene varies as demonstrated for disilane formation in Scheme 11. The basic reactions involve oxidative addition to the metal center (Pt[128]), addition to the multiple bond (Ti[53]), and silylene insertion into SiH (Rh[2]).

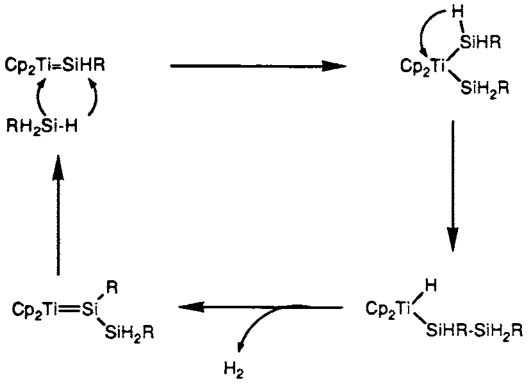
The major problem with the mechanism summarized in Scheme 11 is that metal-silylene complexes are rare. Those that have been reported are all base-coordinated and include $[Cp^*L_2RuSiPh_2.CH_3CN]^+$ BPh_4^-,[116] $(CO)_4Fe=$



Scheme 11.

$Si(OBu^t)_2.B$,[129] $[(CO)_4Fe{=}SiMe_2.B]$,[129] $(CO)_4Fe{=}Si{=}Fe(CO)_4.B$,[129] $(CO)_5Cr{=}Si(OBu^t)_2.B$,[129] and $Cp(CO)[SiMe(OMe)_2]Fe{=}SiMe_2$.[130] At this early stage, there is no reason to expect that base-stabilized metal silylenes and free metal silylenes will exhibit the same reactivity. It is probable, however, that a metal silylene that is not base-coordinated would be more appropriate to test the reaction of intermediates that have been proposed and are represented in Scheme 11.

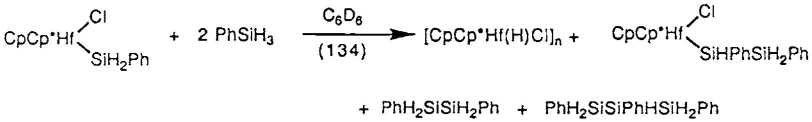
A key feature in the Harrod mechanism for chain growth (illustrated in Scheme 12) is the sequence of α-hydride elimination, addition, rearrangement, α-hydride elimination, etc. Such a process would allow for continued chain growth until reductive elimination removes the chain. The difficulty with the mechanism is that it requires that secondary silanes terminate at the disilane stage. Because it has been shown that secondary silanes can at least get to the trisilane stage with Cp_2MR_2 (M = Ti, Zr), this suggests that either a separate mechanism operates for secondary silanes or that α-hydride elimination is not a key step in the process that leads to oligomers/polymers. Harrod has extended his dehydrogenative coupling studies to germanes.[131] In the presence of Cp_2TiMe_2, diphenylgermane gives tetraphenyldigermane, which apparently dimerizes under certain rection conditions to the tetragermane. The formation of the tetragermane argues against the hypothesis that some form of α-hydride elimination is a required step in the catalytic cycle.[131] An



Scheme 12.

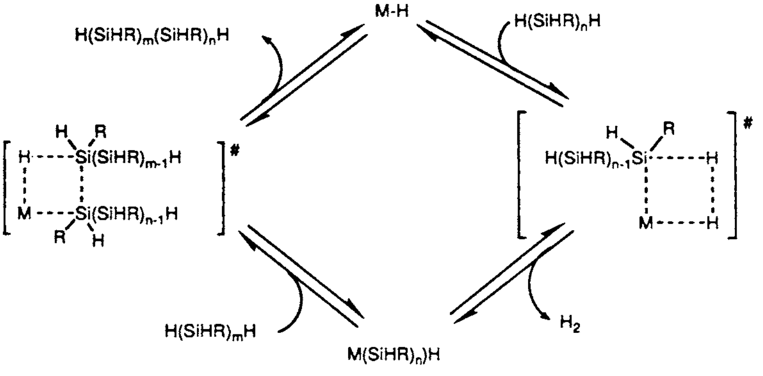
attempt to generate a related zirconium-silylene complex from the elimination of methane from $\mathrm{Cp_2^*Zr(Me)SiHMes_2}$ (the presence of the mesityl groups on silicon would be expected to stabilize the Zr=Si system by analogy to related Si=X systems[132]) gave $\mathrm{Mes_2SiH_2}$ instead.[133]

