

# RECENT ENTERTAINMENTS CONCERNING SILICON TRANSITION METAL SYSTEMS

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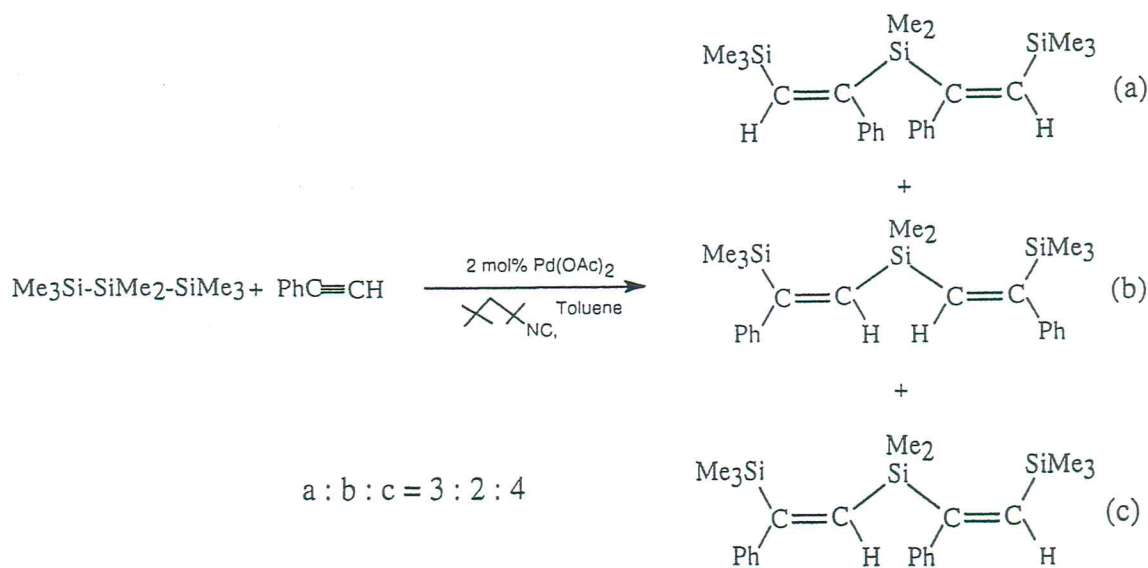
The study of transition metal derivatives of silicon, and the use of transition metals to catalyse organosilicon chemistry, is now a mature, well-documented, area of chemistry.<sup>1, 2</sup> In terms of transition metal-catalysed chemistry, hydrosilylation remains a dominant area of activity; however, other corners of organosilicon chemistry offer interesting insights into the general theme. In this short subjective entertainment some of these catalytic areas are presented together with some new and novel metal-silicon complexes and polymers. The majority of the work discussed was reported during 1993 and 1994, thus providing an up to the minute snapshot of the area; references within each article cited should be consulted to provide a fuller overview.

## Catalytic Systems

### A. Insertions into Si-Si bonds

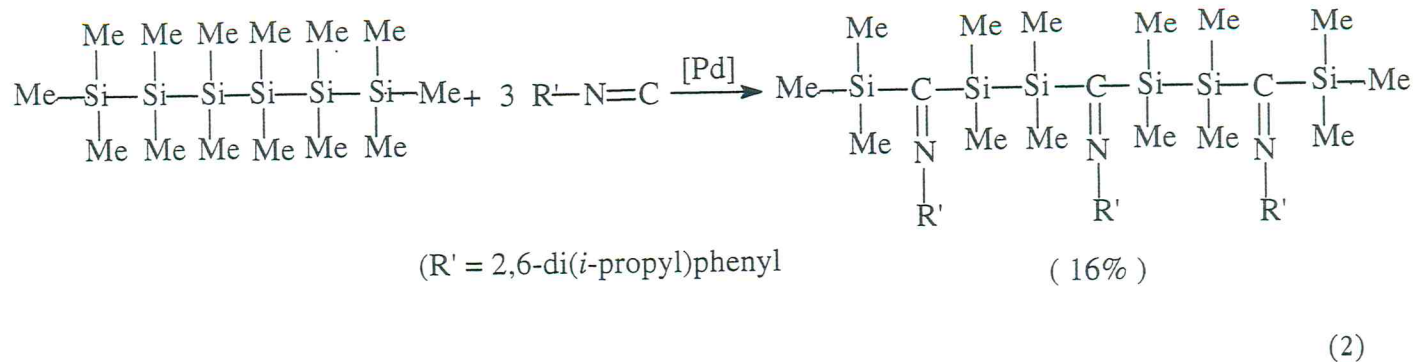
The driving force for the addition of the Si-H bond to unsaturated species, hydrosilylation, is the thermodynamics of the system resulting from the relatively weak Si-H bond strength. Since the Si-Si bond is also a relatively weak bond cf. Si-C, C-C, it is not surprising that addition of the Si-Si bond to unsaturated systems has also developed into an area of fertile chemistry.

