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Communications

Reactivity of the Base-Stabilized Bis(silylene)iron Complex (η^5-C_5H_5)Fe(CO)(η^2-$SiMe_2$-O^tBu-$SiMe_2$): Elevated Temperature Trapping of $SiMe_2$ by R_3EH (R = Me_3Si, E = Si, Ge) and Elimination of $Me_2(O^tBu)SiSiMe_2H$ by *n*-Bu_3SnH

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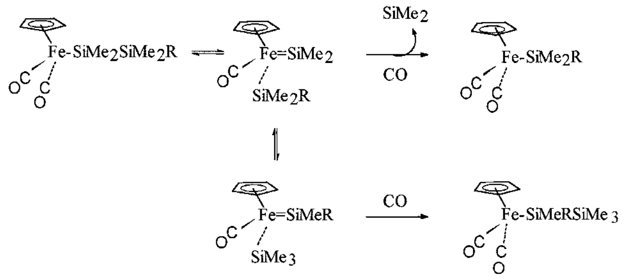
Summary: The base-stabilized silylene complex (η^5-C_5H_5)-Fe(CO)(η^2-$SiMe_2$-O^tBu-$SiMe_2$) is unreactive toward ($Me_3Si)_3EH$ (E = Si, Ge) under photochemical irradiation or at room temperature. However, at 80 °C it reacts, presumably via the equilibrium concentration of base-free complex (η^5-C_5H_5)Fe(CO)($SiMe_2O^tBu$)(=$SiMe_2$), to transfer the silylene group and form ($Me_3Si)_3ESiMe_2H$. Attempts to transfer the $SiMe_2$ group to tributyltin hydride led to formation of bis(tributylstannyl)iron complexes.

The transition-metal silylene complexes LM=SiR_2 have been proposed as transients in a number of metal-mediated silylene group transfers,[1] including metal-catalyzed Si−Si bond formation.[2] Although many metal silylene complexes have been characterized,[3] only scattered reports on their direct reactivity are available.[4] The Tilley group reported that the cationic ruthenium silylene $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2Ru{=}SiPh_2]^+$ transfers the silylene group to alcohols, ketones, and acetic acid,[4b] and the related osmium complex $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2Os{=}SiMe_2]^+$ reacts with benzyl chloride to form the (dimethylchlorosilyl)osmium(III) derivative, a possible clue to the mechanism of the copper-catalyzed Direct Process.[4c] We report the elevated-temperature reaction between the base-stabilized bis(silylene)iron complex (η^5-C_5H_5)Fe(CO)(η^2-$SiMe_2$-O^tBu-$SiMe_2$) (**1b**) and R_3EH (R = Me_3Si, E = Si, Ge; R = ^nBu, E = Sn), which demonstrates silylene transfer from such base-stabilized complexes forming Si−Si and Si−Ge bonds.

Scheme 1



The photolysis of (η^5-C_5H_5)Fe$(CO)_2SiR_2SiR_3$ results in initial CO expulsion, followed by α-elimination to form transient iron silyl silylene complexes that can isomerize via a series of 1,3-alkyl/aryl migrations.[5a] Continued irradiation results in silylene elimination or recombination isomerizations when the silicon chain exceeds 2, e.g. R = $Me_3Si(SiMe_2)_n$ (*n* = 1, 2, etc.) in Scheme 1.[5b,c]

We have isolated the iron−silylene intermediates as intramolecular aryl$Cr(CO)_2$ species,[5e] and the Ogino group has demonstrated that the presence of an alkoxy group on silicon results in the formation of stable alkoxy-stabilized bis(silylene)iron complexes, (η^5-C_5H_5)-Fe(CO)(η^2-SiR_2-OR′-SiR_2).[6] The latter complexes do not undergo photochemical silylene elimination reactions, and in general, they are very stable complexes. The Ogino group also showed that the base-stabilized complexes readily react with methanol[4d] and using VT NMR

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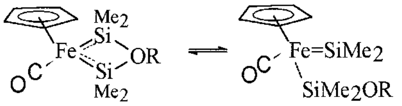
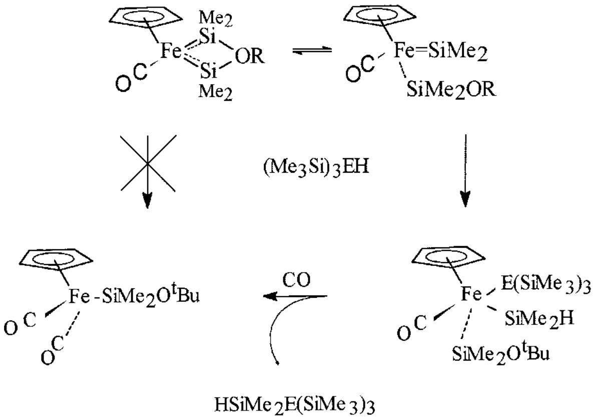
spectroscopy showed that at elevated temperatures these complexes exist in equilibrium with the base-free form, (η^5-C_5H_5)Fe(CO)(SiR_2OR)(=SiR_2)[6c] (eq 1).



