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Activation of the Si–Si Bond by Transition Metal Complexes

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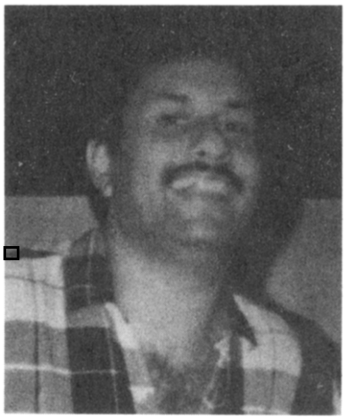
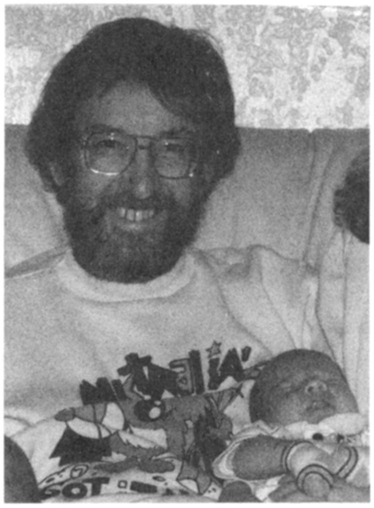


Hemant K. Sharma received his M.Sc. degree in 1977 at Roorkee University, Roorkee, India, and the Ph.D. degree in 1982 in inorganic chemistry from Kurukshetra University, Kurukshetra, India. Then, he joined Panjab University, Chandigarh, India, as a CSIR research associate in Professor S. P. Narula's group from 1982 to 1986. In 1986, he joined the faculty of M. D. University, Rohtak, India, as a Lecturer and worked in organotin chemistry. In 1988, he immigrated to the United States and joined Professor Pannell's group as a research scientist. His research interests have included synthetic and mechanistic transition metal chemistry, photochemistry, molecular rearrangements, and polymers involving group 14 elements.



Keith Pannell grew up in Wimbledon and attended Rutlish School. He took his B.Sc. and M.Sc. degrees from Durham University (University College, "Castle") and his Ph.D. from the University of Toronto. After postdoctoral experiences at the Universities of Georgia and Sussex, he moved to the University of Texas at El Paso. He is a frequent visitor to Mexico, especially the University of Guanajuato. His research interests focus upon the synthesis and study of compounds with intra group 14 element–element bonds, and he is currently enjoying the search for catorcane molecules containing the periodic linkage C–Si–Ge–Sn–Pb.

I. Introduction

The chemistry of transition metal–silicon complexes has become a significant facet of the general chemistry of silicon, and there exist excellent reviews, both ancient and modern, concerning the topic.[1] Another important and in many ways more fundamental feature of silicon chemistry that has attracted researchers is the nature of the Si–Si bond. It is the purpose of this review to bring together these two distinct areas of silicon chemistry. The first reports of a transition metal complex either activating or containing a silicon–silicon bond were in 1965 and

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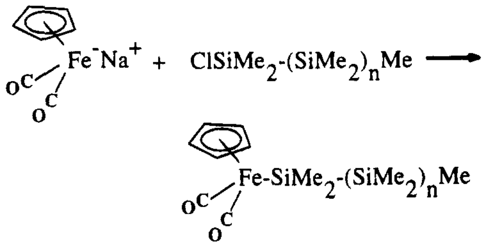
1969, respectively.[2,3] Subsequent to these seminal studies a significant amount of work was scattered in the literature, but it has been in the past 5 years that a dramatic focusing on the area has occurred. In this review we shall emphasize two major aspects of such studies: metal complexes containing a silicon–silicon linkage, either involving a direct metal–silicon bond or via an ancillary ligand, and the use of metal complexes to catalyze chemical transformations of the Si–Si-bond. A review of the stoichiometric reactions between Si–Si-bonded compounds and metal centers is also included since this plays a major initiation role in the catalytic systems.

II. Synthesis and Reactivity of Complexes Containing Si–Si Bonds

A. Complexes with Direct Metal–Si Bonds

1. Acyclic Oligosilyl Complexes with Direct Metal–Si Bonds

Synthesis. The first transition metal complexes containing a silicon–silicon bond were reported in 1969 using a salt elimination reaction,[3] subsequently a popular route to such systems (eq 1).[4–13]



(1)

Manganese and rhenium complexes were obtained in low yields by the high-temperature reaction between silicon hydrides and $M_2(CO)_{10}$ (M = Mn, Re) (eq 2).[5,14]

$$M_2(CO)_{10} + 2\ Me_3SiSiMe_2H \rightarrow 2\ M(CO)_5SiMe_2SiMe_3 + H_2 \quad (2)$$

Since these early studies a series of such complexes has been reported, normally using the salt elimination reaction between oligosilyl halides and the salt of the following transition metal groups: $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$, (M = Cr, Mo, W);[4] $[(\eta^5\text{-}C_9H_7)Fe(CO)_2]^-$;[7] $[(\eta^5\text{-}C_5R_5)M(CO)_2]^-$, (M = Fe, Ru, Os).[8,9,34] Bimetallic complexes have also been reported from the reaction between α,ω-dihalooligosilanes and the corresponding transition metallate salts to produce $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(SiR_2)_n$, (R = H, Me), $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2(SiH_2)_n$, and $[Co(CO)_3(PPh_3)]_2(SiMe_2)_n$.[3,10,40,41,46a]

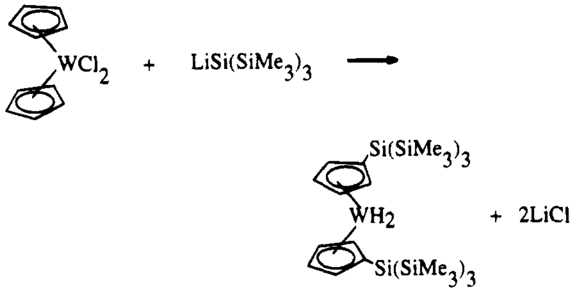
The reaction between Si–Si-bonded compounds and coordinatively unsaturated transition metal centers usually leads to bis(silyl)metal complexes and this specific reaction is discussed in detail below because of its role in metal-catalyzed addition reactions. However, oxidative addition/reductive elimination of the disilanes H_3SiSiH_3 and 1,2-dimethyldisilane to 1,2-bis(dicyclohexylphosphino)ethaneplatinum hydride, P_2PtH_2 (P_2 = dcpe) led to stable isolable disilanyl complexes of platinum, $P_2PtH(SiHRSiH_2R)$.[15] Although related disilanyl complexes had been earlier reported using $(PCy_3)_2Pt$,[16] it is the use of the dcpe chelating ligand that provided entry into stable, and hence readily studied, systems. The pentamethyldisilylplatinum complex $(PEt_3)_2Pt(I)SiMe_2SiMe_3$ was synthesized by the oxidative addition of Me_3SiMe_2SiI to $Pt(PEt_3)_2$.[157]

Related to the linear oligosilane metal complexes described above are a series of tris(trimethylsilyl)silane (*sisyl*) derivatives, $LMSi(SiMe_3)_3$, where LM is a wide range of metal complexes.[5,14,17–26] Such complexes are best prepared by the inverse of the salt elimination noted above using the sisyllithium reagent with a transition metal halide, and several examples are provided in eq 3, although both routes noted above in eqs 1 and 2 are also applicable.

$$[(Me_3Si)_3Si]^-Li^+ + LMX \rightarrow LMSi(SiMe_3)_3 \quad (3)$$

LMX = $Re(CO)_5Br$;[14]
$(\eta^5\text{-}C_5H_5)_2MCl_2$ (M = Zr, Hf);[17,18] Np_3ZrCl;[19]
$dcpePtCl_2$,[24] R_3PAuCl[21]

Such reactions do not always lead to the expected compound. The reaction of 2 equiv of sisyllithium with Np_3TaCl_2 (Np = neopentyl) resulted in the isolation of a stable alkylidene complex, $Np_2Ta(=CHBu^t)Si(SiMe_3)_3$.[19] Furthermore, the reaction of sisyllithium with $(\eta^5\text{-}C_5H_5)_2WCl_2$ led to the substitution of the silicon groups onto the cyclopentadienyl rings (eq 4).[20] The mechanism of this process is not clear, but products containing an oligosilyl group bonded to the cyclopentadienyl ring can be obtained by treatment of the metal cyclopentadienyl complexes containing direct metal–silicon bonds with various bases (*vide infra*).[27,46]



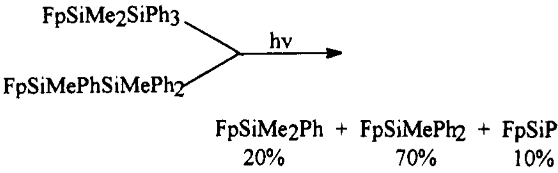
(4)

Reactivity. A significant new reactivity pattern has been observed for the oligosilanes containing a direct Si–transition metal bond. The best developed system is the family of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (Fp) derivatives. The majority of the complexes are low-melting solids that exhibit a reasonable thermal and oxidative stability and may be handled in the air for short periods of time with little apparent degradation. However, they are extremely sensitive to photochemical irradiation and exhibit two primary types of chemical transformation involving silylene expulsion and/or isomerization, illustrated in eqs 5 and 6.[6,12,27–33]

$$\mathrm{Fp{-}SiMe_2SiMe_3 \xrightarrow{h\nu} FpSiMe_3 + [SiMe_2]} \quad (5)$$

$$\mathrm{Fp{-}SiMe_2SiMe_2SiMe_2SiMe_3 \xrightarrow{h\nu} Fp{-}Si(SiMe_3)_3} \quad (6)$$

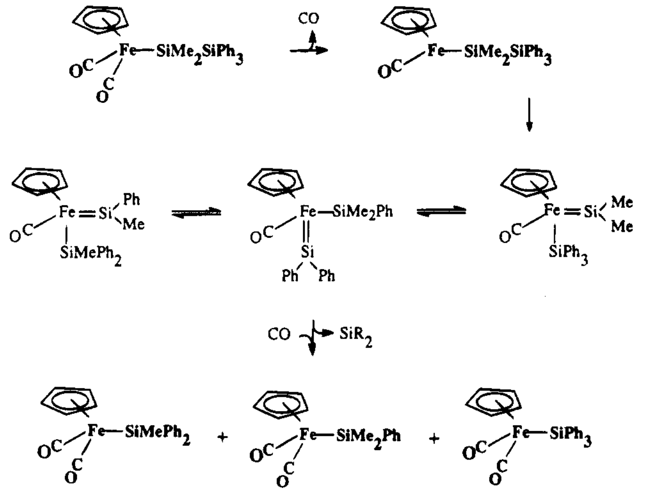
The reactions appear to be quite general regardless of the type of substituents placed upon the silicon atoms. Independent irradiation of various isomers of $\mathrm{FpSi_2Me_nPh_{5-n}}$ yielded the same product mixture of the monosilane complexes, $\mathrm{FpSiMe_nPh_{3-n}}$. This result is illustrated in eq 7 for the isomers $\mathrm{FpSiMe_2SiPh_3}$ and $\mathrm{FpSiMePhSiMePh_2}$ and implied a common intermediate and reaction mechanism.[27,28]



(7)

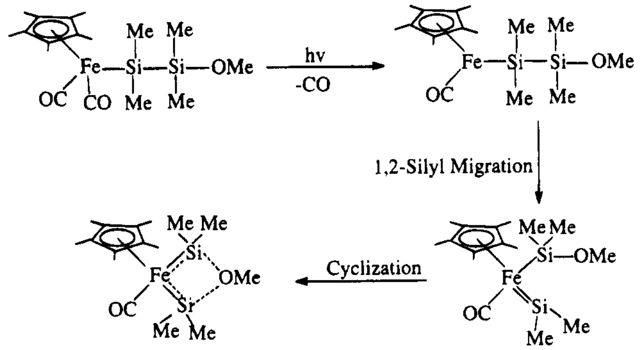
The suggested mechanism for the silylene elimination reactions is outlined in Scheme 1. The mechanism involves the formation of silyl (silylene) intermediates by an α-elimination reaction after initial photochemical elimination of CO from the iron atom. The silyl (silylene) intermediates rapidly equilibrate via a series of 1,3-alkyl and -aryl migrations prior to recoordination of the CO group leading to silylene elimination. The reaction was shown to be intramolecular by suitable labeling experiments.[31,32] Support for this mechanism was provided by the isolation of stabilized bis(silylene) intermediates if one of the substituents on the silicon atoms was a methoxy group, e.g. $[(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Fe(CO)(SiMe_2\cdot\cdot OMe\cdot\cdot SiMe_2)}]$, Scheme 2.[34]

Scheme 1

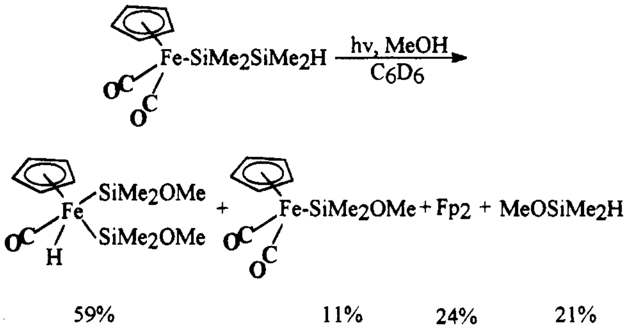


Furthermore, low temperature matrix isolation and laser infrared spectroscopic techniques enabled the intermediate $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)({=}SiMe_2)(SiMe_3)}]$ to be observed directly and also demonstrated that the elimination of $\mathrm{SiMe_2}$ by recoordination of CO was a photochemical, not thermal, event.[35] Phenyl group substituent effects upon product distribution in a series of complexes $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2Si_2Me_4Ar}$ (Ar = $\mathrm{C_6H_4X}$; X = H, *m*-$\mathrm{CF_3}$, *o*-OMe, *p*-OMe, *p*-$\mathrm{NMe_2}$) suggested that in the intermediate silyl (silylene) complexes $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)({=}SiMe_2)(SiMe_2Ar)}]$ and $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)({=}SiMeAr)(SiMe_3)}]$, the electron-donating groups stabilize the intermediate $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)({=}SiMeAr)(SiMe_3)}]$.[29] These results support a highly polarized form of the iron silylene, $\mathrm{Fe{=}Si \leftrightarrow Fe^-{-}Si^+}$, in keeping with the studies on isolated metal silylene complexes.[34,36–39] Related bis(silylene)metal complexes $\mathrm{LM(SiMe_2\cdot\cdot OMe\cdot\cdot SiMe_2)}$ have been isolated for LM = $\mathrm{Mn(CO)_4}$ and $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Ru(PMe_3)}$).[36,37] The latter complex was formed by a thermal reaction between $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Ru(PPh_3)_2Me}]$ and $\mathrm{HMe_2SiSiMe_2OMe}$, and analogous amine stabilized bis(silylene)iron complexes are also established by the same general synthetic procedure.[38] Alkoxy-bridged bis(silylene)iron complexes were found to be unreactive toward conventional silylene traps but with alcohols underwent addition reactions to give hydrido bis(alkoxysilyl)iron complexes, $[(\eta^5\text{-}\mathrm{C_5R_5})\mathrm{FeH(CO)(SiMe_2OR)_2}]$ in quantitative yield.[155]

Scheme 2

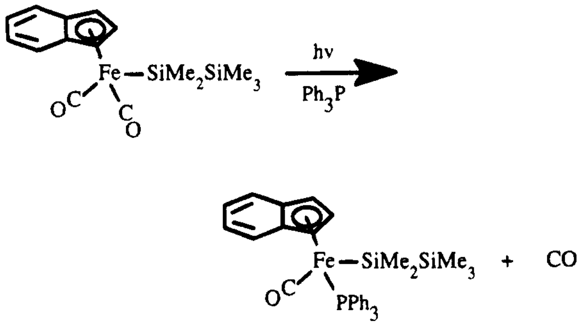


The photolysis of $\mathrm{FpSiMe_2SiMe_2H}$ in methanol produces an interesting mixture of compounds (eq 8).[156] The formation of these compounds suggested that the photolysis of $\mathrm{FpSiMe_2SiMe_2H}$ proceeded through a pathway different from the mechanism suggested in Scheme 1 and involved the transient intermediacy of disileneiron, $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{FeH(CO)(SiMe_2{=}SiMe_2)}]$, and methoxy-bridged bis(silylene)iron, $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)(SiMe_2\cdot\cdot OMe\cdot\cdot SiMe_2)}]$ complexes.



