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Transition-Metal-Catalyzed Silylene Expulsion from, and/or Rearrangement of, Oligosilanes

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Summary: Photochemical treatment of $HSiMe_2SiMe_2R$ ($R = Me$) with a catalytic amount of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$, (1) led to the high-yield formation of Me_2Si, trapped efficiently with $HSi(SiMe_3)_3$. The use of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)SiMe_3$ (2) as catalyst in a thermal reaction does not produce silylene but causes isomerization of the disilane ($R = Ph$). Photochemical treatment of $HSiMe_2SiMe_2SiMe_2SiMe_3$ with a catalytic amount of 1 initially produced $HSi(SiMe_3)_3$ with further transformation to $HSiMe_2Si(SiMe_3)_3$ via silylene insertion. However, thermal catalysis using 2 yielded only $HSi(SiMe_3)_3$. Both thermal and photochemical catalytic processes proceed via equilibrating Fe silyl silylene intermediates.

The photochemical transformation of disilyl and trisilyl derivatives of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ (Fp), resulting in the elimination of SiR_2, is well-established (eq 1).[1–3] In contrast, linear and cyclic oligosilyl groups containing four or more Si atoms result predominantly in high-yield isomerization reactions to form tris(silyl)silane derivatives (eq 2).

$$\mathrm{FpSiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{FpSiMe_3} + \mathrm{SiMe_2} \tag{1}$$

$$\mathrm{FpSiMe_2SiMe_2SiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{FpSi(SiMe_3)_3} \tag{2}$$

These reactions proceed via equilibrating silyl silylene complexes, i.e., $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiMe_2)Si_nMe_{2n+1}$, formed by α-elimination subsequent to initial CO expulsion. In the case of the disilane ($n = 1$) the silylene is readily eliminated, whereas for the tetrasilane, and higher homologs, a series of 1,3-silyl and -methyl migrations proceed down a thermodynamic chain, resulting in the photostable tris(silyl)silane product. The desirability of performing such transformations of oligosilanes in a catalytic manner is self-evident. Randolph and Wrighton have reported that silyl exchange is readily effected upon photochemical irradiation of Fp^*SiMe_3 and Et_3SiH, a reaction that proceeds via initial CO loss, oxidative addition of Et_3SiH to the resulting 16-electron intermediate, reductive elimination of Me_3SiH, and recoordination of CO (eq 3).[2,4]

$$\mathrm{Fp^*SiMe_3} + \mathrm{HSiEt_3} \xrightarrow{h\nu} \mathrm{Fp^*SiEt_3} + \mathrm{Me_3SiH} \tag{3}$$

We report that a combination of the above reactions may be used to perform the silylene generation from disilanes (eq 1) and oligosilane isomerization (eq 2) in a catalytic manner using the intermediate $(\eta^5\text{-}C_5H_5)Fe(CO)SiMe_3$ generated photochemically from $FpSiMe_3$ (1) or thermally from $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)SiMe_3$ (2).[5] In a typical silylene generation reaction photochemical treatment of $HSiMe_2SiMe_3$ in the presence of 5% 1 in a sealed Pyrex NMR tube led to the total transformation of the disilane to $HSiMe_3$ and $SiMe_2$. The silylene was trapped by either 2,3-dimethylbutadiene (27% yield) or $HSi(SiMe_3)_3$ (78%) (eq 4).[6a] The catalytic cycle is detailed in Scheme 1 (cycle A), and the results are closely related to the pioneering studies by the Kumada group involving silylene generation from $HSiMe_2SiMe_3$ catalyzed by platinum and nickel complexes.[7]

$$\mathrm{HSiMe_2SiMe_3} + \mathrm{HSi(SiMe_3)_3} \xrightarrow{h\nu} \mathrm{HSiMe_2Si(SiMe_3)_3} + \mathrm{HSiMe_3} \tag{4}$$

Similar photochemical treatment of mixtures of $HSiMe_2SiMe_3$ with either of the trapping agents used above, in Pyrex tubes but without 1, failed to produce any chemistry.

