



**THE MAJOR IMPACT OF JORGE CERVANTES' ARTICLE:
ORGANOMETALLICS, 1986, 5, 1056-1057.**

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I first visited Guanajuato after being invited by Dra. Lena Ruiz to present a paper to the Academia Mexicana de Química Inorgánica in 1981. At that meeting I was introduced to Jorge Cervantes, a member of the faculty at the Universidad de Guanajuato and thus began a collaboration and friendship that thankfully persists today.

Jorge, a chemical engineer by training, with a master in inorganic chemistry was very interested in the tailings from the various mines in the area and had a vision of developing a research program on silicon chemistry, once in his master thesis he was able to obtain silicon tetrachloride (SiCl₄), an important precursor of silicon materials from such tailings. Jorge has the idea to sometime build an industrial pilot plant, using these silicate materials. At that time their main use was for “filling-in” purposes to enable the formation of

football pitches! After my initial visit to Guanajuato, at the end of that year (1981) Jorge spend few weeks in my laboratory at UTEP-El Paso, to start a collaboration based on a project on hydrosilylation reactions of acetylenes. During the next years (1982-1984) we were able to maintain the collaboration while the silicon research program in Guanajuato started to grow with the participation of his colleagues Edmundo Hernández and Alberto Aguilera.

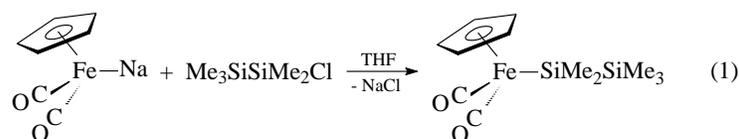
At the end of 1983, Jorge decided to start his doctoral studies under my advice and with the support of Professor Antonio Campero from the chemistry department at the Universidad Autónoma Metropolitana-Iztapalapa we devised a plan involving the newly formed doctoral program at that university to take the requisite academic courses in Mexico City and initiate a research program at the University of



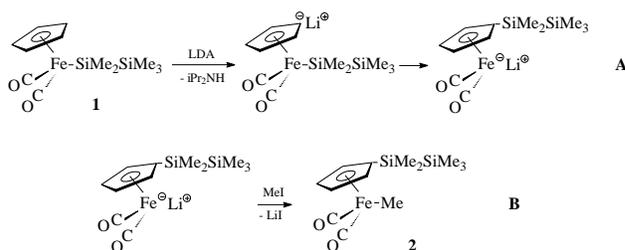
Texas at El Paso. Some years later, Alberto Aguilera also arrive to UTEP-El Paso to study his doctoral program.

At the time of Jorge's arrival in El Paso there was a significant international interest on the photochemical reactivity of polysilanes, $(\text{Me}_2\text{Si})_n$, and this class of compound had found a significant potential as a photoresist materials (Miller and Michl, 1989). It had been well-established that upon photolysis these polysilanes exhibit a stepwise loss of (Me_2Si) fragments until reaching the disilane unit after which no further chemistry had been reported. A particular and important example of such chemistry was the photochemical treatment of the simple trisilane $\text{Me}_3\text{SiSiR}_2\text{SiMe}_3$ that resulted in the elimination of the silylene R_2Si : which dimerized to form the first example of a disilene, $\text{R}_2\text{Si}=\text{SiR}_2$, $\text{R} = \text{mesityl}$ (West et al., 1981). In El Paso we had a strong interest in the chemistry of silicon transition metal complexes with special attention to the chemical implications of creating and energizing silicon-transition metal bonds, in particular those containing the Fe-Si linkage. Thus, it was logical that Jorge's

initial doctoral study involved the synthesis and chemical study of a simple disilyliron complex of the $(\eta^5\text{-cyclopentadienyl})\text{iron dicarbonyl}$ unit, $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{SiMe}_3$, **1** ($\text{FpSiMe}_2\text{SiMe}_3$), using the well-established salt-elimination reaction outlined in equation 1.