(8)

Related π-indenylirondicarbonyl disilane and trisilane complexes exhibited a slightly different photochemistry. For example, the photochemical reaction between $(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Fe(CO)_2SiMe_2SiMe_3}$ and $\mathrm{PPh_3}$ resulted in simple phosphine substitution with no deoligomerization (eq 9);



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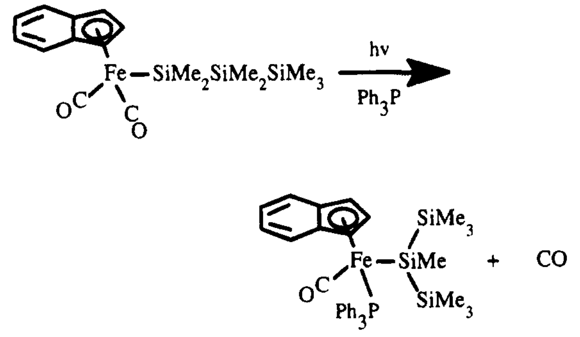
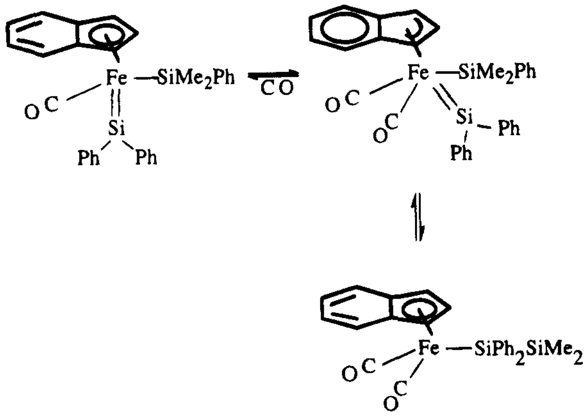


(10)

similar treatment of the related trisilane resulted in isomerization coupled with phosphine substitution, (eq 10).[7]

In neither case was $SiMe_2$ elimination observed; therefore, the results suggested that the π-indenyl ligand profoundly altered the photochemistry of the system. Individual irradiation of the π-indenylirondicarbonyl complexes $(\eta^5\text{-}C_9H_7)Fe(CO)_2Si_2Me_2Ph_3$ isomerized to a mixture of all three isomers prior to SiR_2 eliminations.[152] An η^5 to η^3 ring slippage in the silyl (silylene) intermediate could facilitate CO recoordination, forming a new intermediate that promotes the silyl migration to the silylene, i.e. re-formation of the Si−Si bond, in a manner analogous to the CO insertion reaction[154] (eq 11).

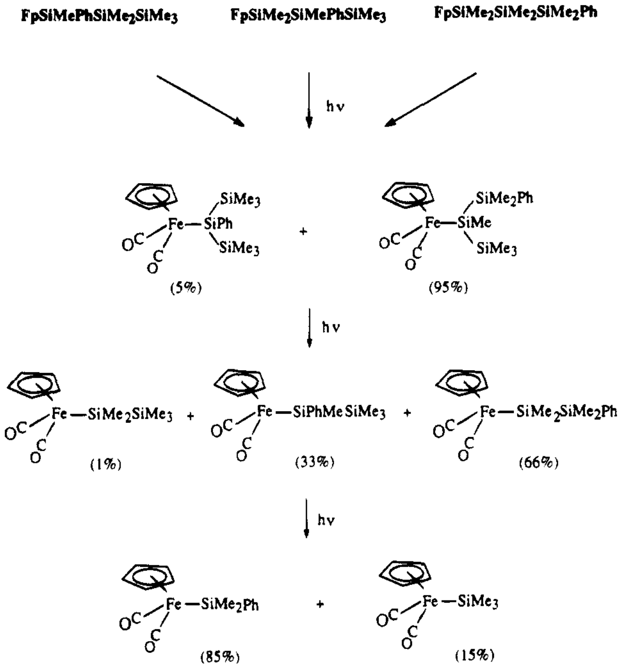


(11)

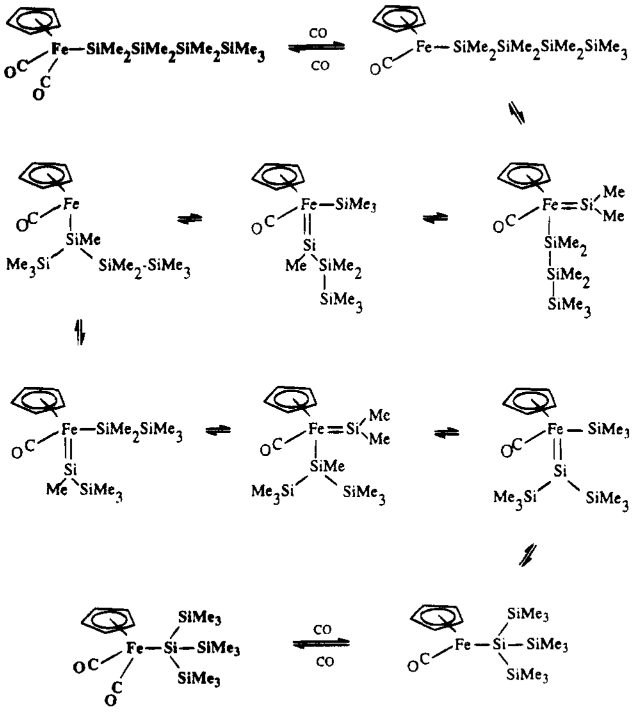
In this manner the recombination of the Si−Si bond can compete with the photochemical silylene expulsion.

Trisilyliron complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}Si_3Me_6R$, $FpSi_3Me_6R$ (R = Me, Ph) are also photochemically labile with respect to silylene elimination; however, prior to SiR_2 loss, isomerization occurs (Scheme 3). Photolysis of the linear Fp trisilyl complexes resulted in the transient formation of intermediate isomeric 2-substituted trisilyl Fp complexes which photodeoligomerized to Fp monosilyl complexes via the intermediacy of Fp disilyl complexes (Scheme 3).[12]

Scheme 3

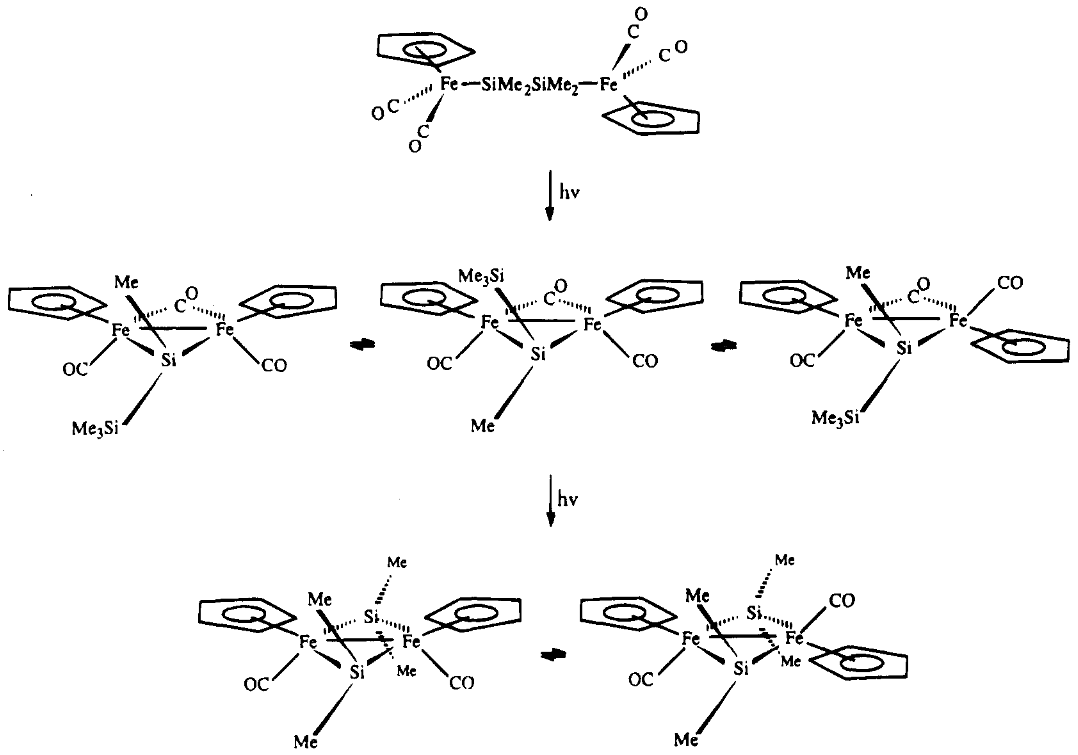


Scheme 4



Linear tetra-, penta-, and hexasilane complexes only exhibit isomerization chemistry with little or no photochemical loss of silylene fragments upon photolysis.[33] The mechanism for the isomerization reaction also proceeds via equilibrating silyl (silylene) intermediates (Scheme 4), involving both methyl and silyl migrations. It appears that silylene iron intermediates with silicon substituents are significantly

Scheme 5



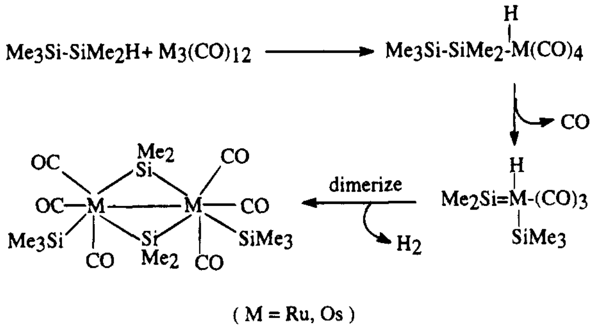
resistive to photochemical substitution, unlike their alkyl analogs.

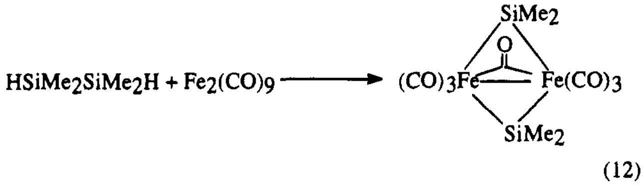
Not all oligosilane metal complexes exhibit the chemistry noted above. For example, the Ru analogs (η^5-C_5H_5)Ru(CO)$_2$–Si$_n$Me$_{2n+1}$ are both thermally and photochemically stable, primarily due to the very low quantum yield for initial CO photoejection.[8] Without the formation of the 16-electron coordinatively unsaturated intermediate, no chemistry occurs, indicating that the photochemistry is not direct oligosilane photochemistry. Indeed, complexes in which the oligosilane is coordinated to the Fe atom in Fp complexes via the cyclopentadienyl ring, [η^5-Me$_3$Si-(SiMe$_2$)$_n$(C$_5$H$_4$)Fe(CO)$_2$R (R = Me), n = 1–5, exhibit no significant photochemistry under the conditions identical to those used in eqs 5–7.[27,46a] The irradiation conditions used, medium-pressure mercury lamp and pyrex glassware, were shown not to sustain normal oligosilane photochemistry.

The bimetallic complexes Fp–(SiMe$_2$)$_n$–Fp also exhibit interesting photochemistry that involves silyl (silylene) intermediates. Via equilibrating bridged-silyl (silylene) intermediates, [(η^5-C$_5$H$_5$)Fe(CO)]$_2$(μ-CO)(μ-SiMe(SiMe$_3$)), the photochemistry resulted in the formation of bimetallic bis-μ-silylene complexes [(η^5-C$_5$H$_5$)Fe(CO)]$_2$(μ-SiMe$_2$)$_2$ that are mixtures of equilibrating *cis* and *trans* isomers (Scheme 5).[40–42]

The ready formation of the silyl (silylene) intermediates probably also explains earlier observations from the reactions between disilanes and metal carbonyl complexes. The thermal or photochemical reaction between pentamethyldisilane and metal carbonyls, M$_3$(CO)$_{12}$ (M = Ru, Os), resulted in the formation of low yields of silylene-bridged metal dimers, [Me$_3$SiM(CO)$_3$]$_2$(μ-SiMe$_2$)$_2$, probably via dimerization of silyl (silylene) intermediates (Scheme 6).[43] Similar bridging silylene complexes were obtained from the reactions of 1,2-tetramethyldisilane and Fe$_2$(CO)$_9$ and Co$_2$(CO)$_8$ (eqs 12 and 13) via related intermediates.[44]

Scheme 6





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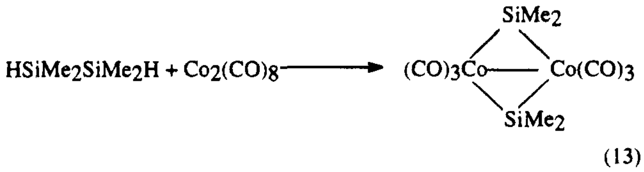
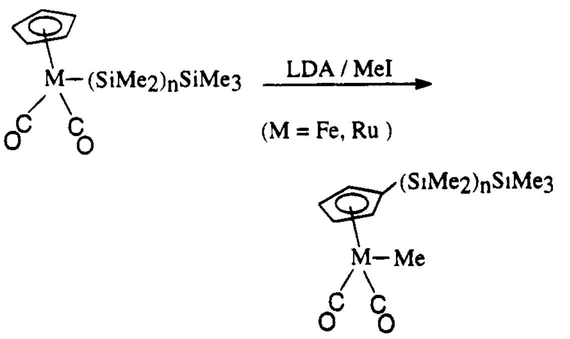


(13)

Oligosilyl complexes of Fe and Ru, (η^5-C$_5$H$_5$)M(CO)$_2$–(SiMe$_2$)$_n$SiMe$_3$, undergo migration of the intact oligosilyl group from the metal to the cyclopentadienyl ring upon treatment with base, lithium diisopropylamide (LDA) (eq 14).[8,27,46]

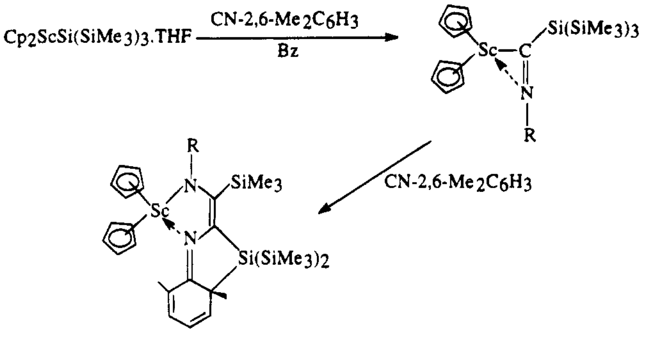


(14)

As noted above, these migration products do not exhibit any photochemistry under the conditions used to study their metal−silicon-bonded precursors.

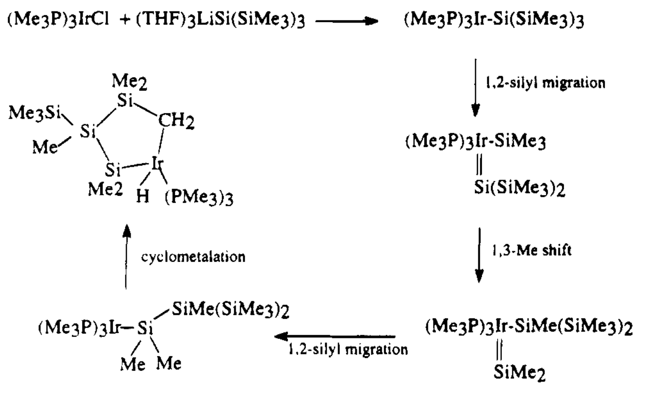
The reactivity of the tris(silyl)silane−transition metal complexes $(Me_3Si)_3Si-ML$ is significantly less dramatic than that of the linear oligosilane complexes; indeed, such bulky, and generally unreactive ligands, are used primarily to stabilize unusual transition metal−silicon bonds. For example, sisyllithium has been effectively used to stabilize the reactive intermediate, lithium silylcuprate, $[Li(thf)_4Cu_5Cl_4\{Si(SiMe_3)_3\}]$.[23] The metal−silicon bond in early transition metal−silicon derivatives is reactive toward insertion of a variety of unsaturated molecules such as carbon monoxide, isocyanides, nitriles, and alkenes.[1f,17] The Sc−Si bond in $Cp_2ScSi(SiMe_3)_3{\cdot}THF$ reacts with $CN\text{-}2,6\text{-}Me_2C_6H_3$ (CNR) to form an η^2-iminosilaacyl complex $Cp_2Sc[\eta^2\text{-}CN(R)Si(SiMe_3)_3]$. This isolable intermediate further reacts with CNR to form a trimethylsilyl group migration product (Scheme 7).[22]

Scheme 7



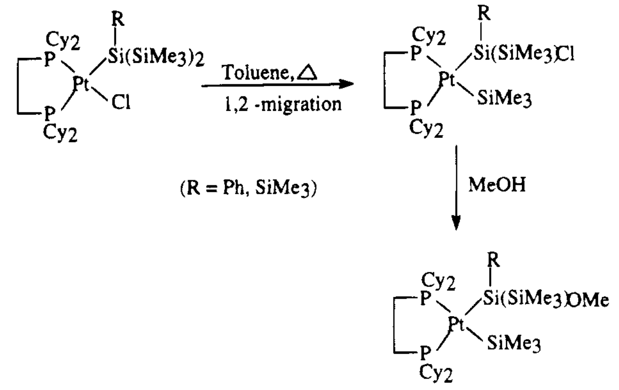
Recently the Tilley group reported the synthesis of an Ir heterocyclic complex involving an interesting rearrangement reaction outlined in Scheme 8.[161] The process involves the partial reversal of the process outlined in Scheme 4, again involving equilibrating silyl (silylene) intermediates. It is clear that the position of equilibrium in these isomerizations will be metal and metal/ligand dependent.