The *bis*-silylation of acetylenes and dienes has been readily accomplished by several research groups since the initial reports by the Kumada group on the addition of 1,1,2,2-tetramethyldisilane to acetylenes<sup>3</sup> and the Tanaka group's discovery of the use of (PPh<sub>3</sub>)<sub>4</sub>Pd to catalyse addition of disilanes to ethylene.<sup>4</sup> Of particular recent interest is the consecutive addition of oligosilanes to both acetylenes and isonitriles, as illustrated in eq 1 and 2 using the catalytic system Pd(OAc)<sub>2</sub>/t-BuNC.<sup>5, 6</sup>



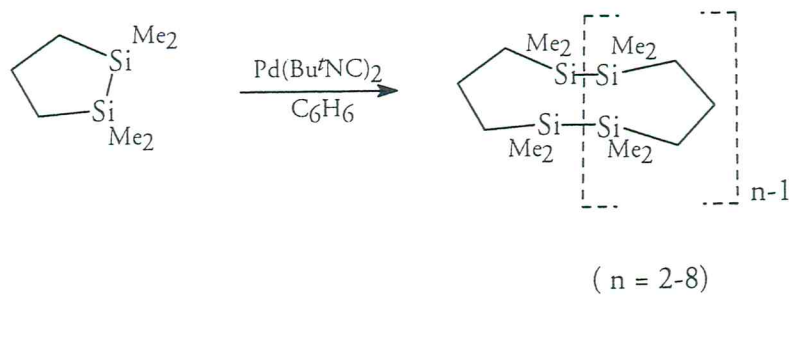
(1)

in "Silicon, Germanium, Tin and Lead Compounds, Metal Alkoxides, Diketonates and Carboxylates, ed. by B. Arkles, Gelest Inc. 1995.



Intramolecular bis-silylation of alkenes and alkynes are readily achieved using Pd catalysts resulting in the stereo- and regio-selective synthesis of organosilicon compounds.<sup>7, 8</sup>

Extensions of this chemistry to the cyclic disilane 1,1,2,2-tetramethyl-1,2-disilacyclopentane resulted in the formation of interesting oligomers, eq. 3.<sup>9</sup>



The stoichiometric reaction between the disilane and Pd(*t*-BuNC)<sub>2</sub> resulted in the formation of the oxidative addition product involved in the suggested catalytic cycle, figure 1.

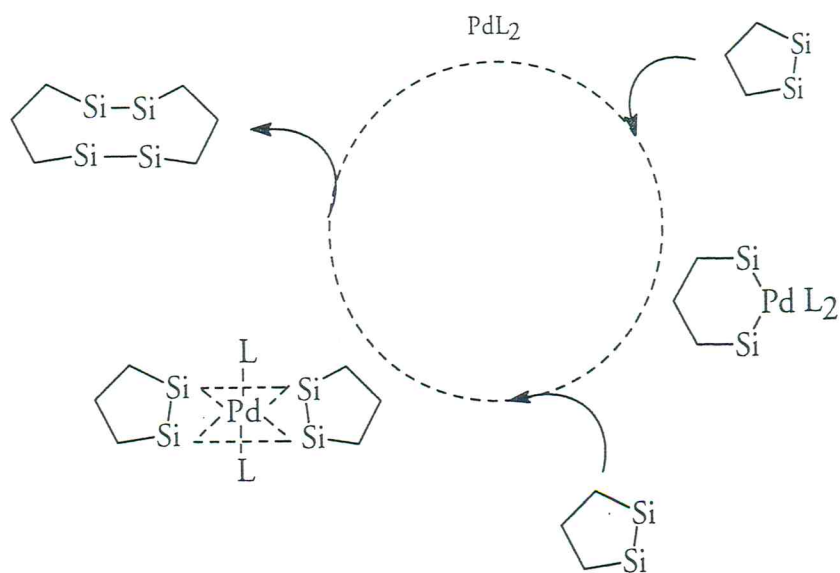
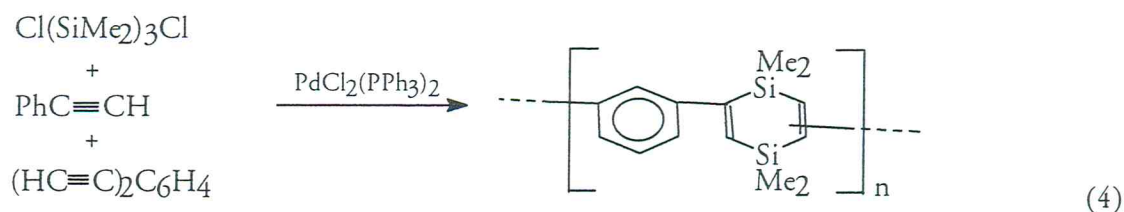