The most interesting proposal for the oligomerization of primary silanes has evolved from the study of the "slow" catalytic reactions of primary silanes with zirconocene and hafnocene catalysts developed by Tilley and co-workers. The basic catalytic system contains $\mathrm{CpCp^*M[Si(SiMe_3)_3]Cl}$. The presence of the chloro substituent appears to slow the coupling reaction of the primary silane sufficiently to monitor the stepwise process shown in equation 6.[134] After one day (33% conversion), the ratio of the silylhafnium complex to disilane to trisilane was about 3 : 2 : 3.



$$\mathrm{CpCp^*Hf(Cl)(SiH_2Ph)} + 2\,\mathrm{PhSiH_3} \xrightarrow[(134)]{\mathrm{C_6D_6}} [\mathrm{CpCp^*Hf(H)Cl}]_n + \mathrm{CpCp^*Hf(Cl)(SiHPhSiH_2Ph)} + \mathrm{PhH_2SiSiH_2Ph} + \mathrm{PhH_2SiSiPhHSiH_2Ph} \qquad (6)$$

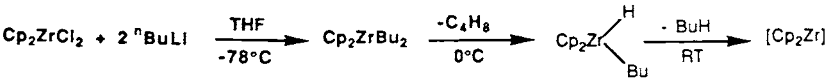
The starting silylhafnium complex shown in equation 6 undergoes thermal decomposition by a second-order process to a hafnium hydride and silicon polymer.[69b] This observation can be explained in terms of the four-centered intermediate shown as the product in step 2 of equation 5 where MX is $\mathrm{HfSiH_2Ph}$ and the reacting silane is now HSi(Hf)PhH.[69b] The alternative, addition of the primary silane to a hafnium-silylene complex (Hf=Si), was eliminated by carrying out the decomposition of $\mathrm{CpCp^*Hf(SiH_2Ph)Cl}$ in the presence of traditional silylene traps such as $\mathrm{HSiEt_3}$. No effect on the rate of decomposition was found with these trapping agents. Finally, when excess $\mathrm{PhSiH_3}$ is present (pseudo-first-



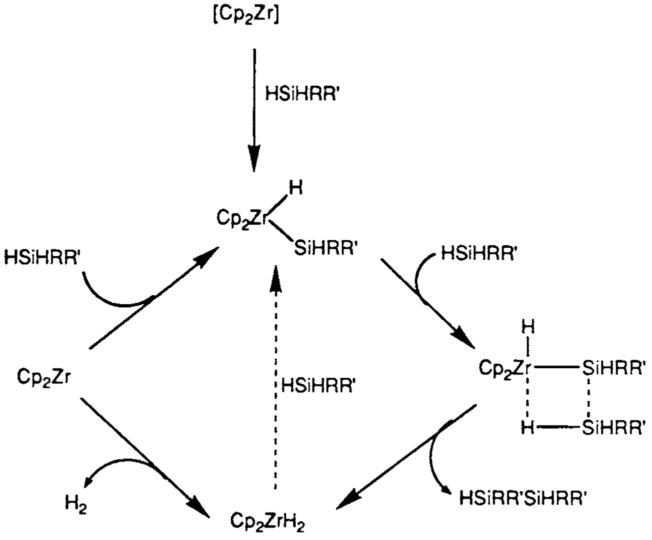
Scheme 13.

order conditions for equation 6) the disappearance of the starting hafnium complex is first-order in both reactants. The results suggest an unusual chain-growth mechanism through a series of sigma-bond metathesis steps as summarized in Scheme 13. This suggestion represents a new polymerization mechanism in that it involves step growth rather than chain growth.[134]