Scheme 8



Related migration chemistry occurs in the case of a bis(silyl)silane platinum complex (Scheme 9);[24]

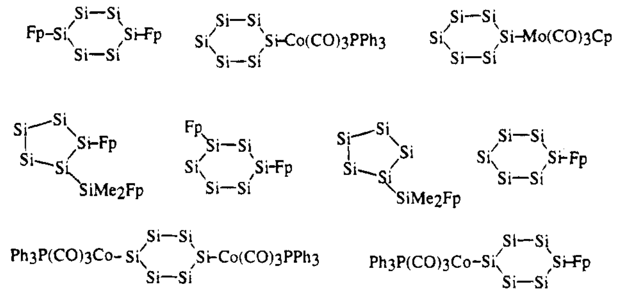
Scheme 9



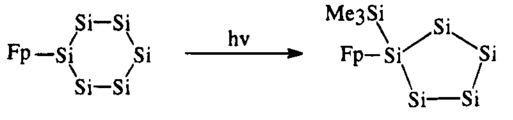
however, beyond these examples the bulky bis- and tris(silyl)silane ligands have not yielded significant silicon-based chemistry.

2. Cyclic Oligosilyl Complexes Containing Direct Metal−Si Bonds

Transition metal-substituted cyclic permethylated-oligosilanes are reported to be formed via salt elimination reactions, and typical examples are illustrated below.[33,47,48]



These complexes are thermally stable crystalline solids; however, they are as photochemically active as their linear analogs. For example, photochemical treatment of the Fp−cyclohexasilyl complex resulted in a skeletal redistribution to form the ring-contracted cyclopentasilyl Fp complex (eq 15).[33]

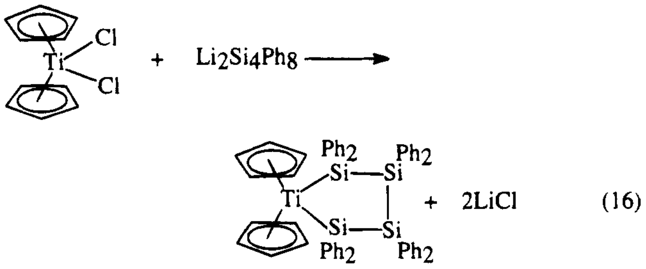


(15)

(Methyl groups are omitted for clarity)

Photochemical treatment of the unsubstituted cyclohexasilane results in Me_2Si elimination and ring contraction to cyclopentasilane and subsequently to cyclotetrasilane; thus, the metal substituent significantly alters the chemistry of the cyclic molecules.[49] The transformation outlined in eq 15 is analogous to $AlCl_3/FeCl_3$-induced ring contractions of cyclic polysilanes,[50] and the mechanism of this transformation involving an α-elimination and a series of 1,3-silyl shifts is essentially the same as the isomerization reaction denoted in Scheme 4 *(vide supra)*.

Heterocyclic metallo-oligosilanes, LM(SiPh$_2$)$_n$ (M = Ti, Pt), are reported (eq 16)



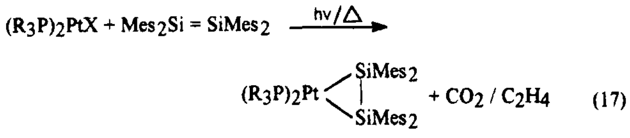
(16)

and are readily reduced by sodium to give relatively stable anion radicals.[51–54]

3. Transition Metal Disilene Complexes

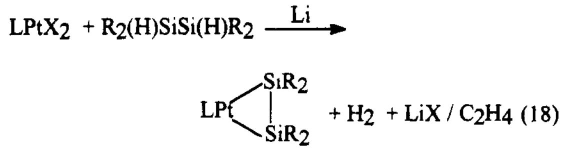
The synthesis and characterization of disilenes (Si═Si) (and their silene cousins (Si═C)) has been one of the major accomplishments of recent organosilicon chemistry.[55,56] Given the well-established ability of π systems to coordinate to transition metals, it is not surprising that a significant chemistry of disilene–metal systems has recently developed.

Pham and West reported that η^2-disilene complexes of platinum were formed by direct reaction of the stable disilene Mes$_2$Si═SiMes$_2$ (Mes = mesityl) with diphosphine platinum(0) olefin or diphosphine Pt(II) oxalato complexes (eq 17).[57] However, a more general alternative chemistry involving 1,2-dihydrodisilane precursors was also established as an efficient route for complexes of the disilenes that are not normally isolable (eq 18).[57]



(17)

(R = Et, Ph; X = C$_2$H$_4$, C$_2$O$_4$)

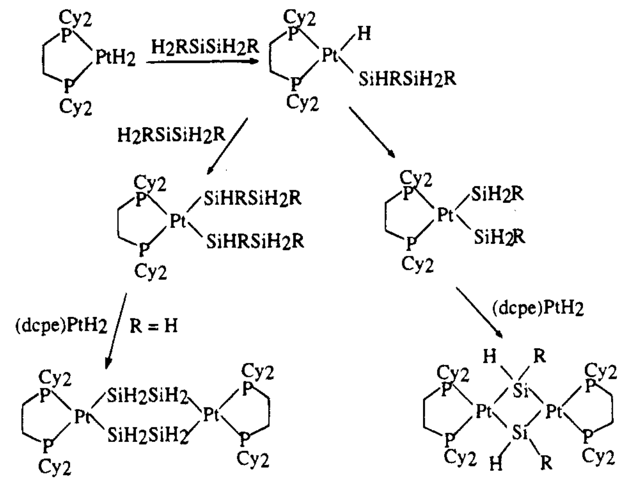


(18)

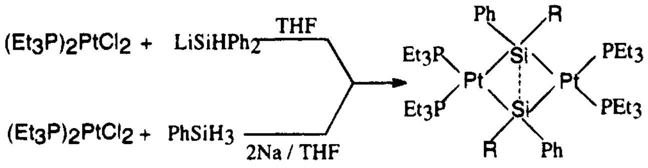
(L = dcpe, dppe; X$_2$ = C$_2$H$_4$, Cl; R = Me, *i*-Pr, Ph)

In related chemistry, disilene-type complexes have been synthesized from the oxidative addition/reductive elimination of monosilanes with various phosphinoplatinum complexes. The disilanylplatinum complexes described earlier, P$_2$Pt(H)SiHRSiH$_2$R (P$_2$ = dcpe), exhibit two secondary reactions, formation of bis(disilyl) complexes P$_2$Pt(SiHRSiH$_2$R)$_2$ by further reaction with a disilane or reaction with P$_2$PtH$_2$ to form bimetallic metallocycles containing the Pt$_2$Si$_2$ ring (Scheme 10).[15]

Scheme 10



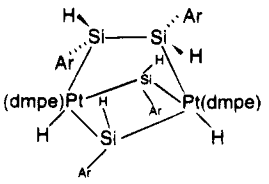
The exact nature of these bimetallic platinum complexes is open to interpretation. Formally they seem to be analogs of many previously known bimetallic bis(μ-silylene) complexes, e.g. LM(μ-SiR$_2$)$_n$ML, LM = Co(CO)$_3$, [(η^5-C$_5$H$_5$)Fe(CO)].[41,43,44,58] The distinction rests upon the degree of Si••Si and LM••ML interaction that exists. No structural data were reported for the [dcpePtSiH$_2$]$_2$ complexes; however, there are several other binuclear platinum–silicon complexes (also obtained from dehydrogenative coupling of silanes with Pt phosphine complexes) that do appear to have considerable disilene character (eq 19).[59]



(R = H, Cl) (19)

Whereas previously known bis(μ-silylene) bimetallics possess Si••Si interactions between 3.8 and 4.2 Å, the crystal structures of the platinum complexes above reveal short cross-ring Si–Si separations (2.272–2.602 Å), suggesting coordination of a disilene by two metal centers.[59] Bimetallic complexes of the type [(dmpe)Pt(SiH$_2$Ar)$_2$]$_2$(μ-dmpe) (Ar = Ph, *p*-Tol) containing the chelating phosphine Me$_2$PCH$_2$CH$_2$PMe$_2$ (dmpe) thermally transform to (dmpe)HPt(η-SiHAr)$_2$[(μ-η^1,η^1-ArHSiSiHAr]Pt(H)(dmpe) (Figure 1), which possesses an η^1,η^1-disilene ligand and two bridging silylene ligands. The molecular structure (Figure 1) shows the disilene bridges the two Pt atoms, causing a 10° puckering of the PtSiPtSi ring.[60]

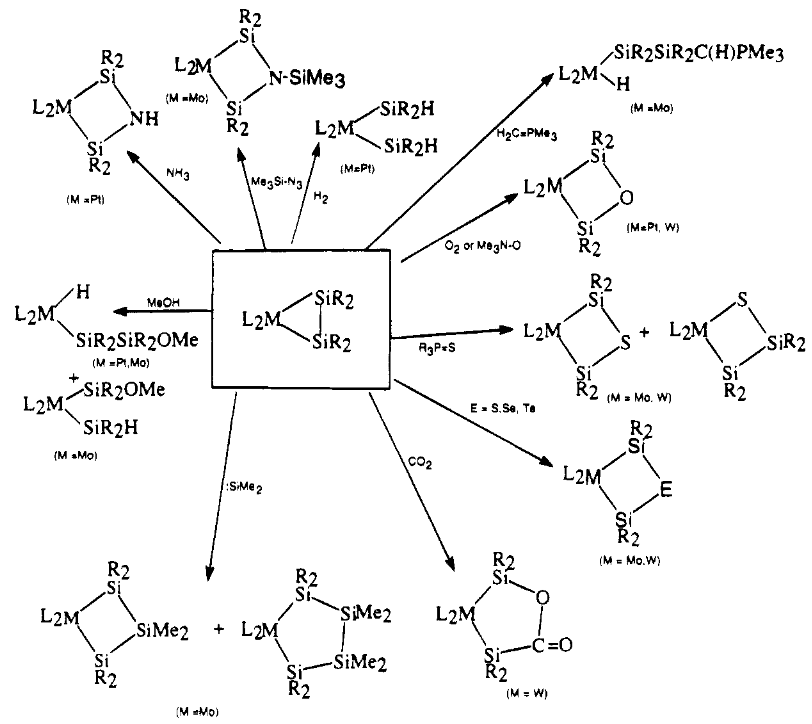
The cross-ring Si–Si distance of 2.882 Å is significantly longer than that found in the platinum complexes noted above but short enough to warrant the claim of significant interaction and, hence, formulation as a silene complex. The complexes undergo a



(Ar = Ph, *p*-Tol)

Figure 1.

Scheme 11

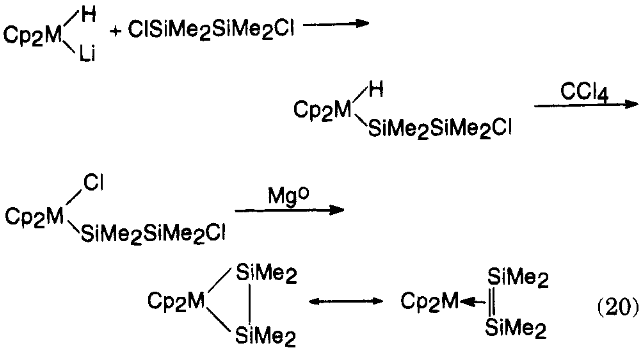


(L2= (Et3P)2, dppe, Cp2; R = Mes, i-Pr, Me)

reversible reaction with $PhSiH_3$ to form Pt(IV) silyl complexes, $(dmpe)Pt(H)(SiH_2Ph)_3$, along with the elimination of disilane. A related rhodium complex, $Rh_2(\mu\text{-}SiRH)_2H_2(CO)_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane), has also been reported, with a Si··Si interaction distance of 2.75 Å, supporting the idea of significant silene character.[61] Theoretical calculations have suggested that in the bis(silylene–disilene) range of complexes the Si–Si distance is dependent upon the nature of the transition metal and, not surprisingly, when Mn and Pt are compared, it is the latter metal that favors disilene complexes.[62]

The significance of these short-range Si··Si interactions **formed at the metal centers from monosilanes** and the disilene vs bis(silylene) dichotomy is the role such systems play in the dehydrogenative coupling catalysis. Since the initial observation by the Harrod group that group 4 metal complexes could oligomerize monosilanes, $RSiH_3$, to materials with molecular weights in the 10^3 range, there has been a significant effort by several groups to use metal complexes to form true high molecular weight polysilanes. The area is the subject of several reviews.[63,64]

Disilene molybdenum and tungsten complexes have been synthesized by a reductive-coupling method involving prior formation of a tungsten disilane complex via a salt elimination reaction (eq 20).[13] The molecular structure of the tetramethyldisilene tungsten complex has been determined[13] and shows a Si–Si bond distance of 2.260 Å, a value that falls in the middle of the range expected for a single (2.35 Å) and a double bond (2.14 Å), suggesting a degree of multiple bonding persists in the complex. Such a result is in keeping with the trends observed for a large number of alkene and alkyne metal complexes, where a significant double- or triple-bond character remains upon coordination. Another measure of the disilene character is the extent of pyramidalization at the silicon atoms. The sum of the angles at each silicon atom was determined to be 348.3°, between the extremes of 360° and 329° expected for sp^2 and sp^3 hybridization, respectively.



(20)

(M = Mo, W)

As might be expected, the η^2-disilene complexes of Pt, Mo, and W exhibit a rich and varied reaction chemistry. They react with both nucleophilic and electrophilic reagents under relatively mild conditions. The principal reactions involve insertions into the Si–Si or M–Si bond. There does not appear to be a great distinction between the reactivity of the two metal systems, i.e. Pt vs Mo (W), and a general Scheme for the reactivity is presented in Scheme 11.[57,65–67]

The reactions with elemental chalcogens, E = O, S, Se, or Te, yielded products resulting from insertions into the Si–Si bond to form principally metallocyclic products. The reactivity of the disilene complexes decreased in the order O > S > Se > Te.

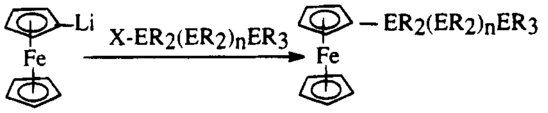
Thus, the reaction with oxygen is instantaneous at room temperature, whereas that with Se and Te requires several hours of heating. The reaction with chalcogen transfer agents, e.g. $R_3P{=}S$, yields both the symmetrical and unsymmetrical products obtained by cleavage of the Si–Si and M–Si bond, respectively. The ratio of the two products is dependent upon the size of the R group; bulky R groups prevent the formation of unsymmetrical product. The nucleophilic attack by methylene trimethylphosphorane on $Cp_2Mo(\eta^2\text{-}SiMe_2{=}SiMe_2)$ leads to the opening of the $MoSi_2$ ring, resulting in the formation of η-bonded disilylylide. The reactions with trimethylsilyl azide, CO_2, dimethylsilylene, and trimethylamine oxide all result in simple insertions into the Si–Si bond.[65,66]

B. Complexes without Direct Metal–Si Bonds

The occurrence of transition metal complexes in which the oligosilane group is bonded to the metal center via another ligand appears to be limited to oligosilylcyclopentadienyl and oligosilylmethyl systems; both exhibit some unique chemical properties.

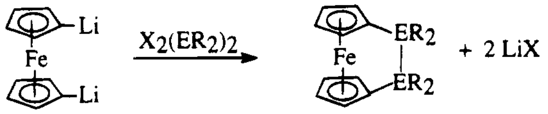
1. Metallocenedisilanes and Oligosilanes

Kumada and co-workers synthesized an array of ferrocenyl, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, and ferrocenylene, $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$, derivatives containing Si–Si, Si–Ge, or Ge–Ge bonds by treating chloro- or alkoxysilanes/germanes with lithiated ferrocene (eqs 21a, 21b).[2,68]



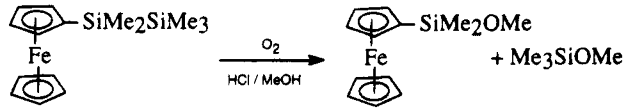
(21a)

(E =Si , Ge, R = Me, Et, Fc, X = Cl or alkoxy)

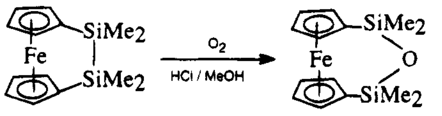


(21b)

These ferrocene derivatives, both the ferrocenyl and ferrocenophane systems, undergo oxidative alcoholysis in the presence of oxygen and traces of an acid or ferric chloride (eqs 22a, 22b).[69,70]



(22a)



(22b)

Ferrocenium ions were postulated as intermediates since via a strong electron-withdrawing effect they could facilitate the nucleophilic attack by alcohol on the highly polarized Si–Si bond. A similar oxidative methanolysis was observed recently for the bimetallic FcSiMe$_2$SiMe$_2$Fc under photolytic conditions and in the presence of ferric chloride.[40]

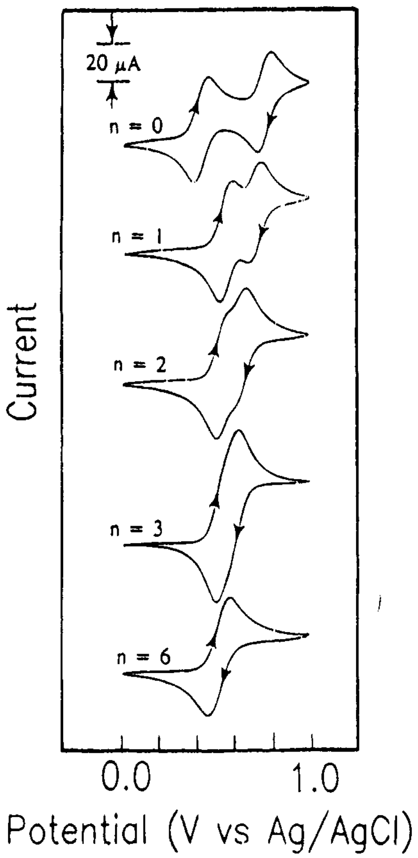


Figure 2.