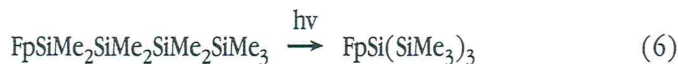
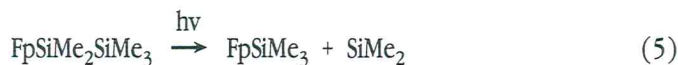
Figure 1

Low molecular weight polymers containing 1,4-disilacyclohexa-2,5-dienylene rings in the backbone were obtained in the palladium-catalyzed generation of  $\text{SiMe}_2$  from 1,3-dichlorohexamethyltrisilane,  $\text{Cl}(\text{SiMe}_2)_3\text{Cl}$ , in the presence of arylacetylenes, eq 4.<sup>10</sup>



### B. Isomerization and silylene expulsion from oligosilanes

Photochemical treatment of oligosilanes containing the substituent  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ , Fp has revealed several rearrangements, isomerizations, and in the case of short oligosilanes,  $\text{Si}_2$  and  $\text{Si}_3$ , deoligomerizations involving silylene formation, eqs 5, 6.<sup>11</sup>



Such transformations on the parent oligosilanes, e.g.  $\text{Me}_3\text{SiMe}_2\text{SiH} \rightarrow \text{Me}_3\text{SiH} + \text{Me}_2\text{Si}$  and  $\text{Me}_3\text{SiMe}_2\text{SiMe}_2\text{SiMe}_2\text{SiH} \rightarrow (\text{Me}_3\text{Si})_3\text{SiH}$ , have now been achieved catalytically using a variety of metal catalysts, but most obviously, and cheaply, using  $\text{FpSiMe}_3$  and/or  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)$  as the precursor to the catalytic  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{SiMe}_3)$ . The general scheme for the isomerization of oligosilanes is outlined in Figure 2.