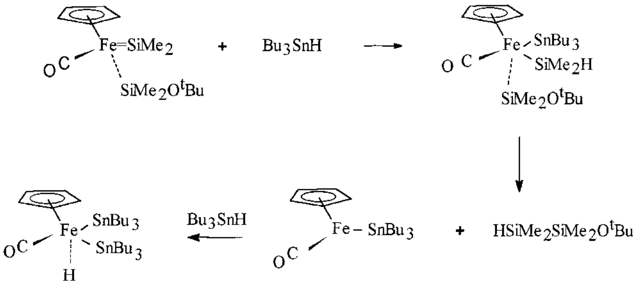
(1)

The presence of $(Me_3Si)_3SiH$ during the photochemical irradiation of (η^5-C_5H_5)Fe$(CO)_2SiMe_2SiMe_2$-O^{t}Bu (**1a**) does not interfere with the direct formation and isolation of the base-stabilized complex, and no further chemistry is observed. This is in contrast to non-base-stabilized analogues formed as transients upon photochemical treatment of (η^5-C_5H_5)Fe$(CO)_2SiR_2SiR_3$, where the silylene could be readily intercepted by $(Me_3Si)_3SiH$.[5d] However, we reasoned that the equilibrium concentration of the base-free silylene was too small for a significant reaction to occur and have repeated related reactions at elevated temperatures, 80 °C, where significant concentrations are present. After the room-temperature photochemical irradiation of **1a** in the presence of $(Me_3Si)_3SiH$ to form **1b**, we stopped irradiating, raised the temperature of the mixture, and monitored the ensuing reaction by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy.[7] Such analysis demonstrated the formation of $(Me_3Si)_3Si-SiMe_2H$,[8] $(Me_3Si)_3Si-Si(SiMe_3)_2$,[9] Fp-$Si(SiMe_3)_3$,[5b] and Fp-$SiMe_2O^t$Bu. We suggest that the mechanism outlined in Scheme 2 satisfactorily accounts for this product distribution, and it is relevant that the addition of SiH to metal silylenes to form disilylmetal complexes has been successfully modeled using density functional theory.[2d]

Scheme 2



Scheme 3



The formation of high yields of $(Me_3Si)_3SiSi(SiMe_3)_3$ suggests that addition of the Si−H bond to the metal silylene may involve a radical process, reminiscent of benzyl chloride addition to the Os-silylene complex noted above.[4c] Similar results were obtained using $(Me_3Si)_3GeH$ as the trapping reagent. Both the bulky silane and germane we used are useful reducing agents with weak E−H bonds.[11]

We attempted to perform a similar trapping experiment with the well-known organotin reducing agent ^{n}-Bu_3SnH. We monitored the reaction by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy and did not observe the formation of the $SiMe_2$ insertion product $^nBu_3SnSiMe_2H$. The observed reaction products and proposed reaction sequence is outlined in Scheme 3.

The hydridobis(stannyl)iron complex CpFe(CO)$(SnBu_3)_2$(H) (**2**) was isolated in 16% yield by column chromatography.[13,14] The other major product identified by NMR spectroscopy, $HSiMe_2SiMe_2$-O^{t}Bu, was synthesized independently to confirm its spectroscopic assignments.[15,16] It seems that, after addition of the SnH bond to the Fe=Si linkage, the greater strength of the Fe−Sn bond precludes reductive elimination of $^nBu_3SnSiMe_2H$ and favors elimination of the disilane. Fur-

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(7) In a typical experiment, a 5-mm Pyrex NMR tube was charged with 0.04 g (0.11 mmol) of $FpSiMe_2SiMe_2O^t$Bu[6a] and 0.081 g (0.32 mmol) of $(Me_3Si)_3SiH$ in 1.0 mL of degassed C_6D_6 and sealed under vacuum. Photolysis using a 450 W medium-pressure mercury lamp, at a distance of 5 cm, was monitored by NMR spectroscopy. After 4 h of irradiation, **1b** was cleanly formed. No side products were noted. Thermolysis of the product mixture was carried out at 80 °C in an oven. The progress of the thermolysis reaction was monitored by NMR spectroscopy. After 16 h, ^{29}Si NMR spectroscopy showed the complete consumption of **1b** and the formation of $(Me_3Si)_3SiSiMe_2H$,[8a] $(Me_3Si)_3SiSi(SiMe_3)_3$,[9b] $FpSi(SiMe_3)_3$,[5b] $FpSiMe_2O^t$Bu[7b] along with unreacted $(Me_3Si)_3SiH$ and trace amounts of unidentified silicon-containing compounds. GC/mass spectroscopic analysis of the reaction mixture also confirmed the formation of $(Me_3Si)_3Si-SiMe_2H$ (17% yield) and $(Me_3Si)_3Si-Si(SiMe_3)_3$ (33% yield), respectively. The solvent was removed from the reaction mixture under vacuum, and 5 mL of hexane was added. The solution was filtered and passed through a small column (silica gel, 1 × 2 cm), and the resulting solution was evaporated to dryness. The solid residue was recrystallized twice from hexanes to yield $(Me_3Si)_3SiSiMe_2H$ (0.01 g, 10% yield), whose spectroscopic and physical properties were identical with those reported.[5d,8a] Using the same general procedure, $(Me_3Si)_3GeSiMe_2H$[8b] was isolated in 15% yield from the thermolysis reaction of **1b** with $(Me_3Si)_3GeH$. Similar results were obtained by starting with a pure sample of **1b** rather than forming it in situ. However, in this case the relative yield of $FpSiMe_2O^t$Bu was greatly reduced and is presumably formed by the liberation of CO from general decomposition pathways of the complexes involved in the chemistry. (b) Attempts to make this material by a direct route, e.g. $[Fp]^-Na^+ + ClSiMe_2O^t$Bu, led to the desired product, bp 100−110 °C (0.01 mm/Hg), contaminated by an uncharacterized material which, to date, has defied separation. NMR (ppm, 300 MHz, C_6D_6): ^1H, 4.16 (C_5H_5), 1.29 (^{t}Bu), 0.70 ($SiMe_2$); ^{29}Si, 56.0. Mass spectrum (*m/z*, % ion current): $FpSiMe_2O^t$Bu, molecular ion peak, $M^+ = 308$ (6%), 280 (M − CO) (6%), 252 (M − 2 CO (5%), 235 (M − ^{t}BuO, 8%), 196 (M − C_4H_8, 18%), 180 (M − C_4H_8O, 6%), 131 ($SiMe_2O^t$Bu, 7%), 121 (C_5H_5Fe, 8%), 56 (Fe, 4%).