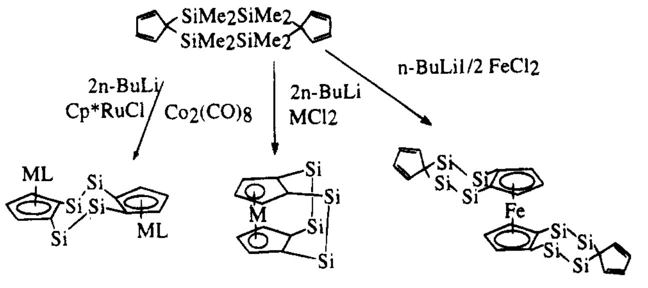
A series of bimetallic α,ω-diferrocenyloligosilanes, Fc–$(SiMe_2)_n$–Fc, $n = 1–6$, have been synthesized from ferrocenyllithium and the corresponding α,ω-dichlorooligosilanes.[68,71] Cyclic voltammetric electrochemical analysis illustrated that with small values of $n = 0–3$ initial oxidation of one Fc unit resulted in an increase in the potential needed for oxidation of the other unit; hence, two distinct redox events could be observed. For the longer chain complexes, $n = 4–6$, only a single redox process was observed, (Figure 2). With a single C atom bridge, i.e. Fc–CH_2–Fc, a single redox process has been observed,[72] whereas with bridging alkene and alkyne groups two processes have been observed.[73] Therefore, these data indicate that transmission of Coulombic effects is efficient through a short silicon chain. The observations reinforce many studies suggesting that a single Si atom has properties similar to the π-system of an alkene. A similar transmission of electronic effects has been noted in bimetallic paramagnetic Cr and V complexes bridged by disilanes (*vide infra*).[74]

[n]-Ferrocenophanes containing an oligosilane bridge are readily synthesized via the use of dilithioferrocene and the appropriate α,ω-dichlorooligosilane.[68,71,76,80,82] Single-crystal X-ray structural analyses revealed that [1]-silylferrocenophanes possess a strained cyclopentadienyl ring tilted structure (dihedral angle of approximately 20°).[75,76,79c] The corresponding tilt angle for the [2]-tetramethyldisilylferrocenophane, $(\eta^5\text{-}C_5H_4)_2Fe(SiMe_2)_2$, was found to be only 4.3°.[71,76] This latter tilt angle is only slightly greater than that present in (η^5-SiMe$_3$SiMe$_2$C$_5$H$_4$)$_2$Fe, in which the bridge between Cp rings is absent.[77] Any potential strain in the [2]-ferrocenophane disilane is relieved by Si–Si, and Si–C, bond elongation rather than by significant angular distortion. The Si–Si bond in the [2]-ferrocenophane disilane is longer than that in the nonbridged (η^5-SiMe$_3$SiMe$_2$C$_5$H$_4$)$_2$Fe, 2.351 *vs* 2.34 Å, respectively.[71,77] The result of the ring strain difference is reflected in the thermal stability of the systems. Whereas strained [1]-silylferrocenophanes, (η^5-C$_5$H$_4$)$_2$Fe(SiR$_2$), undergo facile thermal ring-opening polymerization to yield high molecular weight polyferrocenylenesilanes,[76,78,79] the oligosilane-bridged complexes, (η^5-C$_5$H$_4$)$_2$Fe(SiR$_2$)$_n$, do not.[71,76] The [2]-disilylruthenocenophane, with a dihedral angle of 7.8°, does not exhibit thermal ring-opening polymerization.[80]

A cyclic voltammetric study of the electrochemical properties of mono-, di-, and trisilyl-bridged ferrocenophanes showed a marked dependency upon the oligosilyl bridge size. Monosilyl-bridged complexes undergo irreversible decomposition upon oxidation, while the disilyl-bridged complex exhibited partial reversibility and the trisilane-bridged ferrocenophane showed completely reversible oxidation process.[71] This trend reflects the capacity of the three bridges, Si, Si$_2$, and Si$_3$, to incorporate the increase in Fe–cyclopentadienyl ring distance that is established to occur upon oxidation to ferrocenium ions.[81]

Jutzi and co-workers have obtained an entertaining series of bis(disilyl)-bridged metallocene complexes from 1,2-bis(cyclopentadienyltetramethyldisilane) (Scheme 12).[82]

Scheme 12

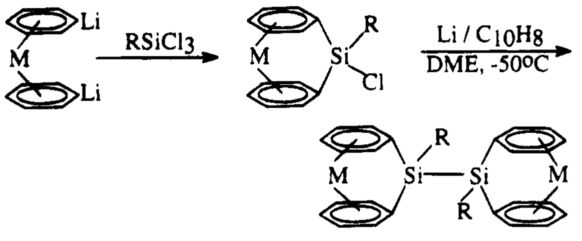


(M = Ru or Co; M= Fe or Ru, L = Cp* or (CO)2)

(Methyl groups are omitted for clarity)

The structures of both [2],[2]-bis(disilyl)ferrocenophane and ruthenocenophane(η^5-C$_5$H$_3$)$_2$M(SiMe$_2$SiMe$_2$)$_2$ (M = Fe, Ru) have been determined by single-crystal X-ray diffraction.[80,82] The tilt angles between the planes of the cyclopentadienyl rings are 7.2° (Fe) and 12.9° (Ru), both significantly greater than the tilt angle of analogous mono(disilyl) analogs, 4.3° (Fe) and 7.2° (Ru). The Si–Si bond distances in the complexes are similar, 2.365(4) Å (Fe) and 2.363(1) Å (Ru), and are longer than that for the typical permethylated metallocene complexes, e.g. 2.351 Å for FcSiMe$_2$SiMe$_2$Fc.[71] The [2],[2]- bis(disilyl)ruthenocenophane was found to be resistant to thermal polymerization.[80]

Bimetallic *ansa*-metallocene disilane complexes of V and Cr have been synthesized by reductive coupling of the respective [1]-silylmetallocenophanes (M = V, R = Ph, *n*-propylphenyl; M = Cr, R = Ph) (eq 23).[74] The structure of the V complex was determined by X-ray diffraction.[74] The molecule assumes an antiperiplanar configuration with nearly parallel bis(arene) vanadium units of similar geometry. The Si–Si bond distance is 2.362 Å, and the V–V separation is 7.60 Å. The EPR properties of the complexes suggest a weak magnetic exchange between the metals mediated through the Si–Si bridge. Such exchange via the silicon bridge is in accord with electrochemical studies on α,ω-diferrocenyloligosilanes noted above.[71]



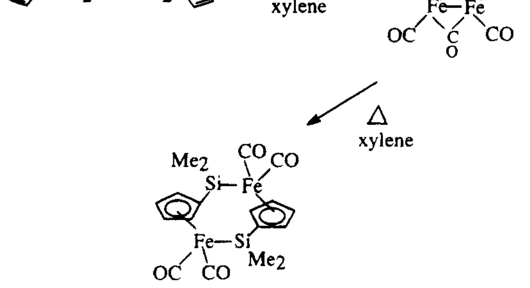
(23)

(M = V, Cr; R = Ph, 4-*n*-propyl-Ph)

Several miscellaneous oligosilylcyclopentadienyl metal complexes have been reported and often characterized using X-ray techniques.[83,84] They do not exhibit any unusual chemistry related to the Si–Si bond. Typical of this group are various di- and trisilyl-bridged complexes of the type [(η^5-C$_5$H$_4$)$_2$E]MCl$_2$ (M = Ti, Zr, Hf, E = (Me$_2$Si)$_2$, (Me$_2$Si)$_3$), and some of their reaction chemistry at the transition metal center has been studied and shown to be typical of such systems. The disilyl bridged complex of Zr and the trisilyl-bridged complex of Ti have been characterized by X-ray diffraction.[83] The structure of the iron complex, [(η^5-Me$_3$SiMe$_2$SiC$_5$H$_4$)Fe(CO)$_2$]$_2$, has been determined, and it was used to generate the anion, [(η^5-Me$_3$SiMe$_2$SiC$_5$H$_4$)Fe(CO)$_2$]$^-$Na$^+$, which was further used to synthesize a variety of derivatives.[84]

The thermal reaction between Fe(CO)$_5$ and 1,2-bis(cyclopentadienyl)tetramethyldisilane provides a ring-bridged bis(cyclopentadienyl)tetracarbonyldiiron complex in which two Cp rings are linked by a disilyl group. The complex isomerizes thermally via cleavage of Si–Si and Fe–Fe bonds to form a symmetrical cyclic complex containing two Fe–Si bonds (Scheme 13). The mechanism of this complex rearrangement is not reported.[85]

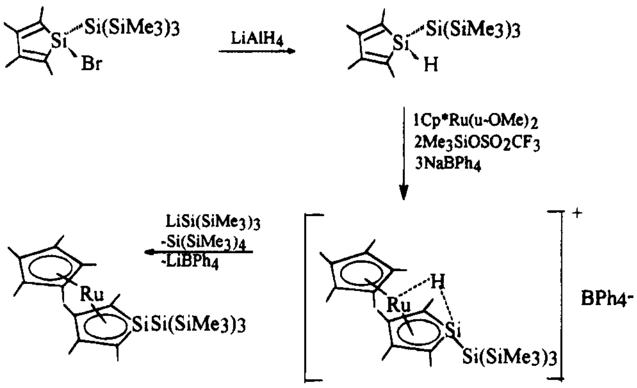
Scheme 13



2. $(Me_3Si)_3Si$–Silacyclopentadiene Complexes

The first stable and isolable η^5-silacyclopentadienyl transition metal complex was recently synthesized by taking advantage of the $Si(SiMe_3)_3$ group as a substituent on the ring silicon atom (Scheme 14).[86]

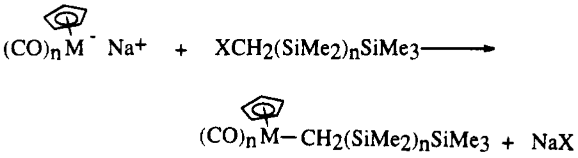
Scheme 14



The structure of the salt, $\{Cp^*Ru(H)[\eta^5\text{-}Me_4C_4SiSi(SiMe_3)_3]\}[BPh_4]$, determined by X-ray analysis showed the cation to be a protonated ruthenocene and the five-membered ring, C_4Si, to be planar with the sum of the angles at the ring Si being 355.1°, indicating sp^2 hybridization. An agostic Si··H··Ru arrangement, $J_{Si-H} = 41$ Hz, was observed. The ^{13}C NMR chemical shifts data for the η^5-silacyclopentadienyl ruthenocene at 73.1, 88.5 (Me_4C_4Si), and 86.0 (C_5Me_5) show aromaticity in both rings and are similar to those reported for the related η^5-germacyclopentadienyl complex, $(\eta^5\text{-}C_5Me_5)Ru[\eta^5\text{-}Me_4C_4GeSi(SiMe_3)_3]$.[87]

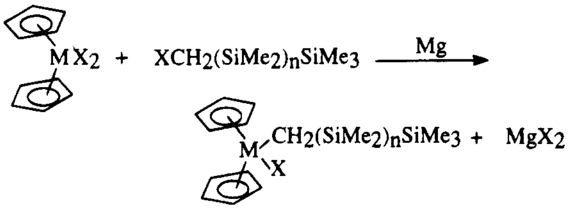
3. Oligosilylmethyl Complexes, $LM-CH_2(SiMe_2)_nSiMe_3$

Using salt elimination reactions a series of oligosilylmethyl–transition metal complexes have been synthesized (eqs 24 and 25).[6,88–91] The spectroscopic properties of the complexes are in accord with their structural assignments and typical of metal–carbon-bonded complexes, as is their thermal chemistry. However, the CO-containing complexes derived from the chemistry in eq 24 possess interesting new photochemistry involving isomerization to metal–silicon-bonded complexes (eq 26).[88–90] The proposed mechanism for this rearrangement involving a β-elimination and formation of silene intermediates is outlined in Scheme 15.



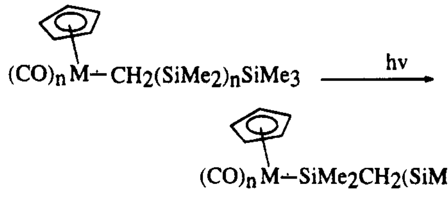
(24)

(M = Fe, Ru, W)



(25)

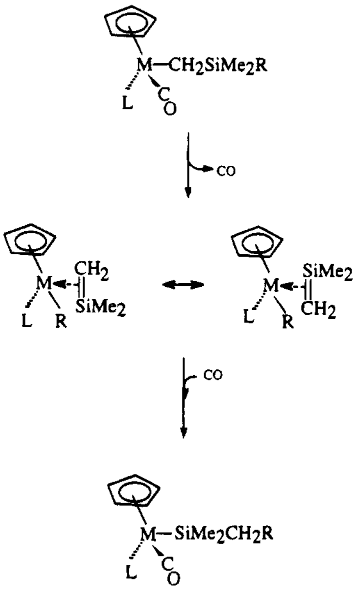
(M = Ti, Zr)



(26)

(M = Fe, W)

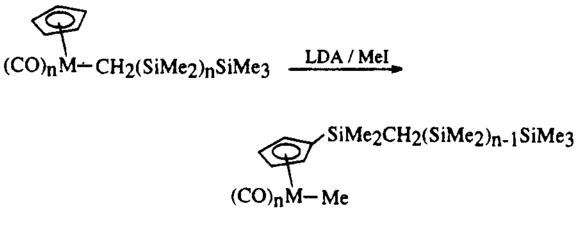
Scheme 15



Similar chemistry was observed with a germylsilylmethyl tungsten complex $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2GeMe_2SiMe_3$, which rearranged to $(\eta^5\text{-}C_5H_5)W(CO)_3GeMe_2CH_2SiMe_3$. The isomeric $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2SiMe_2GeMe_3$ underwent a direct β-elimination reaction to form $(\eta^5\text{-}C_5H_5)W(CO)_3GeMe_3$ and $Me_2Si{=}CH_2$, and the liberated silene was readily trapped.[91] Metal–silene complexes have been isolated and characterized by single-crystal X-ray crystallography.[92]

The group 4 metal complexes $(\eta^5\text{-}C_5H_5)_2M(Cl)CH_2SiMe_2SiMe_3$ (M = Ti, Zr) do not exhibit the same rearrangement chemistry, and when subjected to the same photochemical conditions noted in Scheme 15, they underwent a M–C bond cleavage that resulted in the formation of $Me_3SiSiMe_3$, probably via a free radical process.[89]

Treatment of oligosilylmethyl complexes of iron and tungsten, $(\eta^5\text{-}C_5H_5)M(CO)_nCH_2(SiMe_2)_nSiMe_3$, with n-BuLi or lithium diisopropylamide (LDA) led to ring metalation and, on quenching the reaction with MeI, resulted in the migration coupled with rearrangment of the oligosilylmethyl group (eq 27).[88,89]

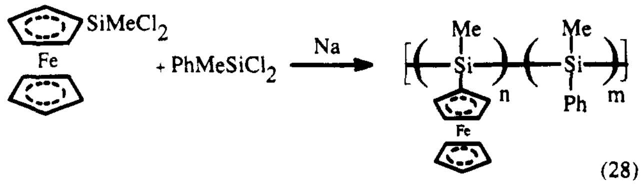


(27)

(M = Fe, W)

4. Polysilanes Containing Transition Metal Complexes

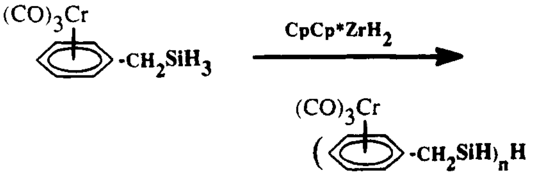
High molecular weight ferrocenyl-substituted polysilanes were synthesized, as copolymers, via the Wurtz-type coupling reaction outlined in eq 28.[93,94]