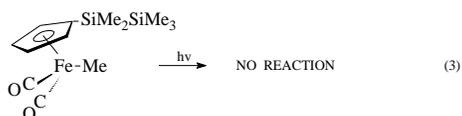
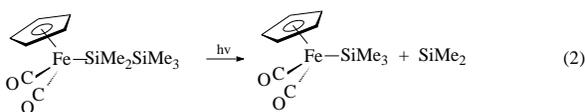


With this molecule available, photochemical and base treatment reactions were initiated. A key reaction was the treatment of **1** with lithium diisopropylamide, LDA, $\text{LiN}(\text{iPr})_2$, which led to the smooth high yield migration of the disilyl group to the cyclopentadienyl ring with no evidence for base cleavage of the Si-Si bond. Careful infrared analysis of the reaction showed that a new metallate ion had formed as noted in step **A** of Scheme 1. Quenching of this ferrate with methyl iodide led to a stable, readily isolable new organometallic $(\eta^5\text{-pentamethylidisilyl-cyclopentadienyl})\text{iron}(\text{dicarbonyl})\text{methane}$, **2**, step **B** of Scheme 1.



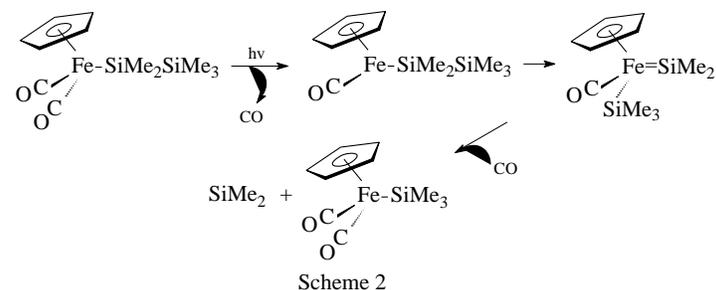
Scheme 1

Now we had two disilyl-substituted iron complexes, **1** and **2** in which the Si₂ group was in two very distinctive environments, attached directly to the metal center, **1**, or attached to another ligand of the metal, **2**. This permitted, for the first time, a study of the Si-Si bond in the coordination sphere of a metal and to discern any difference in chemistry based upon the positioning within the coordination sphere of the metal. The photochemical reactivity of **1** and **2**, as discovered in our laboratory, is outlined in equations 2 and 3, respectively.



It was immediately clear that having the Si₂ group directly bonded to the Fe center had a major impact, namely directly activating the Si-Si bond of the disilane group. This groundbreaking result formed the basis of much subsequent research over the following years.

A mechanism for this new activation of the Si-Si bond in disilanes was proposed and is outlined in Scheme 2.

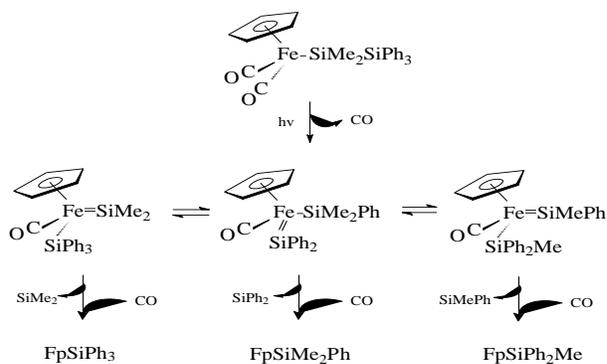


The initial step of the proposed mechanism involved the well-established elimination of the CO group to transform the 18-electron starting material to a reactive 16 electron species. The next step we proposed was novel and unprecedented. It involved the 1,2-migration of the Me₃Si group to the iron centre and the concomitant formation of the two-electron donor silylene-Fe linkage, to return to an 18 electron metal system. We proposed this silyl(silylene)iron complex to be a transient species and that the CO

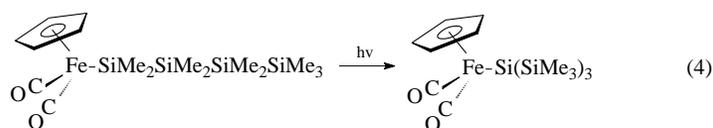


eliminated in the first step further displace the Me_2Si group to form the isolated monosilyl complex. This mechanism clearly indicated why the metal-silicon bond was essential to the Si-Si bond activation.