In all of the cases reported thus far for the titanium triad-catalyzed coupling processes a preformed catalyst has been employed. In our studies, we have taken a different approach based on an assumed species which could initiate the catalytic cycle. The presumed species is zirconocene, Cp_2Zr, a 14-electron Zr(II) species which has not been isolated in monomeric form. A species which is presumed to be zironocene is generated from commercially available Cp_2ZrCl_2 and *n*-BuLi. The original report employed tetrahydrofuran as a solvent[70] and the sequence shown in equation 7 was proposed. Formation of Cp_2ZrBu_2 was monitored by NMR spectroscopy. The β-elimination in the next step was favored based on the formation of 1-butene in 80–90% yield. The last step, reductive elimination from the hydroalkyl to give "Cp_2Zr", was inferred from trapping reactions with $PMePh_2$, enynes, dienes, and diynes. In a later report, it was shown that the zirconocene could be trapped by the olefin generated (butene in equation 7) if a phosphine ligand was present.[71] The zirconium derivatives, $Cp_2Zr(H)R$, are not considered thermally stable.[70b]


$$Cp_2ZrCl_2 + 2\,{}^nBuLi \xrightarrow[-78^\circ C]{THF} Cp_2ZrBu_2 \xrightarrow[0^\circ C]{-C_4H_8} Cp_2Zr(H)(Bu) \xrightarrow[RT]{-BuH} [Cp_2Zr] \quad (7)$$

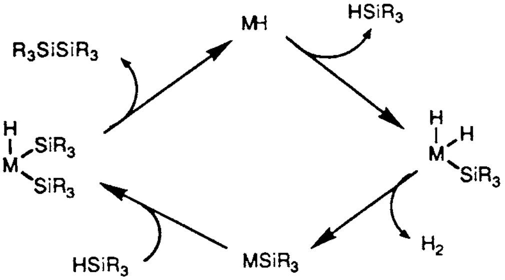
The premise when we began this work was that a zirconocene species would react like a carbene (although it is not isolobal to a carbene) and insert into the Si–H bond to give $Cp_2Zr(H)(SiHRR')$. Our original thought was that the newly formed



Scheme 14.

complex would eliminate dihydrogen to give Zr = Si and enter the catalytic cycle proposed by Harrod shown in Scheme 12. Although we have not yet performed kinetic studies or other experiments to support any particular mechanism, the alternative proposed in Scheme 14 seems more attractive in view of the results summarized in Scheme 13. The advantage of the zirconium catalyst could lie in the presence of the empty orbital present in the Zr(IV) species formed. This could lead to an η^2-interaction of the H–Si bond with zirconium which then provides the necessary configuration for a sigma-bond metathesis such as that proposed by Tilley and co-workers.[134] After the sigma-bond metathesis step Cp_2ZrH_2 would be formed. The dihydride has been reported as an insoluble polymer and thus the reactivity of a monomeric "Cp_2ZrH_2" is unknown. Shown in Scheme 14 are two possibilities including reductive elimination of dihydrogen and the equivalent of a σ-bond metathesis similar to that proposed by Tilley. If Cp_2ZrH_2 is produced, the reductive elimination and/or metathesis reactions would have to occur at a rate faster than or competitive with oliogmerization of the zirconocene dihydride.

It is probable that the mechanisms for the coupling of hydrosilanes from the preformed derivatives of zirconium, Cp_2ZrR_2 (R = Me,Ph), and the combination of Cp_2ZrCl_2 and nBuLi are not the same. However, the evidence for this suggestion comes from the studies of the related catalyst, Cp_2TiR_2 (R = Me, Ph). In the absence of olefins secondary silanes do not couple with Cp_2TiMe_2.[135] In the presence of cyclooctene the conversion of $MePhSiH_2$ to coupled products increases and the trisilane product becomes highly favored.[57] Addition of an appropriate olefin to the combination, Cp_2ZrCl_2/*n*-BuLi could "trap" the intermediate Cp_2Zr



Scheme 15.[141]

species and circumvent the dehydrogenative coupling reaction. Indeed, when cyclooctene and $PhMeSiH_2$ are added in a 1 : 1 ratio to the species generated from Cp_2ZrCl_2/*n*-BuLi, the HSi/HSi coupling reaction is completely suppressed and the products produced are a 1 : 1 ratio of $C_8H_{13}SiHPhMe$ (CH/HSi coupling) and $C_8H_{15}SiHPhMe$ (hydrosilation). When the ratio of cyclooctene to silane is decreased, the major products are those of dehydrogenative coupling of HC/HSi and HSi/HSi.[62]