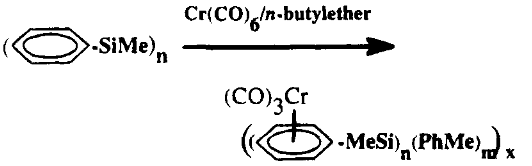
(28)

The copolymers exhibited the characteristic photochemical depolymerization noted for polysilanes, a source of their potential as photoresist materials. However, the presence of the Fc substituents resulted in a significant retardation of this depolymerization, presumably due to the ability of ferrocene to quench the triplet states responsible for the polysilane photochemistry.[94] The ferrocenyl(methyl)silane-co-phenyl(methyl)silane polymers are electroactive and exhibit reversible redox properties in the same potential range as ferrocene and polyvinylferrocene, 0.45–0.50 V.[95] There was no evidence for electronic interactions between the Fc units (which would be separated by an oligosilyl group) or between the pendant Fc group and the polysilane chain segments. The low molecular weight poly(dodecamethyl-1,6-hexasilyl)-1,1′-ferrocenediyl polymer, $\{\eta^5\text{-}C_5H_4)_2Fe(SiMe_2)_6\}_n$, obtained via the condensation of 1,1′-dilithioferrocene with $Cl(SiMe_2)_6Cl$ exhibited significant conductivity on doping with I_2 and $SbCl_5$.[96]

Polysilanes containing $Cr(CO)_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ groups are also reported. Incorporation of the metal was both at the monomer stage prior to polymerization and by reaction of the polymers with the metal systems (eqs 29 and 30).[30,97,98]



(29)



(30)

Only low molecular weight oligomers were obtained from the dehydrogenative coupling reaction (eq 29), $M_n = 1091$ ($M_w/M_n = 1.2$),[97] whereas with the second approach (eq 30), high molecular weight materials were obtained, but with only 10–20% incorporation of $Cr(CO)_3$ groups onto the aryl rings.[98] Tungsten and molybdenum analogs have also been reported and used as preceramic materials.[99–101] Pyrolysis to 1200 °C of a W-containing polysilane [WPS, formed from the photochemical treatment of $(PhMeSi)_n$ and $W(CO)_6$] produced a ceramic material that contained α-SiC and β-SiC and unidentified phases (eq 31).[101] Thermal treatment of a preceramic tungsten–polysilane prepared from $(CH_3CN)_3W(CO)_3$ led to β-SiC and the tungsten silicides W_5Si_2 and WSi_2 (eq 32).[100]

$$(PhSiMe)_n + W(CO)_6 \rightarrow WPS \xrightarrow{\Delta} \alpha\text{-SiC}(26\%) + \beta\text{-SiC}(50\%) + ?(20\%) \quad (31)$$

$$(PhSiMe)_n + (CH_3CN)_3W(CO)_3 \rightarrow WPS \xrightarrow{\Delta} \beta\text{-SiC}(50\%) + WSi_2(30\%) + W_5Si_2 \quad (32)$$

The exact nature of the polymers was not detailed, and the metal content varied from 2 to 20%. A range of other metal-substituted materials was reported including Cr, Hf, Mo, Nb, Ta, Ti, V, W, Y, and Zr.[99–101]

C. ^{29}Si NMR and Crystal Structural Properties of Metal-Substituted Oligosilanes

A detailed discussion of these aspects is outside the main thrust of the present review; however, sufficent data exist to permit a brief general overview to be presented.

^{29}Si NMR is a useful tool both for structural analysis of metal-substituted oligosilanes and for following their chemical transformations. Inspection of selected data presented in Table 1 permits some generalizations to be offered. The data are for pentamethyldisilane and octamethyltrisilane derivatives of five metal systems: $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2$- (Fp*), $(\eta^5\text{-}C_9H_7)Fe(CO)_2$-, $(\eta^5\text{-}C_5H_5)Ru(CO)_2$-, and $Re(CO)_5$-. By far the greatest set of data exists for the Fp, Fp*, and indenyl analogs, and the trends noted are quite general in these systems. Comparison of the ^{29}Si NMR chemical shifts of the Si atoms in the individual complexes to their permethylated analogs, i.e. Me_6Si_2 and Me_8Si_3, shows that the silicon attached to the metal center, Si_α, exhibits a significant low field shift of $\Delta\delta = 35–45$ ppm. The shift noted for the Si_β atom is approximately 8 ppm, while that of the Si_γ atom is 1 ppm. The differing nature of the η^5-ligand is significant only for the Si_α atom. Inspection of the data for the second-row transition metal derivatives illustrates a similar trend; however, the magnitude of $\Delta\delta$ for the Si_α atom is markedly reduced to 20 ppm, while for the third-row elements an **upfield** shift ($\approx$20 ppm) is noted. In the latter examples the Si_β and Si_γ atoms still exhibit downfield shifts similar to those noted for the Fe complexes, and indeed such atoms also exhibit the same $\Delta\delta$ values regardless of the nature of the α atom, e.g. for $Fp\text{–}CH_2\text{–}SiMe_2SiMe_3$ the $\Delta\delta$ values are 11 and 1.0 ppm, respectively.[7–9,27,46,88–90,102,146]

The extent of the shifts noted for a specific oligosilane is dependent upon the isomer structure. This is typified by the data from the family of Fp complexes for which a change of the Si_α from primary to secondary to tertiary progressively decreases the magnitude of the shift: Fp**SiMe**$_2$–Si ($\Delta\delta = 40$ ppm), Fp**SiMe**($SiMe_3$)–Si ($\Delta\delta = 25$ ppm), Fp**Si**($SiMe_3)_2$–Si ($\Delta\delta = 5$ ppm).

In general, a typical permethylated Si–Si bond length is 2.35 Å. From the Fp, Fp*, and (η^5-indenyl)-Fe family of oligosilyl complexes,[7,11,47,145,146] the structural parameters of the Si–Si bond adjacent to the Fe-Si bond chain exhibit a small elongation to 2.36–2.39 Å, (Table 2). The effect seems to be cumulative

Table 1. ^{29}Si NMR Data for Permethylated Metal Oligosilanes and [δLM−(Si)$_n$ − δMe−(Si)$_n$] ($\Delta\delta$) in Parts per Million, C_6D_6

$LMSi_n$	Si_α	Si_β	Si_γ	Si_δ	$\Delta\delta$:Si_α, Si_β, Si_γ, Si_δ	ref
$LM\text{-}Si_\alpha Me_2Si_\beta Me_3$						
Fp*	14.2	−12.5			*33.9, 7.2*	146
Fp	16.9	11.3			*36.6, 8.4*	102
$(\eta^5\text{-}C_9H_7)Fe(CO)_2$	25.1	−11.9			*44.8, 7.8*	7
$(\eta^5\text{-}C_5H_5)Ru(CO)_2$	2.5	−12.2			*22.2, 7.5*	8
$(\eta^5\text{-}C_5H_5)Os(CO)_2$^{a}	−34.3	−13.9			*−14.7, 5.8*	9
$Re(CO)_5$	−43.9	−9.9			*−24.2, 9.8*	8
$LM\text{-}Si_\alpha Me_2Si_\beta Me_2Si_\gamma Me_3$						
Fp*	19.0	−37.9	−14.7		*35.1, 10.7, 1.4*	146
Fp	21.2	−36.5	−15.1		*37.4, 12.1, 1.1*	102
$(\eta^5\text{-}C_9H_7)Fe(CO)_2$	30.0	−36.6	−15.1		*46.1, 12.0, 1.0*	7
$(\eta^5\text{-}C_5H_5)Ru(CO)_2$	6.2	−37.5	−15.1		*22.3, 11.1, 1.0*	8
$Re(CO)_5$	−38.8	−36.7	−14.6		*−22.7, 11.9, 1.5*	8
$LMSi_\alpha Me(Si_\beta Me_3)_2$						
Fp*	−27.0	−9.3			*21.6, 6.8*	146
Fp	−23.2	−8.1			*25.4, 8.0*	102
$(\eta^5\text{-}C_9H_7)Fe(CO)_2$	−12.7	−8.7			*35.9, 7.4*	7
$(\eta^5\text{-}C_5H_5)Ru(CO)_2$	−37.6	−9.2			*11.0, 6.9*	8
$LMSi_\alpha Me_2Si_\beta Me_2Si_\gamma Me_2Si_\delta Me_3$						
Fp	22.9	−32.5	−42.8	−14.5	*38.1, 12.4, 1.9, 0.7*	33
$(\eta^5\text{-}C_9H_7)Fe(CO)_2$	31.0	−32.8	−43.2	−15.1	*46.2, 12.1, 1.7, 0.1*	146
$LMSi_\alpha(Si_\beta Me_3)_3$						
Fp	−82.6	−5.7			*5.5, 6.8*	33
$(\eta^5\text{-}C_9H_7)Fe(CO)_2$	−69.5	−6.3			*18.6, 6.2*	146
bimetallic complexes						
$FpSiMe_2SiMe_2Fp$	29.2				*48.9*	46
$Fp(SiMe_2)_3Fp$	32.4	−24.7			*48.5, 23.9*	10a
$Fp(SiMe_2)_4Fp$	23.7	−31.2			*38.9, 13.7*	10a

[a] The designations Si_α and Si_β were changed by K.H.P. from those reported in the literature.

Table 2. Structural Parameters for Selected Transition Metal Disilanes

complex	*d*, Si−Si, Å	ref
$Fp^*SiMe_2SiMe_3$	2.364(2)	146
$(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMe_3$	2.361(3)	7
$(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)SiMe_2SiMe_3$	2.393(2)	7
$FpSiMe_2SiMe_2Fp$	2.390(4)	46a
$[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}SiMeSiMe_3)(\mu\text{-}CO)$	2.371(1)	41

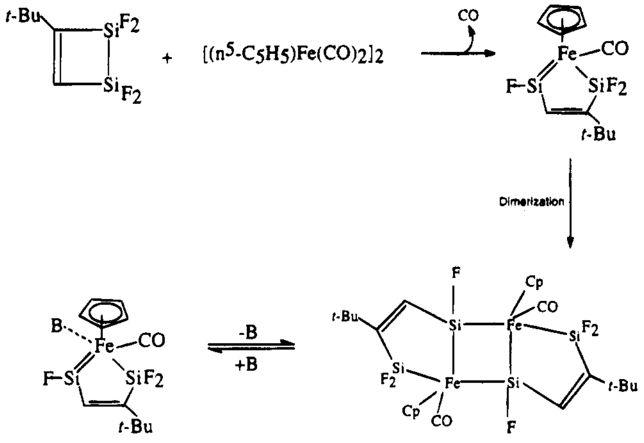
since the upper limit is noted for the bimetallic complex $FpSiMe_2SiMe_2Fp$, 2.390(4) Å;[46a] however, overall the bond length elongations are very minor.

III. Oxidative Addition of Si–Si Bonds to Transition Metals

Oxidative addition of the Si−H bond to a metal center was one of the earliest synthetic methods for Si−M bond formation. Given the relative weakness of the Si−Si bond, similar reactivity of this bond was to be expected. As noted in section II, several early examples of the formation of bridged silylene complexes from the reactions of disilanes and metal carbonyl complexes have been established that involved rupture of the Si−Si bond (Scheme 6; eqs 12 and 13). However, it is probable that these reactions proceeded via initial Si−H addition as depicted. More recently, several reactions have been reported that involve the clean oxidative addition of disilanes to metal centers to form bis(silyl)metal complexes.[15,106,111,112,119a,120,139,148,149,157,162]

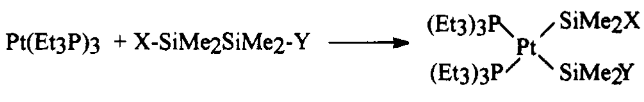
An interesting example is the reaction between highly reactive tetrafluorodisilacyclobutene and Fp_2 that resulted in the formation of a disiladiferracyclic ring compound, Fe_2Si_2, via the intermediacy of a silylene complex. In the presence of donor solvents, the Fe_2Si_2 ring was cleaved and donor-stabilized silylene complexes were obtained (Scheme 16).[45]

Scheme 16

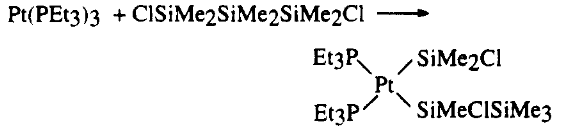


(B = HMPA, THF, MeCN)

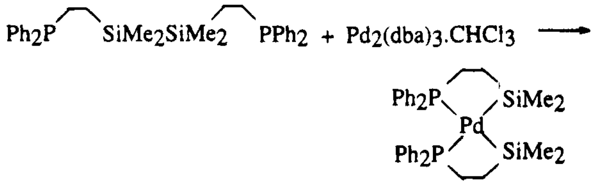
The reactions between disilanes and the platinum/palladium family of complexes have been shown to lead to bis(silyl) complexes.[15,106,111,112,119a,120,139,148,149,157,162a] The reaction of the disilanes HRMeSiSiMeRH (R = H, Me) with the palladium complex $(P_2Pd)_2(\mu\text{-}H)_2$ (P = dcpe) resulted in the formation of stable bis(silyl) complexes $P_2Pd(SiMeHR)_2$.[112] In a similar manner the reactions outlined in eqs 33−36 typify such chemistry, and, as noted in the following section, often represent the catalytically active intermediates associated with the addition of Si−Si bonds to unsaturated substrates.[106,119a,139,157]



X, Y = Cl, Br, F (33)

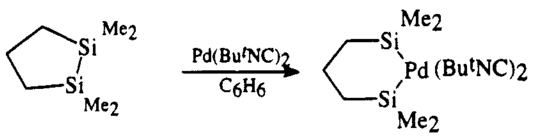


(34)



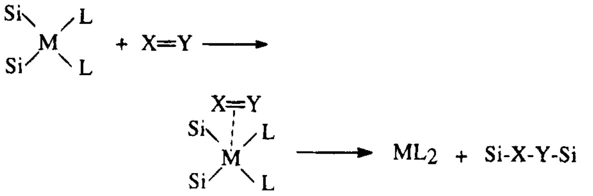
(35)

dba = dibenzylideneacetone



(36)

The chemistry outlined in eq 34 illustrates both the oxidative addition of the Si–Si bond and the isomerization process detailed above for the Fp–oligosilane complexes (Schemes 3 and 4). Each of the above examples is directly involved in catalytic cycles resulting in the addition of the Si–Si bond to unsaturated molecules, illustrated in eq 37 and discussed in the next section.



(37)

IV. Transition Metal-Catalyzed Reactions of the Si–Si Bond

From the above it is clear that the reaction of many transition metal centers with molecules containing Si–Si bonds results in much new chemistry. Oxidative addition of the Si–Si bond to the metal center offers the potential for formation of bis(silyl), silyl (silylene), silylene, and disilene complexes, often in equilibrium with each other. Given the general reactivity of transition metal systems with respect to further coordination, intramolecular migrations, and rearrangements, followed by reductive eliminations, a range of potential catalytic processes can be envisaged. Indeed, addition of the Si–Si bond to unsaturated molecules, isomerizations, silylene generation, and polymerizations may be expected. In this section we review such metal-catalyzed chemistry.

A. Insertion into the Si–Si Bond

The addition of a disilane to acetylene to give the corresponding bissilylated olefin is an exothermic process (*ca.* 40 kcal/mol) on the basis of thermochemical considerations.[103] Thus, the addition of Si–Si bonds to substituted acetylenes, olefins (dienes, allenes, etc.), should provide an attractive regioselective route to functionalized organosilicon compounds. Transition metal complexes have been used to catalyze this chemistry, and it has developed into an active area of research in organosilicon chemistry. The mechanism of these reactions often involves initial oxidative addition of the Si–Si bond to the transition metal center as noted above. We shall review the general trends of this area, where a remarkable range of product distributions are reported from seemingly similar reactions, dependent upon the specific substituents upon the silicon compounds, the substrates, and the catalyst used. An outline of the major reaction types, with yields and stereochemistry, where reported, is presented in Tables 3–5.