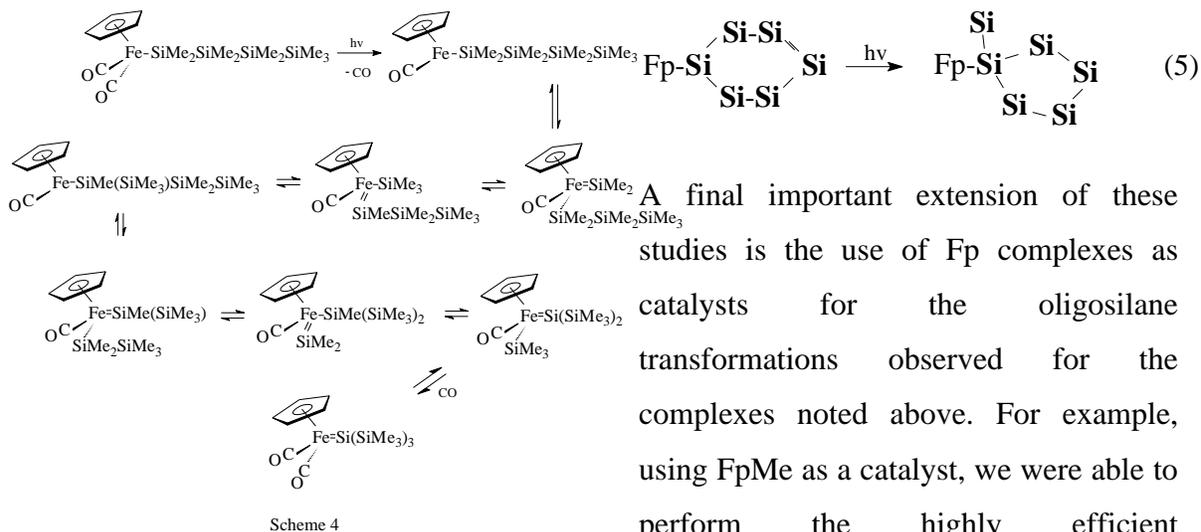
Enlargement of the type of disilyl group to include mixed substituents, e.g. $\text{FpSiMe}_2\text{SiPh}_3$, and study of their photochemistry yielded another pivotal and seminal result. The products obtained from such photochemistry were a mixture of FpSiMe_2Ph , FpSiMePh_2 and FpSiPh_3 , a totally unexpected result. This indicated that the silyl(silylene) transient persisted long enough, even in the presence of CO, to be involved in a dynamic equilibrium involving 1,3 Si to Si alkyl/aryl shifts such that eventual silylene displacement by CO gave the observed products, Scheme 3.



Extension of this study to trisilyl- and tetrasilyl-Fp derivatives illustrated a further major discovery due to the original research by Jorge. Irradiation of the tetrasilyl-Fp complex exhibited a dramatic rearrangement to form a tertiary tetrasilyl product, equation 4 (Pannell et al., 1989), with no SiMe_2 elimination.