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(6) (a) A 5-mm Pyrex NMR tube was charged with 0.1 g (0.76 mmol) of $HSiMe_2SiMe_3$, 0.1 g (0.40 mmol) of $HSi(SiMe_3)_3$, and 5 mol % of 1 in 1.5 mL of dry benzene and sealed under vacuum. Photolysis using a Hanovia 450-W lamp at a distance of 10 cm was monitored by ^{29}Si NMR spectroscopy. After 10 h the $HSiMe_2SiMe_3$ had been consumed and resonances associated with the insertion product $HSiMe_2Si(SiMe_3)_3$ were observed (−9.15, −33.0, and −136.4 ppm) together with a minor amount of $HSiMe_2SiMe_2Si(SiMe_3)_3$ (−9.17, −15.7, −39.9, −132.2 ppm). GC/MS indicated the formation of the two products in 89% and 11% yields, respectively. The NMR solution was diluted into 10 mL of hexane and passed through a small column (1 × 2 cm) of silica gel and the resulting solution evaporated to dryness. The solid white residue was recrystallized from hexane to yield pure $HSiMe_2Si(SiMe_3)_3$ (0.096 g, 78%), whose spectroscopic and physical properties were identical with those reported.[8] (b) In a manner identical with that above 0.2 g (0.81 mmol) of $HSiMe_2SiMe_2SiMe_2SiMe_3$ was irradiated for 13 h with ^{29}Si NMR monitoring. The disappearance of the starting material was noted along with the appearance of $HSi(SiMe_3)_3$ and also $HSiMe_2Si(SiMe_3)_3$. Resonances indicating the formation of small amounts of other silane species were also apparent. Upon completion of the reaction GC/MS analysis showed the presence of $HSiMe_2Si(SiMe_3)_3$ (67%), $HSi(SiMe_3)_3$ (6%), $HSiMe_2SiMe_2Si(SiMe_3)_3$ (6%), and small amounts of HSi_3Me_7, ferrocene, and $FpSi(SiMe_3)_3$. Chromatography of the mixture via a silica gel column (2 × 10 cm) yielded a white solid that was 87% and 13%, respectively, $HSiMe_2Si(SiMe_3)_3$ and $HSiMe_2SiMe_2Si(SiMe_3)_3$ (0.14 g). (c) A 5-mm Pyrex NMR tube was charged with 0.11 g (0.44 mmol) of $HSiMe_2SiMe_2SiMe_2SiMe_3$ and 5 mol % 2. The tube was sealed under vacuum and placed in an oven maintained at 120 °C. The progress of the reaction was monitored by ^{29}Si NMR, and after 24 h no starting material was present, having been converted to $HSi(SiMe_3)_3$ with trace amounts of $HSiMe_2SiMe(SiMe_3)_2$. Workup as described above resulted in the isolation of 0.097 g (88%) of $HSi(SiMe_3)_3$.

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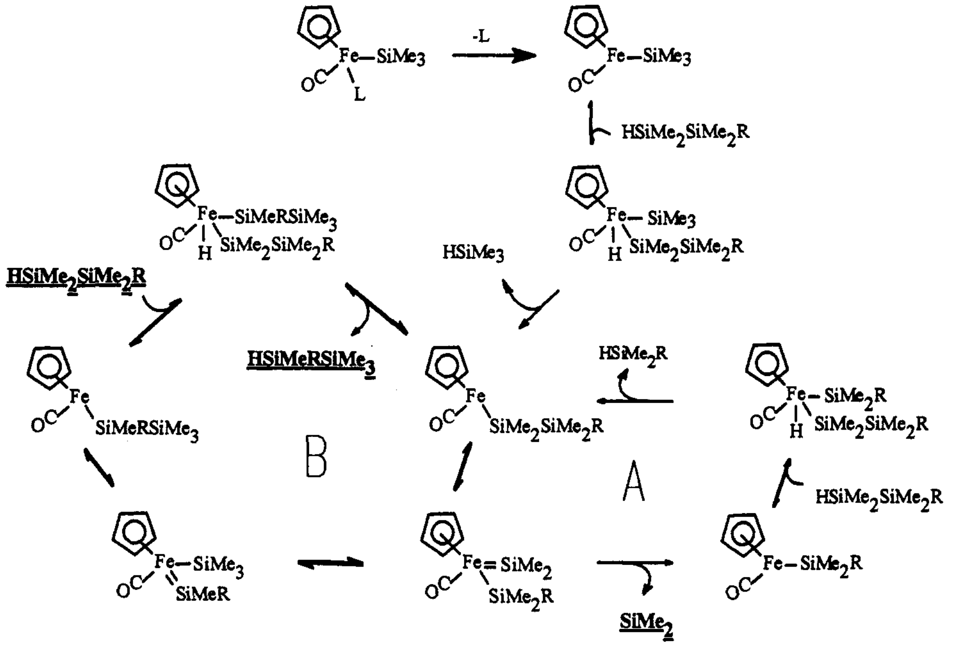
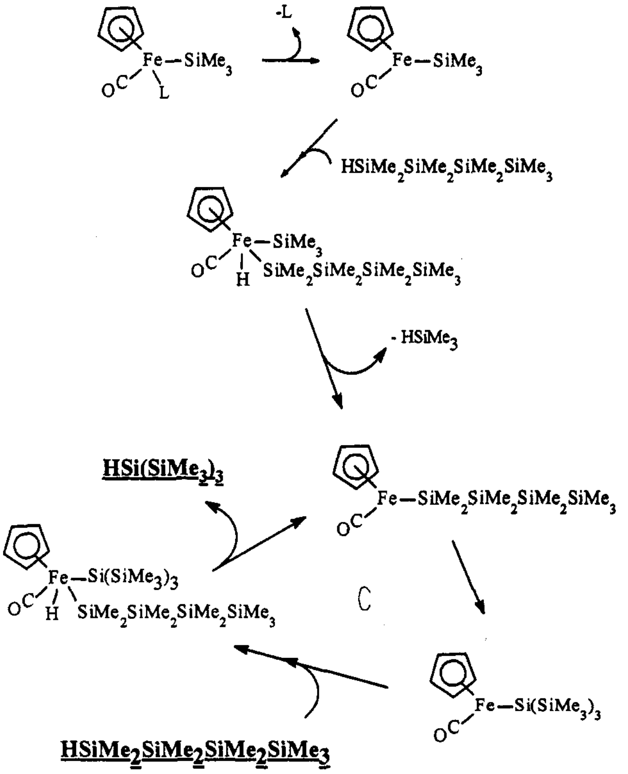
Scheme 1. Catalytic Process for Silylene Generation: Photochemical with Catalyst 1 (Cycle A; R = Me) and Thermal Isomerization with Catalyst 2 (Cycle B; R = Ph)