Table 3. Selective Data on the Catalytic Bissilylation of Alkynes in the Presence of Palladium Catalysts

entry	disilane	alkyne	catalyst	yield	Z:E	ref
1	$HMe_2Si{-}SiMe_2H$	$MeO_2CC{\equiv}CCO_2Me$	$PdCl_2(PEt_3)_2$	40		104
2	$HMe_2Si{-}SiMe_2H$	$PhC{\equiv}CH$	$PdCl_2(PEt_3)_2$	25		104
3	$HMe_2Si{-}SiMe_3$	$MeO_2CC{\equiv}CCO_2Me$	$PdCl_2(PEt_3)_2$	43		104
4	$Me_3Si{-}SiMe_3$	$PhC{\equiv}CH$	$Pd(OAc)_2$/*a*	82	96:4	110
5	$Me_3Si{-}SiMe_3$	$Hex^nC{\equiv}CH$	$Pd(OAc)_2$/*a*	81	95:5	110
6	$Me_3Si{-}SiMe_3$	$PhC{\equiv}CPh$	$Pd(dba)_22P(OCH_2)_3CEt$	91	100:0	147
7	$PhMe_2Si{-}SiMe_2Ph$	$Hex^nC{\equiv}CH$	$Pd(OAc)_2$/*a*	96	100:0	110
8	$PhMe_2Si{-}SiMe_2Ph$	$HC{\equiv}CH$	$Pd(OAc)_2$/*a*	98	97:3	110
9	$F_2PhSi{-}SiMe_3$	$PhC{\equiv}CPh$	$Pd[\eta^3\text{-allyl})Cl]_2/PMe_2Ph$	95	99:1	120
10	$F_2PhSi{-}SiMe_3$	$PhC{\equiv}CH$	$Pd[\eta^3\text{-allyl})Cl]_2/PMe_2Ph$	94	89:11	120
11	$F_2PhSi{-}SiMe_3$	$Hex^nC{\equiv}CH$	$Pd[\eta^3\text{-allyl})Cl]_2/PMe_2Ph$	94	87:13	120
12	$F_2MeSi{-}SiMeF_2$	$PhC{\equiv}CPh$	$PdCl_2(PPh_3)_2$	85	100:0	107
13	$FMe_2Si{-}SiMe_2F$	$PhC{\equiv}CPh$	$PdCl_2(PPh_3)_2$	61	100:0	107
14	$F_2MeSi{-}SiMe_3$	$PhC{\equiv}CPh$	$PdCl_2(PPh_3)_2$	27	100:0	107
15	$Cl_2MeSi{-}SiMeCl_2$	$HC{\equiv}CH$	$Pd\,(PPh_3)_4$	96	79:21	108
16	$Cl_2MeSi{-}SiMe_2Cl$	$HC{\equiv}CH$	$Pd\,(PPh_3)_4$	34	80:20	108
17	$ClMe_2Si{-}SiMe_2Cl$	$HC{\equiv}CH$	$Pd\,(PPh_3)_4$	78	89:11	108
18	$ClMe_2Si{-}SiMe_3$	$HC{\equiv}CH$	$Pd\,(PPh_3)_4$	55	93:7	108
19	$(MeO)_2MeSi{-}SiMe(OMe)_2$	$PhC{\equiv}CH$	$Pd\,(PPh_3)_4$	71	96:4	108
20	$(MeO)_2MeSi{-}SiMe(OMe)_2$	$BuC{\equiv}CH$	$Pd\,(PPh_3)_4$	54	100:0	108
21	$MeOMe_2Si{-}SiMe_2OMe$	$PhC{\equiv}CH$	$Pd\,(PPh_3)_4$	78	92:8	108
22	$MeOMe_2Si{-}SiMe_2OMe$	$BuC{\equiv}CH$	$Pd\,(PPh_3)_4$	76	84:16	108
23	$MeOMe_2Si{-}SiMe_3$	$BuC{\equiv}CH$	$Pd\,(PPh_3)_4$	59	98:2	108

[a] *tert*-Alkyl isocyanide.

Table 4. Selective Data on the Catalytic Bissilylation of Alkenes

entry	disilane	alkene	catalyst	yield	Z:E	ref
1	$FMe_2Si-SiMe_2F$	$CH_2=CH_2$	$Pt(PPh_3)_4$	95	100:0	119
2	$ClMe_2Si-SiMe_2Cl$	$CH_2=CH_2$	$Pt(PPh_3)_4$	49	100:0	119
3	$MeOMe_2Si-SiMe_2OMe$	$CH_2=CH_2$	$Pt(PPh_3)_4$	53	100:0	119
4	$F_2PhSi-SiMe_3$	1-octene	$Pd[\eta^3\text{-allyl})Cl]_2/PMe_2Ph$	64	63:37	120
5	$F_2PhSi-SiMe_3$	styrene	$Pd[\eta^3\text{-allyl})Cl]_2/PMe_2Ph$	67	28:72	120

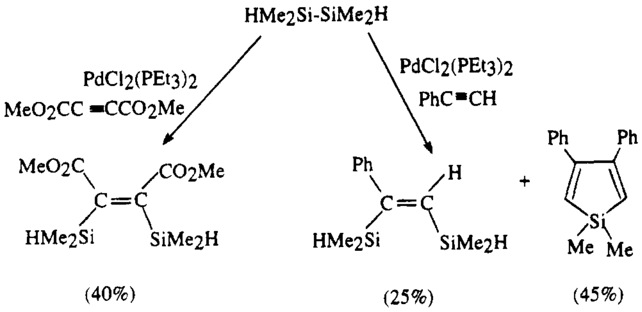
Table 5. Selective Data on the Catalytic Bissilylation of α,β-Unsaturated Ketones, α-Diketones, and Enones

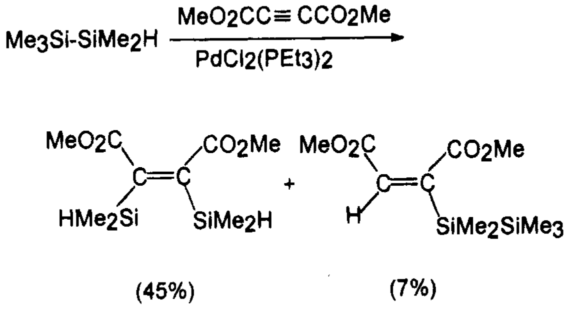
entry	disilane	ketone	catalyst	yield	ref
1	$FMe_2Si-SiMe_2F$	*p*-benzoquinone	$PdCl_2(PPh_3)_2$ or$Pd(PPh_3)_4$	41	107b
2	$FMe_2Si-SiMe_2F$	methyl vinyl ketone	$PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$	81	107b
3	$PhCl_2Si-SiMe_3$	(*E*)-4-phenyl-3-buten-2-one	$Pd(PPh_3)_4$	78	134
4	$Me_3Si-SiMe_3$	*p*-benzoquinone	$PdCl_2(PEt_3)_2$	100	151
5	$Me_3Si-SiMe_3$	benzil	$PdCl_2(PMe_3)_2$	99	158
6	$Me_3Si-SiMe_3$	methyl phenyl ketone	$PdCl_2(PMe_3)_2$	64	158

1. Bissilylation of Acetylenes

Acetylenes in the presence of a variety of Pd catalysts undergo bissilylation with 1,1,2,2-tetramethyldisilane (Scheme 17).[104] Under identical reaction conditions, pentamethyldisilane reacted to form a similar addition product, but also significant amounts of the simple hydrosilylation product (eq 38). This result represents a rare example of an oligosilyl hydride addition *(vide infra)*.[104]

Scheme 17

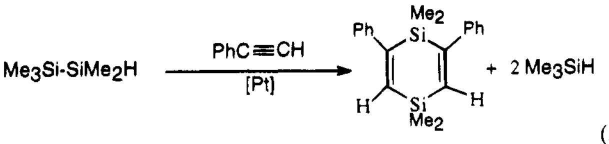




(38)

The reactivity of organodisilanes in such addition chemistry is enhanced by electronegative substituents fluorine, chlorine, and alkoxide and becomes comparable with strained cyclic Si–Si-bonded compounds. A large variety of stereo- and regioselective functionalized organosilicon compounds have been formed by such chemistry.[107–109] Selected data on the bissilylation of alkynes in the presence of Pd catalysts are presented in Table 3.

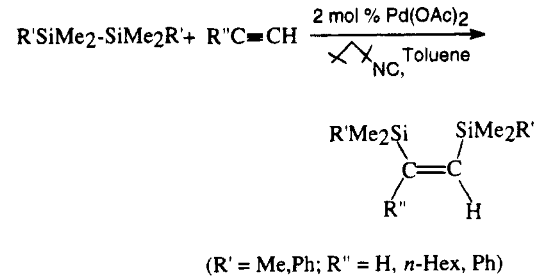
The significant formation of 1-silacyclopentadiene in Scheme 17 suggested the elimination of Me_2SiH_2 and Me_2Si: occurred, and such chemistry has been shown to occur with several metal systems from disilanes. For example, the reaction of pentamethyldisilane with phenylacetylene in the presence of phosphineplatinum or $NiCl_2(PEt_3)_2$ catalysts also underwent an α-elimination to extrude dimethylsilylene, which was trapped by phenylacetylene to produce 1,4-disilacyclohexadiene in excellent yields (for example, eq 39).[104–106,138]



(39)

In the presence of a variety of Pd catalysts 1,3-dichlorohexamethyltrisilane did not undergo bissilylation, but generated silylene species thermally, which were trapped by 2 equiv of acetylenes to produce 1,4-disilacyclohexa-2,5-dienes in 20–82% yields along with Me_2SiCl_2.[106]

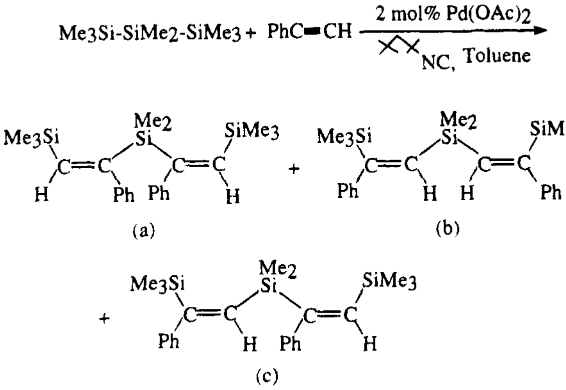
The palladium(II) acetate/*tert*-alkyl isocyanide and $Pd(dba)_2\cdot 2P(OCH_2)_3CEt$ complexes efficiently catalyze the bissilylation of alkynes with otherwise unreactive disilanes such as hexamethyldisilane and 1,1,2,2-tetramethyl-1,2-diphenyldisilane.[110,147] In general, Z isomers, which arise from the *cis* addition of the Si–Si bond to alkynes, were formed predominantly in excellent yields (eq 40).[110,147] The bissilylation of alkynes using the palladium(II) acetate/*tert*-alkyl isocyanide or $Pd(dba)_2 2P(OCH_2)_3CEt$ catalysts was also successfully applied to permethylated tri- and tetrasilanes; thus, the reaction of octamethyltrisilane with phenylacetylene gave a mixture of regioisomeric double-silylated products in high yield (Scheme 18).[110,147]



(40)

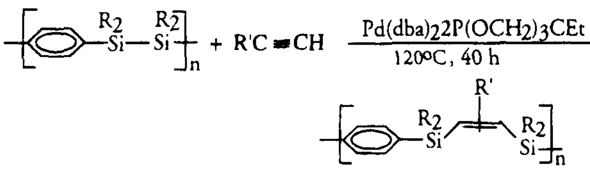
A similar reaction with decamethyltetrasilane resulted in addition of each Si–Si bond in 47% yield

Scheme 18



a : b : c = 3 : 2 : 4

together with bisdisilylated products, a and b above, formed by cleavage of the Si–Si bond of tetrasilane and loss of Me$_2$Si. The Pd catalyst, Pd(dba)$_2$·2P(OCH$_2$)$_3$CEt, was found to have high activity for the insertions of alkynes into the Si–Si bonds of the polymers, like poly(*p*-disilanylene)phenylene, M$_w$ = 2.3 × 10^3 (eq 41).[147]



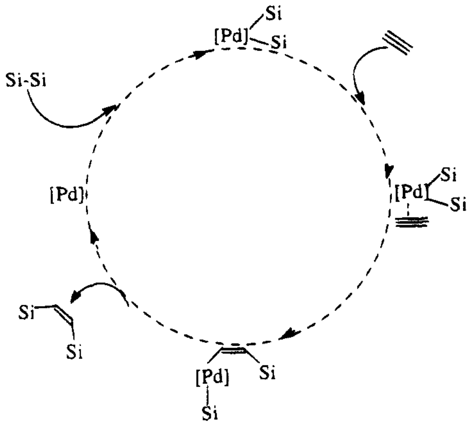
(41)

(R= Me, Ph; R' = Hex, Ph)

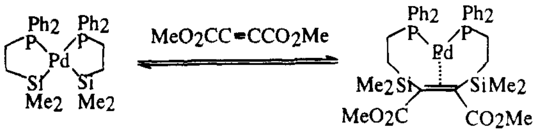
The cyclic bis(silyl)palladium bis(*tert*-alkyl isocyanide) complexes recently isolated from the activation of two Si–Si bonds of bis(disilyl)alkane with Pd(CNR^t)$_2$ (eq 37) exhibit reactivity toward acetylenes to give cyclic bissilylated products in quantitative yield.[148]

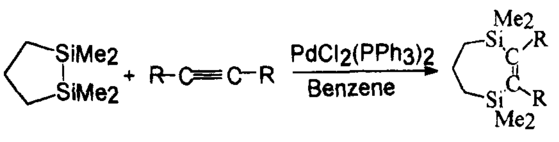
The mechanism of these addition reactions is envisaged to proceed via oxidative addition of the disilane followed by insertion of acetylene into one of the resulting Si–Pd bonds and finally reductive elimination of 1,2-bis(silyl)ethene from the silyl(*β*-silylethylene)pladium intermediate (Scheme 19). Support for such a mechanism was provided by synthesis and study of two palladium complexes, [bis(trialkylsilyl)alkene]palladium(0) and bis(trialkylsilyl)palladium(II). It was found that the two complexes were readily interconverted under the reaction conditions (Scheme 20).[111] Similar results were obtained by the Fink group with the (dcpe)Pd(SiMe$_2$H)$_2$/RC≡CR (R = CO$_2$Me) system.[112] A range of cyclic silicon compounds, both carbosilanes containing a Si–Si bond and oligosilanes, also add to acetylenic bonds in reactions catalyzed by (PPh$_3$)$_2$PdCl$_2$ (e.g. eq 42).[113,114]

Scheme 19



Scheme 20





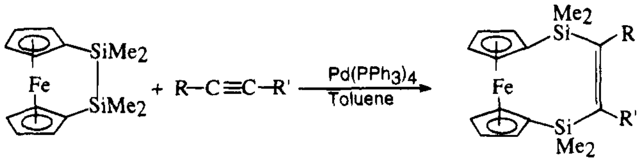
(42)

(R =H, CO2Me)

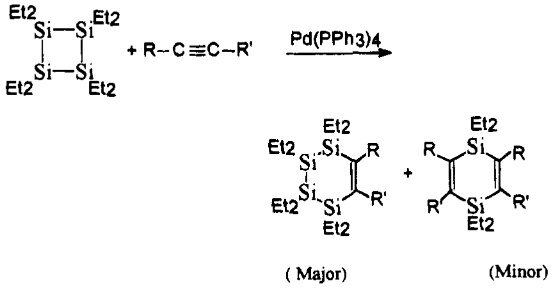
The mechanism for the process involving octamethyldisilacyclobutane was illustrated by performing the reaction with stoichiometric amounts of the disilane and (PPh$_3$)$_2$PdCl$_2$. After initial reduction to (PPh$_3$)$_2$Pd, it was possible to trap the intermediate PdSi$_2$ complex and further effect the reductive elimination of the product and regeneration of the catalyst (Scheme 21).[114]

The simple metal carbonyls Ni(CO)$_4$, Fe$_2$(CO)$_9$, and Ru$_3$(CO)$_{12}$ also catalyze such addition reactions, and in the case of the iron and ruthenium systems intermediate disilyl metal complexes were isolated.[115–116]

Moderately ring strained 1,1′-ferrocenediyltetramethyldisilane also underwent a facile insertion of acetylenes and 1,3-dienes in the presence Pd(PPh$_3$)$_4$ at 110 °C to yield cyclic organometallic ring systems (eq 43).[117] The strained cyclotetrasilane (Et$_2$Si)$_4$ reacted with alkynes in the presence of (PPh$_3$)$_4$Pd to yield 3,4,5,6-tetrasilacyclohexenes and 1,4-disilacyclohexa-2,5-dienes, the latter product stemming from incidental silylene formation (eq 44).[118]



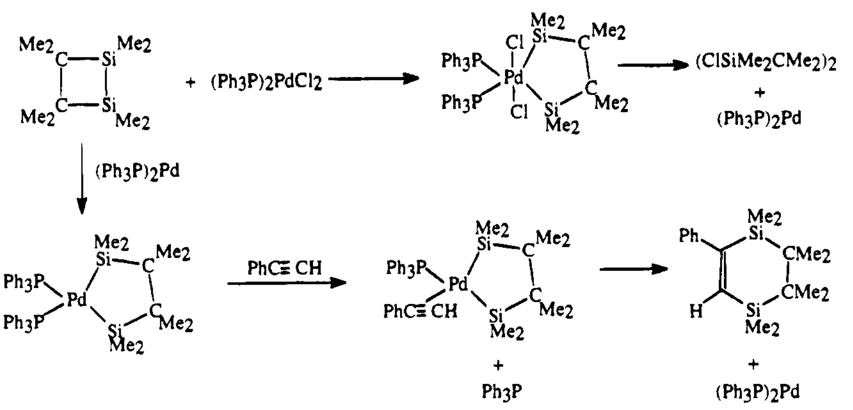
(R = R' = H; R = H, R' = Ph) (43)



(44)

(Major) (Minor)

Scheme 21



2. Bissilylation of Ethylene and Other Olefins

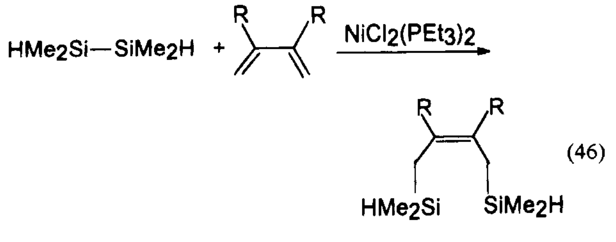
The Tanaka group reported the first successful bissilylation of ethylene with disilanes in the presence of platinum phosphine complexes to give 1,2-bis(silyl)ethanes (eq 45).[119] The reactivity of the

$$XSiMe_2SiMe_2X + CH_2{=}CH_2 \xrightarrow{Pt(PPh_3)_4} XSiMe_2CH_2CH_2SiMe_2X \quad (45)$$

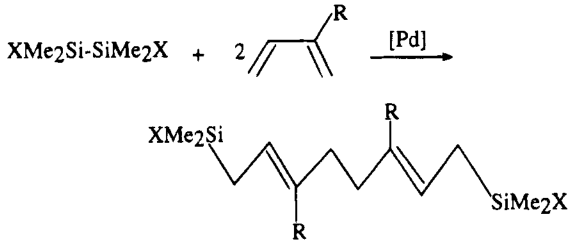
disilanes is considerably enhanced by the introduction of electronegative and sterically less demanding substituents on the silicon atom. The order of reactivity of the disilanes, $XSiMe_2SiMe_2X$, was X = F > OCH_3 > Cl > CH_3 > p-$CF_3C_6H_4$ > C_6H_5 > p-$CH_3C_6H_4$. The stereochemistry of the addition was established by the reaction of norbornene with disilanes which gave *cis* addition of disilanes with respect to the C=C bond. Selected data on the bissilylation of alkenes are presented in Table 4. The catalysis is thought to proceed via a cycle similar to that for Si–Si bond addition to acetylenes (Scheme 19).