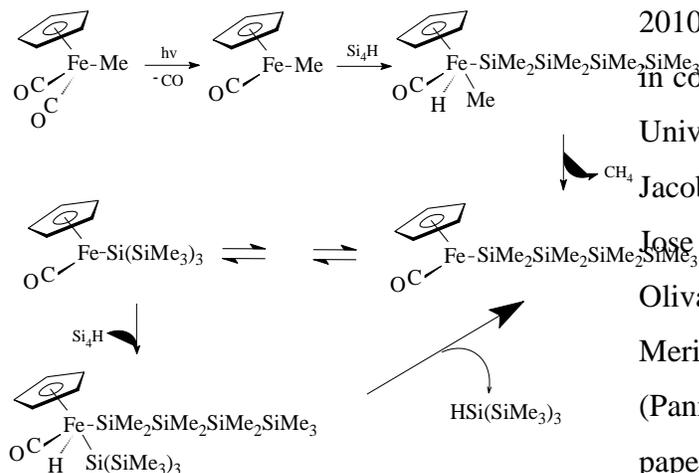


This result, very distinctive, suggested that the various sterically encumbered silyl(silylene) iron transients were resistant to silylene displacement in the presence of CO. Furthermore, it was possible to demonstrate isomerization processes occurring via both 1,3-alkyl shifts as well as the 1,2 Si shifts. Such results opened up another new chemistry for the Si-Si bonded metal system, unprecedented in the non metal-substituted analogs.



This tetrasilyl isomerization is very efficient and the process can be monitored by NMR but no intermediates can be observed. It is a quite remarkable transformation. It led directly to studies of other oligosilyl-Fp systems, for example the cyclic permethylated-hexasilyl-Fp system upon irradiation isomerizes to the ring contracted product outlined in equation 5, but with maintenance of the 6 silicon atoms. Upon photochemical irradiation the non-metal substituted cyclohexasilane eliminates SiMe₂ to form the corresponding ring contracted cyclopentasilane thereby illustrating another aspect of the very specific metal atom activation of the oligosilane systems.

A final important extension of these studies is the use of Fp complexes as catalysts for the oligosilane transformations observed for the complexes noted above. For example, using FpMe as a catalyst, we were able to perform the highly efficient photochemical transformation of the permethylated linear tetrasilane Me₃SiMe₂SiMe₂Me₂SiMe₂SiH (Si₄H) to the tertiary isomer (Me₃Si)₃SiH (Pannell et al., 1994). The mechanism proposed for the formation of this useful and popular reducing agent is illustrated in Scheme 5 and is based upon the irreversible elimination of methane during the process (Pannell et al., 2010).



Scheme 5

This very brief description of new chemistry directly related to Jorge's pioneering studies is illustrative of the advances in the understanding and use of transition metals in modifying the properties of oligosilanes. Other extensions and sidelines derived from this research led Jorge to investigate the mass spectral and single crystal structural analysis of disilanes (Pannell et al., 1990; Guerrero et al., 1992; Guerrero et al., 1994); the photochemical properties of ferrocenylpolysilanes (Villegas et al., 2003); and expansion of the LDA induced migrations to Ge, Sn and Pb derivatives of the Fp and related system (Cervantes et al., 1989; Sharma et al., 1995) and quantum chemical predictions on unusual Si-Si bonded fragments (Ortega-Moo et al.,

2010). Much of this work was performed in collaboration with his colleagues at the Universidad de Guanajuato including Jacobo Gomez Lara, Antonio Guerrero, Jose Luis Mata-Mata, Eulalia Ramirez-Oliva, Antonio Villegas, and Gabriel Merino. The 1986 organometallic article (Pannell et al., 1986) and the following papers related to silicon-transition metals have by now around 300 citations in the chemical literature.

Going back to 1981-1982 initial collaboration with Jorge in the topic of hydrosilylation reactions of acetylenes some papers were published as part of the master thesis of Guillermo González-Alatorre and the work of Eulalia Ramírez-Oliva under the advice of Jorge and me (Ramírez-Oliva et al., 1996; Rivera-Claudio et al., 1996; Cervantes et al., 2000).

Finally, I wish to pay respect to the major contributions of Dr. Francisco Cervantes-Lee, to the research at U. T. El Paso in the area of silicon metal chemistry and other aspects of our program. Paco was a friend and dedicated to his art of single crystal X-ray analysis with a diligence, creativity and intellectual rigor that reflects



magnificently on his education that commenced at the Universidad de Guanajuato. You should be proud of his contributions to science, just as you are of those of Jorge Cervantes Jauregui.

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