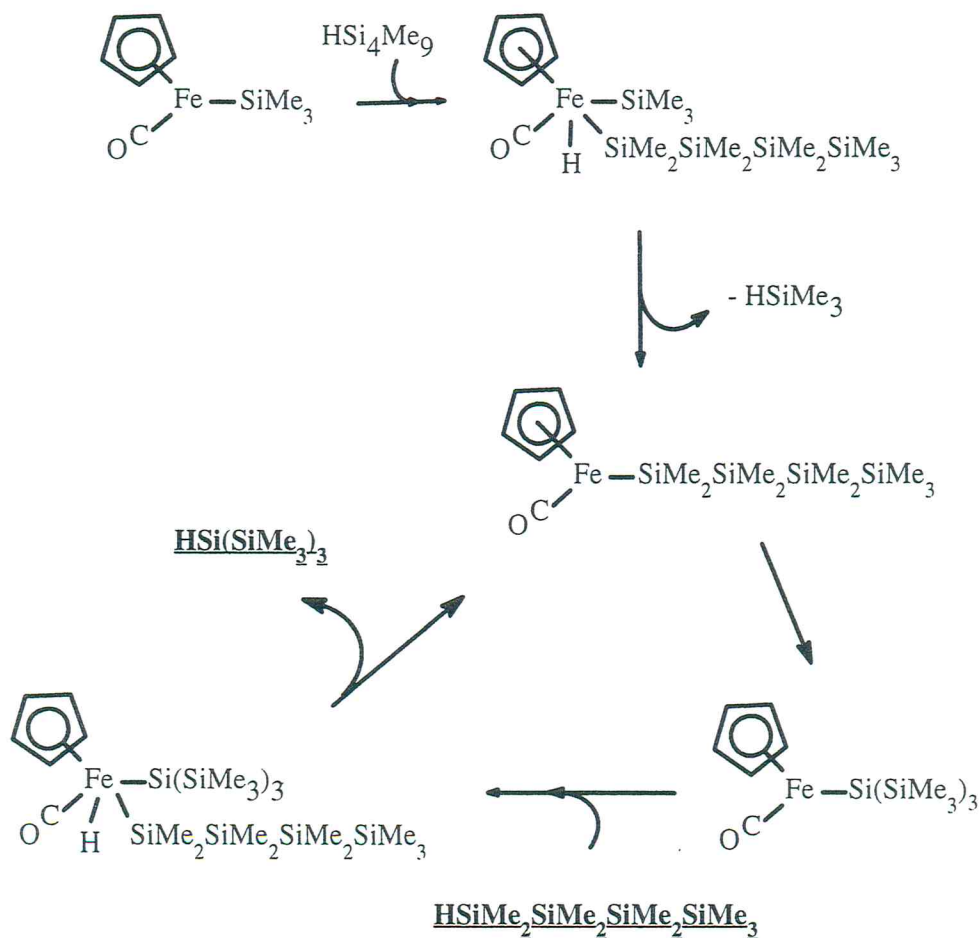
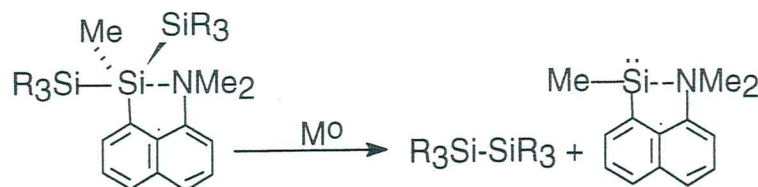


Figure 2

Thermal activation of trisilanes containing 8-(dimethylamino)-1-naphthyl group bonded to central Si atom resulting in silylene eliminations has also been reported using Ni or Pd catalysts, eq 8.<sup>13</sup>



(7)

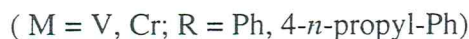
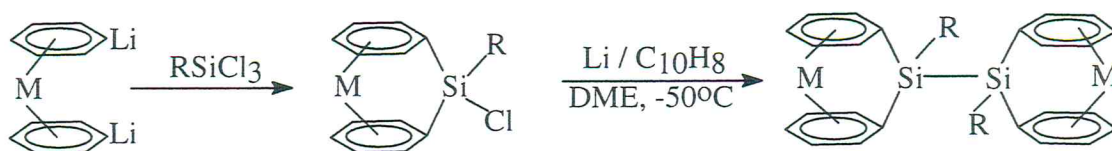
### Ferrocenyl/Ferrocenylene Complexes and Polymers

There has been a recent flurry of interest in silicon complexes, monomers, oligomers and polymers, in which the group 14 element is connected to a  $\sigma$ -bonded cyclopentadienyl group. Specifically the properties of ferrocenyl, ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>), Fc, and ferrocenylene, ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>), FC, silanes have been the subject of electrochemical and thermal studies.

The Kumada group was the first to synthesize ferrocenyl-, ferrocenylenesilanes and -germanes in the early 1970's via simple salt-elimination reactions between ferrocenyllithium (or ferrocenyldilithium) and the appropriate chlorooligosilanes.<sup>14, 15</sup>

Recently detailed electrochemical studies have been performed on  $\alpha, \omega$ -bis-(ferrocenyl)oligosilanes.<sup>16</sup> When the bridge between the two ferrocene units contains 1, 2 or 3 silicon atoms, cyclic voltammetric analysis resulted in the observation of two discrete redox processes. Longer-chain silicon bridges resulted in loss of discrimination between the two Fc units. By way of contrast, a single saturated carbon bridge, CMe<sub>2</sub>, does not permit distinction of the two Fc unit,<sup>17</sup> although the unsaturated linkage of CH = CH does.<sup>18</sup> Such data reveals the capacity of Si atoms to transmit electronic information, presumably via a  $\pi^*/3d$  orbital admixture.