The reaction between the non-symmetrically substituted disilane, Me_3SiSiF_2Ph, and various olefins, norbornene, styrene, and 1-octene, in the presence of $(R_3P)_2PdL_2$ (R_3 = Me_2Ph, Me_3) resulted in ready addition of the Si–Si bond to the alkene. The disilane formed *trans*-$Pd(SiMe_3)(SiF_2Ph)L_2$ complexes which are reactive toward olefins, again demonstrating the nature of the catalytic cycle involved in this apparently quite general chemistry.[120]

The double silylation of 1,3-butadienes by *sym*-1,1,2,2-tetramethyldisilane was reported to be catalyzed by $NiCl_2(PEt_3)_2$ to give 1,4-bis(dimethylsilyl)-but-2-enes (eq 46).[105] Use of Pd catalysts changed the outcome of such reactions, dependent upon the substituents on silicon. Coupled to the 1,4-addition of the Si–Si bond to produce 1,4-disilyl-2,3-butenes, a new dimerization-addition reaction was observed to form 1,8-disilyl-2,3(6,7)-octadienes. Thus, hexamethyldisilane (and organodisilanes having electron-withdrawing substituents or cyclic carbosilanes) slowly undergo a low yield dimerization–bissilylation with butadienes and isoprene at elevated temperatures (90–120 °C) in the presence of Pd catalysts, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, $Pd(OAc)_2$, or $PdCl_2(ArCN)_2$ (eq.47).[107,112,114,117,118,121,122]



(46)

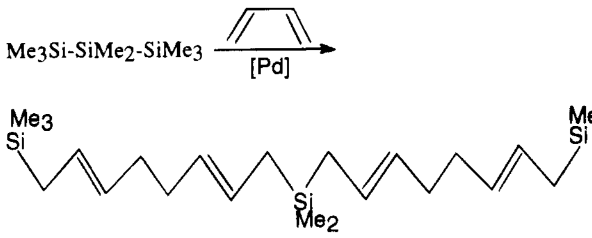


(47)

(X = Me, MeO, Cl; R = H, Me)

Recently, it was observed that many organodisilanes with hydrocarbon substituents (allyl, vinyl, phenyl, and methyl) react with 1,3-butadienes in the presence of $Pd(dba)_2$ to give dimerization–bissilylated products regio- and stereoselectively in high yields at room temperature.[122] With this catalyst no dimerization–double-silylated products were obtained with disilanes having the electronegative substituents fluorine and chlorine; however, with the palladium catalysts, $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$, a mixture of 1,4-addition and dimerization–addition was reported.[107] Furthermore, using $Pt(CO)_2(PPh_3)_2$ as catalyst, phenyl-substituted disilanes quantitatively added to 1,3-butadienes to form only 1,4-addition products.[123] A similar result was noted with vinyl-substituted disilanes using $(PPh_3)_4Ni$ as catalyst.[124] These various results perfectly illustrate the subtle distinctions available with changing catalysts and silicon substituents and thereby both the interest in, and complexity of, such systems.

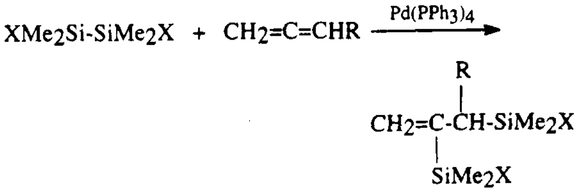
Oligosilanes such as octamethyltrisilane, $Me_3SiSiMe_2SiMe_3$, also reacted with butadiene at room temperature in the presence of $Pd(dba)_2$ to give a single isomer having an all E configuration of double-bissilylated product in 32% yield (eq 48).[122]



(48)

The $(Ph_3P)_4Pd$-catalyzed reaction of strained [2]-disilylferrocenophane with butadiene exclusively yielded a macrocylic product involving **two** sequential insertions, with an approximately 7:3 mixture of *trans–trans* and *cis–trans* isomers.[117] The reaction of cyclotetrasilane $(Et_2Si)_4$ with isoprene resulted in isolation of addition products involving both single- and double-insertion processes.[118]

Several examples of metal-catalyzed 1,2-additions of Si–Si bonds to allenic compounds have been reported (e.g. eq 49).[114,125]



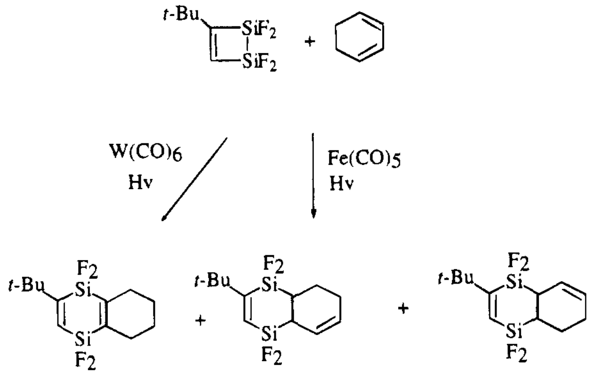
$$XMe_2Si\text{-}SiMe_2X + CH_2{=}C{=}CHR \xrightarrow{Pd(PPh_3)_4} CH_2{=}\underset{\displaystyle SiMe_2X}{C}\text{-}\overset{\displaystyle R}{C}H\text{-}SiMe_2X$$

(49)

(X = Cl, OMe, R = H, Me)

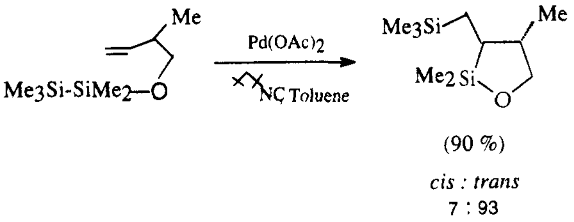
The $Fe(CO)_5$-mediated reaction between tetrafluorodisilacyclobutene and cyclohexadiene resulted in the formation of both isomers of a 1,2-addition along with an unusual H-shift isomerized product. The $W(CO)_6$-mediated addition reaction produced only the H-shift isomerized product (Scheme 22).[126] It is believed that these reactions occur through the intermediacy of an η^4-cyclohexadiene disilametallacycle complex, and such intermediates were isolated and characterized by X-ray diffraction.[126a]

Scheme 22

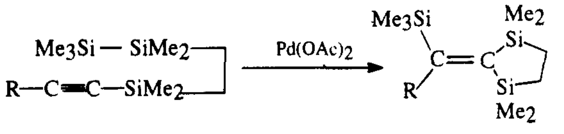


3. Intramolecular Bissilylation of Unsaturated Compounds

Intramolecular bissilylation of C=C and C≡C is an attractive stereo- and regioselective synthesis of organosilicon compounds. The intramolecular bissilylation reactions of C=C bonds (eq 50) led to stereoselective synthesis of 1,2,4-triols.[127] Palladium(II) acetate–*tert*-alkyl isocyanide-catalyzed bissilylations of pentaalkyldisilyl-substituted alkynes undergo intramolecular regioselective *cis* addition of the Si–Si linkage to furnish exocyclic olefins in good yield (eq 51).[110a,128]



(50)

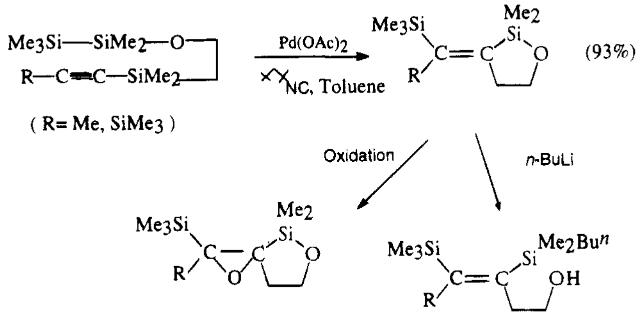


(51)

(R= Me, Ph, SiMe3)

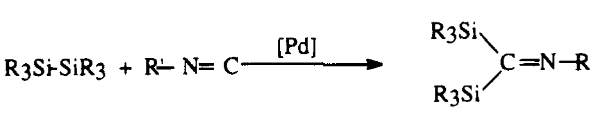
The synthetic transformations of these olefins may be exemplified by ring opening in the presence of *n*-BuLi to yield silyl-substituted homoallylic alcohols or, upon oxidation, epoxides (Scheme 23).[110a,128]

Scheme 23



4. Insertion of Isonitriles, α, β-Unsaturated Ketones, α-Diketones, and Quinones

Isonitriles, R–N=C, undergo insertions readily into the Si–Si bond of disilanes in the presence of Pd catalysts, $Pd(PPh_3)_4$ or $Pd(OAc)_2$, to yield thermally stable, N-substituted bis(organosilyl)imines in fairly good yield (eq 52).[110b,129,130] Isonitriles have inserted regularly into each Si–Si bond of tri-, tetra-, penta-, and hexasilanes; insertion provides oligo(organosilyl)imines.[129] Partial insertion of isonitriles into the oligosilane chain can also be achieved by changing the stoichiometric ratios of polysilane and isonitriles; i.e., the reaction takes place in a stepwise fashion (eq 53).[130]



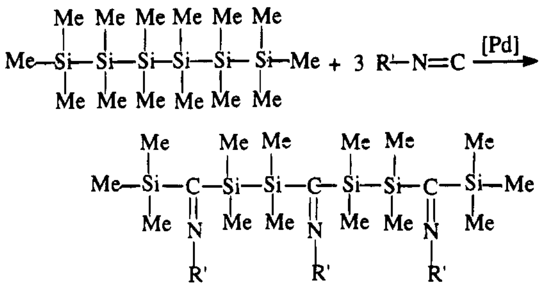
$$R_3Si\text{-}SiR_3 + R'\text{-}N{=}C \xrightarrow{[Pd]} (R_3Si)_2C{=}N\text{-}R'$$

(52)

(R = Me, Ph; R' = 2-tolyl, 2,6-xylyl, *c*-hexyl, 2,6-di-*i*-pr-phenyl)

It has been shown that the macrocyclic molecules containing reactive Si–Si bonds also underwent insertions of isonitriles in each of the Si–Si bonds in a regular fashion in the presence of $Pd(OAc)_2$.[149]

The Pd-catalyzed reaction of tetrasilanes with aryl isocyanides in the presence of 1,1,3,3-tetramethyl-

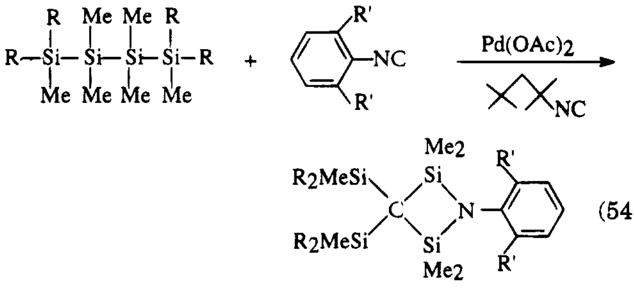


(53)

(16%)

R' = 2,6-di(*i*-propyl)phenyl

butyl isocyanide underwent skeletal rearrangement to yield azadisilacyclobutane products in good yields (eq 54).[131]

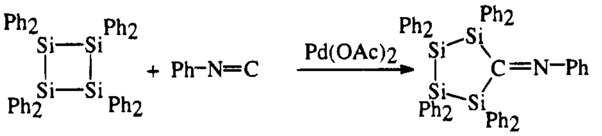


(54)

(R =Me,Ph; R' = Me, *i*-Pr)

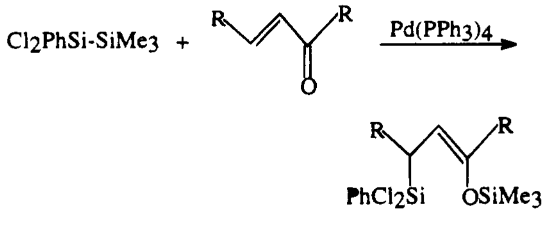
The rearrangement occurred only with aryl isocyanides, not with alkylisocyanides. The mechanism of this complex rearrangement is not yet clear.

Cyclic organosilanes also undergo facile insertions of isonitriles. Direct heating of disilacyclobutane or trisilacyclopropane derivatives with aryl isocyanides provides silacycloimine derivatives.[132] Octaphenylcyclotetrasilane in a Pd-catalyzed reaction with phenyl isocyanide yielded the corresponding tetrasilacyclopentanimine (eq 55).[133]



(55)

Pd-catalyzed reactions between *sym*-substituted fluorodisilanes and methyl vinyl ketone or benzoquinone provided 1,4-disilylated products.[107] However, 1,4-disilylation of α,β-unsaturated ketones in the presence of phosphino-Pd catalysts occurred only with unsymmetrical disilanes $Cl_2PhSiSiMe_3$ and $Cl_3SiSiMe_3$ (eq 56).[134] These disilylated products can be converted to the corresponding optically active α-hydroxyketones in high yields.[134c] No 1,4-disilylated products of α,β-unsaturated ketones were obtained with other unsymmetrical disilanes, $(MeO)_3Si-SiMe_2X$ (X = F, Cl), or symmetrical disilanes, $XMe_2Si-SiMe_2X$ (X = Ph, F, Cl).[134] It was observed that the catalyst $PdCl_2(PEt_3)_2$ is highly effective for the bissilylation of relatively inert disilanes; for example, the reaction of hexamethyldisilane with *p*-benzoquinone in the presence of $PdCl_2(PEt_3)_2$ yielded 100% of bissilylated product[151] (Table 5).

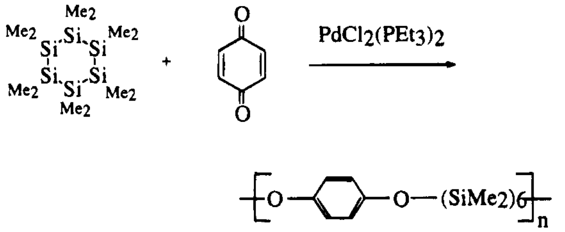


(56)

(R =Me, Ph)

The reactions of α-diketones, e.g. benzil, methyl phenyl diketone, acenaphthenequinone, or camphorquinone, with hexamethyldisilane in the presence of $PdCl_2(PMe_3)_2$ or $Pt_2(dba)_3P(OCH_2)_3CEt$ gave the corresponding 1,2-bis(trimethylsiloxy)ethenes in moderate to excellent yields.[158]

Palladium complexes, $PdCl_2(PEt_3)_2$ and $Pd(dba)_2$-$2P(OCH_2)_3CEt$, have been successfully used for the synthesis of a new class of copolymers involving *p*-quinones, e.g. 1,4-naphthoquinone and *p*-benzoquinone, and cyclic oligosilanes in 60–76% yields (eq 57).[150]



(57)

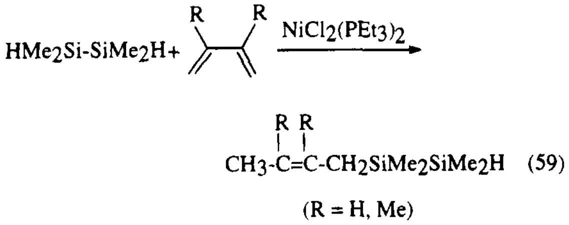
The thermal ring-opening polymerization of cyclic disilanes or polysilanes and insertion of *p*-quinones into the Si–Si bond produced benzene-soluble polymers containing regular alternating units of *p*-(arylenedioxy)silylene groups with molecular weights in the range of 4 000–82 000. Using the same Pd catalysts, the quinones were also inserted into the backbone of poly[(1,2-dimethyl-1,2-diphenyldisilanylene)(*p*-phenylene)] and poly(dimethylsilylene) to yield soluble high molecular weight (M_w 19 000–180 000) copolymers in 83–100% yields.[151] The structure of the polymers can be modified by changing the ratio of *p*-quinones, since the insertion of the quinones in the Si–Si bonds of the parent polymers is almost quantitative. The introduction of the quinone groups in the backbone enhanced the thermal stability of copolymers compared to the parent polysilanes.