Scheme 2. Catalytic Process for Oligosilane Isomerization: Photochemical with Catalyst 1 and Thermal with Catalyst 2



The Turner group has shown that the CO substitution of the silylene from (η^5-C_5H_5)Fe(CO)(=$SiMe_2$)$SiMe_3$ to form $FpSiMe_3$ is a photochemical event.[3] Since the thermal process does not cause silylene expulsion, thermal treatment of $HSiMe_2SiMe_3$ and 2 in the presence of either 2,3-dimethylbutadiene or $HSi(SiMe_3)_3$ resulted in no chemical transformations. To prove that thermally generated equilibrating silyl silylene complexes occurred in the case of disilanes, we treated both isomers $PhSiMe_2SiMe_2H$ (3) and $HPhMeSiSiMe_3$ (4) independently to the same thermal conditions described in the presence of catalyst 2. Both reactions resulted in the formation of a mixture of 3 and 4 in the ratio 65:35, respectively, proving the thermal formation of equilibrating iron silyl silylene complexes (Scheme 1, cycle B).

To effect the isomerization of $HSiMe_2SiMe_2SiMe_2SiMe_3$, irradiation with $FpSiMe_3$ (5%) was performed and led to rapid formation of $HSi(SiMe_3)_3$, and the catalytic scheme is shown in Scheme 2.[6b] However, further transformation to the dimethylsilylene insertion reaction product $HSiMe_2Si(SiMe_3)_3$ was observed and it is apparent that some silylene expulsion occurred from the linear (η^5-C_5H_5)Fe(CO)$SiMe_2SiMe_2SiMe_2SiMe_3$ intermediates, a result that we had not previously observed when following the high-yield reaction described in eq 2 via ^{29}Si NMR.

To retard the silylene elimination and subsequent formation of $HSiMe_2Si(SiMe_3)_3$, we used the thermal route with catalyst 2. Treatment of a toluene solution of $HSiMe_2SiMe_2SiMe_2SiMe_3$ with 2 (5%) in a sealed NMR tube at 120 °C resulted in the quantitative formation of $HSi(SiMe_3)_3$ as the only observed product after 24 h (88% isolated yield).[6c]

Overall we have demonstrated that the chemistry of the Fp–oligosilane systems can be utilized to perform (a) catalytic silylene generation from disilanes (photochemically with catalyst 1), (b) isomerization of disilanes (thermally with catalyst 2), and (c) isomerization of linear oligosilanes using either method, but preferably the thermal route using 2 as catalyst. It is noteworthy that Blinka and West have shown that cyclosilanes may be isomerized by $AlCl_3$ only if 1% $FeCl_3$ is present;[9] however, we have also performed the photochemical isomerization of $HSiMe_2SiMe_2SiMe_2SiMe_3$ using either $Fe(CO)_5$ or $W(CO)_6$ as catalyst and the thermal isomerization using (η^5-C_5H_5)Ru$(PPh_3)_2CH_3$ as catalyst. The photochemical reactions proceed smoothly, however, as with the photochemical catalysts using 1, subsequent to isomerization, some silylene insertion occurred. Using the Ru catalyst,

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[9] Blinka, T. A.; West, R. *Organometallics* **1986**, *5*, 128.

a mixture of $(Me_3Si)_3SiH$ and $(Me_3Si)_2MeSiSiMe_2H$ (55:45) was formed. These results suggest that a variety of metal complexes may be used as the catalytic species in the chemistry described, including preferential isomer formation, and we are actively pursuing this concept.

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