There are several intriguing aspects of SiH/HSi coupling of secondary silanes that remain unresolved. In the case of coupling of $PhMeSiH_2$ with Cp_2TiPh_2 and $ArAr'SiH_2$ with Cp_2ZrMe_2 or $(PPh_3)_3RhCl$, the major product (or the longest chain) produced under forcing conditions is the trisilane. It is tempting to suggest that this is a result of addition of a hydrosilane to a "disilene" metal complex (or to the limiting structure, the metalladisilacyclopropane) which then terminates the chain growth. At this time there is little support for the equivalent of a disilene coordinated to a metal except in the case of the recently reported Pt systems, $(dppe)Pt[SiR_2SiR_2]$ (R = *i*-Pr)[136] and $Pt_2L_4(SiPhCl)_2$[137]. The related transition-metal silene complexes, M(>Si=C<) have been isolated for Ru,[138] and implicated in the beta-hydride eliminations of $L_4Os(H)SiR_3$[139] and in the NiL_4 catalyzed formation of silenes.[140] The difficulty in trying to determine whether HSi will add across a coordinated disilene arises from the fact that to stabilize the complex rather bulky groups on silicon are most likely required. Bulky groups at silicon would probably preclude the addition of the hydrosilane. On the other hand, simplifying the substituents at silicon will be associated with increased difficulty in determining that a disilene complex has been formed.

The coupling of tertiary silanes cannot occur through a silylene complex and may be too sterically hindered to react through a σ-bond metathesis process. In this case, a series of oxidative addition-reductive elimination reactions may be required as suggested by Curtis and Eptstein[141] as shown in Scheme 15.

The catalysts from the titanium triad hold a peculiar position in the successful catalysis of the coupling of Si–H/Si–H bonds as demonstrated in the recent survey of complexes from Groups IV–VI as reported by Harrod and co-workers.[52] This position may be attributed to the presence of the nonbonding a_1 frontier orbital that is present only in the Group IV metallocenes in the M(IV) state. This orbital is either implicated in the α-hydride elimination step favored by Harrod or leads to an interaction required for the σ-bond metathesis process favored by Tilley. It is tempting to suggest that the requirement for a successful coupling catalyst would be the ability to form a 16-electron metal silyl hydride complex. Can this criterion be met only by early transition metals or can such species be generated, perhaps *in situ* by the late transition metals? The question of how the later and heavier transition metals catalyze the coupling reaction is still unresolved. Are metal-silylene complexes the intermediates or is σ-bond metathesis the operative process? Only future studies will be able to resolve these issues.

7. CONCLUSION

The purpose of this chapter has been to introduce the multifaceted aspects of functionalizing hydrosilanes in the presence of transition metal catalysts. As presented in the Introduction, the condensation reaction of SiH/XEl could be a general synthetic method for the functionalization of silicon centers and provide a complement to the condensation reactions of halosilanes. Certainly it cannot be claimed that such synthetic routes would replace those that have been developed for halosilanes but the availability of such alternatives could be important when the reactions of the chlorosilane are difficult to control or where the by-products are undesirable.

The question of which catalysts will be best for specific transformations will require considerable further understanding of the reactions of hydrosilanes (and other silicon derivatives) with transition metals, particularly the low valent complexes. The discovery of appropriate catalysts hinges on this development. To paraphrase a conclusion of Curtis on the difficulties of C–H activation[74]: If productive Si–H activation is to be specific, a fortuitous combination of rates of formation and decomposition of the metal intermediates must be obtained. Although Curtis was addressing C–H activation the same conclusion could be drawn concerning the activation of Si–H towards all of the coupling processes discussed in this review.

There are other transition metal-catalyzed processes that were not included in this review that could have relevance to SiH/HEl coupling. These include redistribution reactions[23] and the oxygenation of Si–Si bonds that is the plague for heavy metal catalysts. The focus was on the catalyzed coupling of SiH/HEl and coupling of SiH/XEl was essentially ignored. However, it is important to point out that hydrosilanes which normally do not couple with Grignard reagents to form silicon–carbon bonds will do so in the presence of $(PPh_3)_2NiCl_2$.[142]

There is also the nagging question of the relationship between C–H activation and Si–H activation or for that matter the possible relationship between olefin interaction with metal centers and the η^2-bonding interaction of hydrosilanes. Such correlations must be left for another review. Also tantalyzing is the prospect of the equivalent of oxidative addition of other silicon-element bonds to transition metal centers. There is at least one example of the successful addition of halosilanes to zero-valent platinum complexes.[143]

8. ACKNOWLEDGMENT

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