B. Hydrosilylation with Disilanes

The ability of the Si–Si bond to be cleaved in the reactions described above and in section II suggests that transition metal-catalyzed hydrosilylation of carbon–carbon multiple bonds using oligosilanes, $R_3(SiR_2)_nH$, would be limited. This is indeed the case. Urenovitch and West in 1965 reported an unsuccessful attempt to hydrodisilylate olefins with pentamethyldisilane using H_2PtCl_6 as catalyst but obtained only the Si–Si bond cleavage products.[135] Kumada et al. carried out the first successful hydrodisilylation of vinyltrimethylsilane with pentamethyldisilane using a Pt catalyst (eq 58).[136]

$$\mathrm{Me_3SiSiMe_2H} + \mathrm{CH_2{=}CH{-}SiMe_3} \xrightarrow{\mathrm{PtCl_2(C_2H_4)(C_5H_5N)}} \mathrm{Me_3SiSiMe_2CH_2CH_2SiMe_3} \quad (58)$$

The reaction of pentamethyldisilane with acetylenes using Pd catalysts produced significant yields of hydrosilylated products[104] (eq 38), and the reaction of *sym*-tetramethyldisilane with butadienes in the presence of a Ni catalyst yielded hydrosilylated products (eq 59).[105]



(59)

(R = H, Me)

Despite these reports, hydrosilylation of oligosilanes remains a relatively little-explored reaction.

C. Polymerization of Hydrodisilanes

The platinum complex $\mathrm{PtCl_2(PEt_3)_2}$ has been used for the formation of linear oligomers from pentamethyl- and tetramethyldisilanes (eq 60).[137]

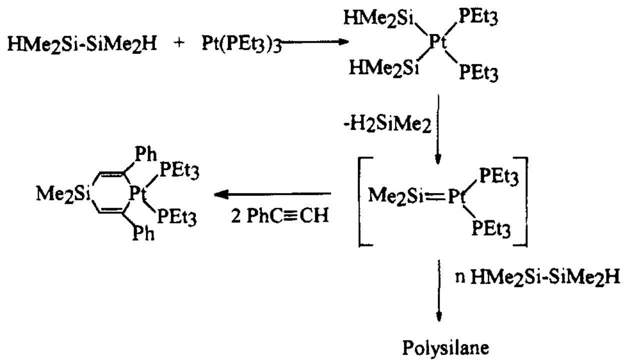
$$\mathrm{RMe_2SiSiMe_2H} \xrightarrow{\mathrm{Pt}} \mathrm{R(Me_2Si)_{\mathit{n}}H} \quad (60)$$

$$(\mathrm{R} = \mathrm{H, Me}, n = 1{-}6)$$

A mechanism was proposed involving an α-elimination of $\mathrm{Me_2Si}$ which subsequently inserts into the Si−H bond present in the disilane. Intermediate silyl (silylene)Pt complexes similar to those illustrated above for the Fp−oligosilane complexes are probably involved. The silylene species produced was readily trapped by diphenyl acetylene to give 1,4-disilacyclohexadiene.[106,138] Analogous results have recently appeared from the coupling of disilanes. Thus, the reaction of tetramethyldisilane and $\mathrm{Pt(PEt_3)_3}$ yielded *cis*-$\mathrm{(HMe_2Si)_2Pt(PEt_3)_3}$, a complex that was shown to be an effective catalyst for disilane polymerization[139] and bissilylations.[157] A platinum−silylene complex is the likely intermediate in these oligomerization reactions and was trapped with phenylacetylene to form 1-platina-4-silacyclohexadiene (Scheme 24).[139]

The dehydrogenative coupling of hydrodisilanes has also been accomplished in the presence of metallocene catalysts.[140,153] The reactions of pentamethyl- and tetramethyldisilanes with $\mathrm{Cp_2MMe_2}$ (M = Ti, Zr) resulted in the formation of a mixture of oligomers. Polymerization of 1,2-dimethyldisilane with $\mathrm{Cp_2MMe_2}$ produced a cross-linked polysilane polymer which upon pyrolysis produced SiC in 88% yield. A mechanism involving the intermediacy of metal−silylene complexes was proposed in these dehydrogenative coupling reactions. The order of reactivity of disilanes toward dehydrogenative coupling is $\mathrm{H_2MeSiSiMeH_2} > \mathrm{HMe_2SiSiMe_2H} > \mathrm{HMe_2SiSiMe_3}$.

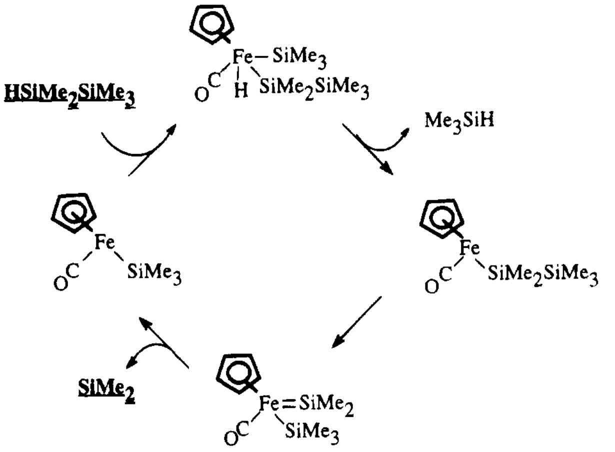
Scheme 24



D. Isomerization of, or Silylene Elimination from, Oligosilanes

Silylenes, $\mathrm{R_2Si}$, were generated from $\mathrm{RSiMe_2SiMe_2H}$ (R = H, Me) catalyzed by palladium, platinum, or nickel complexes (Scheme 17; eq 39). More recently, using the chemistry described in eqs 5 and 6 and depicted mechanistically in Schemes 1, 3, and 4, the photochemically generated catalytic species (η^5-$\mathrm{C_5H_5}$)Fe(CO)($\mathrm{SiMe_3}$) was used to produce silylenes from pentamethyldisilane, $\mathrm{Me_3SiSiMe_2H}$ (Scheme 25).[141]

Scheme 25



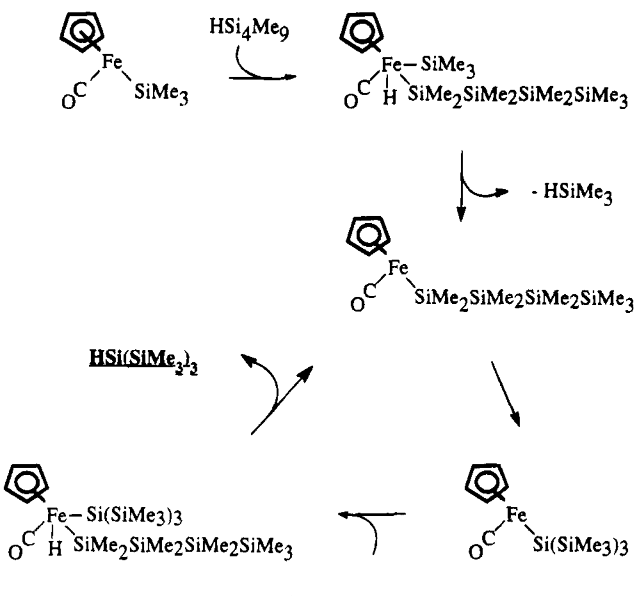
The irradiation was performed in Pyrex glassware, a condition that precluded photochemistry of the disilane itself in the absence of a catalyst. The silylene was trapped either with tris(trimethylsilyl)silane or 2,3-dimethyl-1,3-butadiene (e.g. eqs 61a, 61b). A range of transition metal complexes accomplished this process.

$$\mathrm{Me_3SiSiMe_2H} \xrightarrow[\mathrm{CpFe(CO)_2SiMe_3}]{h\nu\backslash\mathrm{benzene}} \mathrm{Me_2Si{:}} + \mathrm{Me_3SiH} \quad (61a)$$

$$\mathrm{(Me_3Si)_3SiH} + \mathrm{Me_2Si{:}} \rightarrow \mathrm{(Me_3Si)_3SiSiMe_2H} \quad (61b)$$

For the longer chain oligosilanes, the anticipated isomerization to branched silanes (Scheme 4) was readily effected by the same catalytic system. Thus, nonamethyltetrasilane, $\mathrm{Me_3SiSiMe_2SiMe_2SiMe_2H}$, was converted to tris(trimethylsilyl)silane, $\mathrm{HSi(SiMe_3)_3}$, although chain elongation to produce $\mathrm{HSiMe_2Si(SiMe_3)_3}$ via silylene insertion was an important byproduct. Thermal treatment of the tetrasilane in

Scheme 26



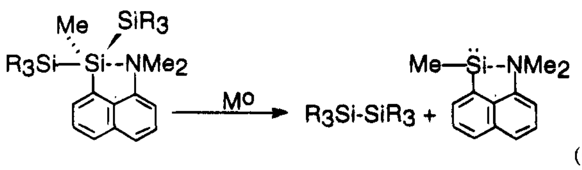
the presence of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)SiMe_3$, which produced the catalytically active 16-electron complex $(\eta^5\text{-}C_5H_5)Fe(CO)SiMe_3$ **thermally** via elimination of PPh_3, resulted in very high yields of only the isomerized product without silylene interference (Scheme 26).[141]

Furthermore, from the thermal reaction of pentamethyldisilane with the same phosphine-substituted catalyst no silylene elimination was observed. Upon a change to the phenyl-substituted disilane $PhMe_2SiSiMe_2H$, a thermally induced isomerization occurred to yield an equilibrium mixture of the starting material and $Me_3SiSiMePhH$ (eq 62).

$$PhMe_2SiSiMe_2H \xrightleftharpoons[CpFe(CO)(PPh_3)SiMe_3]{\Delta\backslash\text{toluene}} Me_3SiSiMePhH \quad (62)$$

The distinction between the different catalyses observed from the thermal and photochemical generation of $(\eta^5\text{-}C_5H_5)Fe(CO)SiMe_3$ lies in the previously mentioned observation by the Turner group that silylene elimination from the various silyl (silylene) intermediates, $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiMe_2)SiMe_3$, is a photochemical event.[35] Both photochemical and thermal catalytic processes proceed via equilibrating iron silyl (silylene) intermediates as noted in Scheme 1.

The reactivity of the Si–Si bond in oligo- or polysilanes is greatly influenced by the nature of groups attached to the silicon. Trisilanes containing an 8-(dimethylamino)-1-naphthyl group bonded to a central Si atom undergo silylene eliminations in Ni- or Pd-catalyzed reactions (eq 63).[142] This chemistry is reminiscent of the generation of silylenes, leading to disilenes, observed from the photochemistry of trisilanes. The silylene liberated from this Pd-catalyzed process was trapped with diphenylacetylene. Metal-silylene complexes are the likely intermediates in these reactions.

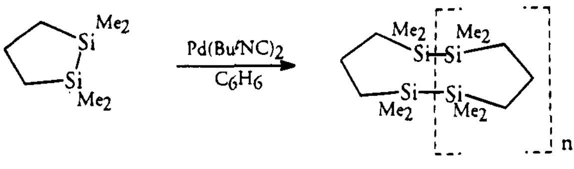


(63)

(R3 = Me3, PhMe2, Ph2Me; M = Ni or Pd)

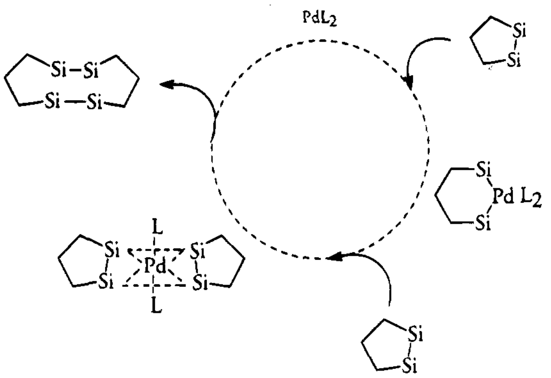
E. Si–Si Bond Metathesis

The Pd catalyst bis(*tert*-butyl isocyanide)palladium(0) was found to be highly effective for the activation of Si–Si bonds through Si–Si σ-bond metathesis and catalyzed the formation of interesting oligomers from 1,1,2,2-tetramethyl-1,2-disilacyclopentane in 93% yield (eq 64).[148] The stoichiometric reaction (eq 36) between the disilane and Pd(*t*-BuNC)$_2$ resulted in the formation of the oxidative addition product involved in the suggested catalytic cycle (Scheme 27).

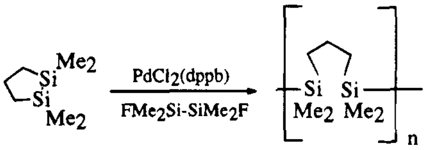


(n = 2-8) (64)

Scheme 27



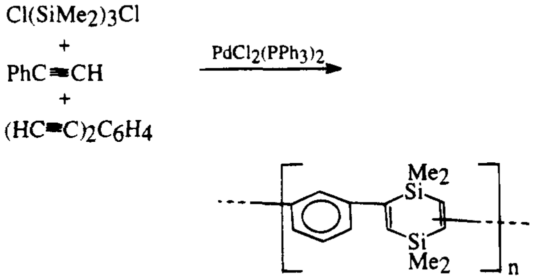
The Si–Si σ-bond metathesis was further supported by the reaction of phenylpentamethyldisilane with 1,1,2,2-tetramethyl-1,2-disilacyclopentane in the presence of Pd(*t*-BuNC)$_2$ to form acyclic oligomers in 48% yield with the successive insertion of $-Me_2Si(CH_2)_3SiMe_2-$ units into the Si–Si bond. No high molecular weight polymers were isolated from these reactions; however, when the catalyst was changed to $Pd(C_5H_5)(C_3H_5)$, the cyclic disilane yielded high molecular weight polymers in 51% yield.[159] Cyclic disilanes also undergo thermal ring-opening polymerizations catalyzed by Pd complexes $PdCl_2$(dppb) or $PdCl_2$(dbpb) and in the presence of initiators such as 1,2-difluoro-1,12,2-tetramethyldisilane to yield high molecular weight polymer ($M_w > 3 \times 10^5$) in 85% yield along with trace amounts of the dimer (eq 65).[160]



(65)

However, in the absence of 1,2-difluorodisilane, only dimerization occurred in 89% yield.

Low molecular weight polymers containing alternating units of 1,4-disilacyclohexa-2,5-dienylene and phenylene rings in the backbone were obtained in the palladium-catalyzed generation of $SiMe_2$ from 1,3-dichlorohexamethyltrisilane, $Cl(SiMe_2)_3Cl$, in the presence of internal arylacetylenes such as *m*- and *p*-diethynylbenzene or *m*-diprop-1-yn-1-ylbenzene (eq 66).[106] The introduction of phenylacetylene in these reactions imparted solubility to the polymer obtained.



(66)

F. Miscellaneous Silylations

The rhodium complex $RhClCO(PMe_3)_2$ catalyzed the direct silylation of arenes with hexamethyldisilane upon UV irradiation (eq 67).[143]

$$ArH + Me_3Si{-}SiMe_3 \xrightarrow{UV} Ar{-}SiMe_3 + Me_3SiH \quad (67)$$

The dehydrogenative monosilylation of alkenes with disilanes gave alk-1-enylsilanes, a useful class of compounds in organic synthesis. The reaction of styrene with 1,2-difluoro-1,1,2,2-tetramethyldisilane in the presence of a Pt catalyst gave (fluorodimethylsilyl)styrene as a major product (eq 68).[144]

$$PhCH{=}CH_2 + FMe_2Si{-}SiMe_2F \xrightarrow{Pt(PPh_3)_4} PhCH{=}CHSiMe_2F + SiMe_2FH \quad (68)$$

V. Conclusions

A substantial amount of the studies presented in this review have taken place during the very recent past. A decade ago, apart from isolated reports, the wealth of the chemistry described herein was not anticipated and indeed many of the reactions are very special. Given the significant increase in the number of research groups participating in the field, we safely predict that the combination of the stoichiometric chemistry, the catalytic chemistry, and the current drive for new materials based upon silicon chemistry will keep us busy, entertained, and enthralled into the next century (funding agencies permitting!).

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