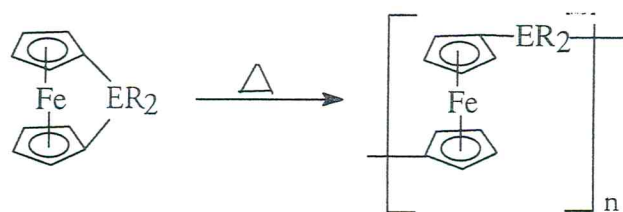
Related to this transmission of effects through silicon chains is a report by Elschenbroich and coworkers on the Si-Si bridged arene complexes of V and Cr outlined below, eq 8.<sup>19</sup>



(8)

These complexes exhibit weak magnetic exchange between the two metal centers via a disilane bridge.

Thermal treatment of the single Si or Ge bridged ferrocenophanes was reported to yield polymers as early as 1970 by Rosenblum,<sup>20</sup> and recent studies have revived interest in these systems, eq. 9.<sup>21, 22</sup>



(E = Si , Ge, R = Me, Et, *n*-Bu, *n*-Hex, Fc, etc.

(9)

The polymers exhibit at least two major redox processes when examined by cyclic voltammetry in accord with the separation of the ferrocene units by a single silicon/germanium bridge as noted above.

The polymers are either partially crystalline or amorphous dependent upon the R groups in the backbone. [They have been converted to ceramic materials by thermolysis,<sup>23</sup> produce electrochromic thin films,<sup>22d</sup> and reversible doping with I<sub>2</sub> of a polymer containing a hexasilyl bridging group was shown to produce conducting materials.<sup>24</sup>]

#### 5-Silacyclopentadienyl Complexes

The first stable and isolable 5-silacyclopentadienyl transition metal complex was recently synthesized, figure 5.<sup>25</sup> The spectral data is consistent with aromaticity in both the rings and are similar to those reported for  $\eta^5$ -germaruthenocene, ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru[h<sup>5</sup>-Me<sub>4</sub>C<sub>4</sub>Ge(SiMe<sub>3</sub>)<sub>3</sub>].<sup>26</sup>

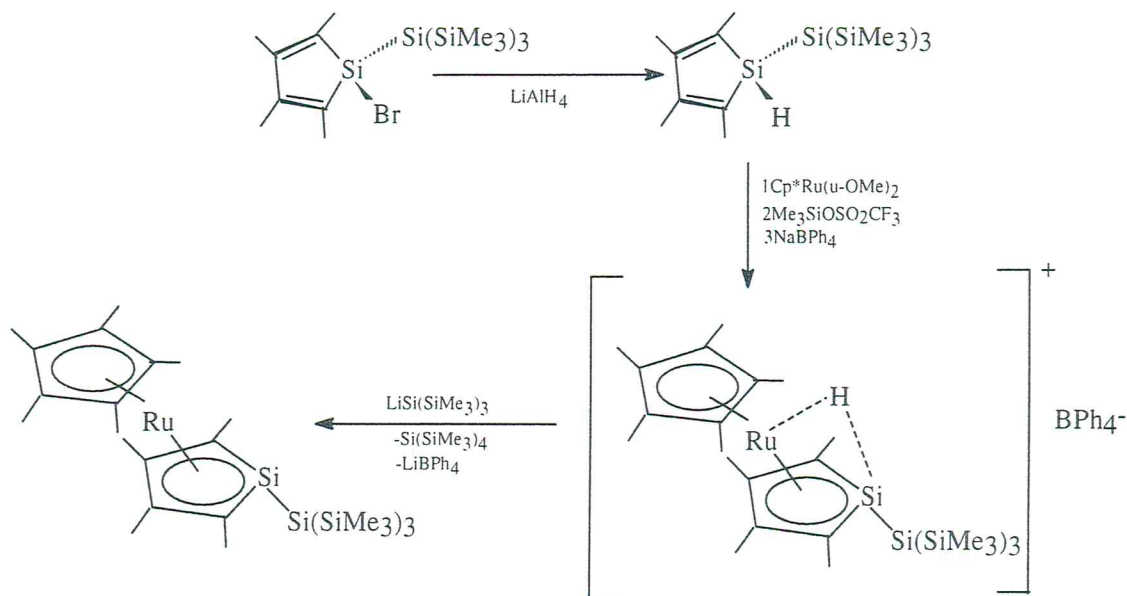


Figure 3

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