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(10) Thermolysis of **1b** with Ph_2MeSiH in the presence of catalytic amounts of benzoyl peroxide was carried at 80 °C in an oven. NMR spectroscopy shows the formation of $FpSiPh_2Me$, $FpSiMe_2O^t$Bu, and unidentified silicon compound(s) with ^{29}Si resonances at 28.2 and −4.3 ppm.

(11) (a) Chatagilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188. (b) Brook, M. A. In *Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley: New York, 1999; p 175.

(12) (a) Dixon, C. R.; Netherton, M. R.; Baines, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 11049. (b) Jones, K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336.

thermore, this result lends credence to the absence of free silylene species generated by the reaction conditions.

To date we have not been able to trap $SiMe_2$ by the reaction of **1b** with unhindered silanes, i.e., Ph_2MeSiH and Et_3SiH, in the presence or absence of radical initiators such as benzoyl peroxide.[10] This has precedents, since both we and the Baines group have used $(Me_3Si)_3SiH$ as a successful trapping agent for silylenes/germylenes in circumstances where the use of Et_3SiH failed.[5d,12]

The results presented illustrate the capacity of a discrete Fe=Si complex to react with E−H bonds (E = Si, Ge, Sn) entailing the ultimate formation of Si−Si bonds, confirming a recent suggestion from less direct evidence.[8b] The results also resolve the apparent distinction in reactivity between the base-stabilized iron silylenes, $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^2\text{-}SiR_2{-}OR'\text{-}SiR_2)$, and the transient non-base-stabilized forms $(\eta^5\text{-}C_5H_5)Fe(CO)(SiR_3)({=}SiR_2)$.

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(13) A 5 mm Pyrex NMR tube was charged with 0.086 g (0.25 mmol) of **1b** and 0.22 g (0.75 mmol) of $^nBu_3SnH$ in 1.0 mL of degassed C_6D_6 and sealed under vacuum. Thermolysis of the mixture was carried out at 80 °C in an oven. The progress of the reaction was monitored by NMR spectroscopy. After 2 h, ^{29}Si NMR spectroscopy showed the resonances at 3.4 and −41.6 ppm due to the formation of 1-*tert*-butoxy-2-hydrido-1,1,2,2-tetramethyldisilane, $HSiMe_2SiMe_2O^tBu$, and another resonance at −4.9 ppm due to $HSiMe_2O^tBu$. The ^{119}Sn NMR showed a resonance at 132.6 ppm due to the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)(^nBu_3Sn)_2H$ (**2**), along with another small resonance at −83.8 ppm due to $Bu_3SnSnBu_3$. After 10 h of thermolysis **1b** was completely consumed and the volatile materials were removed at 50 °C under vacuum. The residue was extracted from 10 mL of hexanes, filtered, and passed through a small column (silica gel, 1 × 3 cm). The orange band was eluted with hexanes, and upon evaporation of the solvent 0.03 g (16% yield) of **2** was obtained. Complex **2** was independently synthesized from the photochemical reaction of $FpSn^nBu_3$ with $^nBu_3SnH$ in a sealed NMR tube. All the spectroscopic data are in agreement with the reported data.[14.]

(14) Akita, M.; Oku, T.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1991**, *10*, 3080.

(15) (a) Tobita, H.; Wada, H.; Ueno, K.; Ogino, H. *Organometallics* **1994**, *13*, 2545. (b) Ueno, K.; Masuko, A.; Ogino, H. *Organometallics* **1997**, *16*, 5023.

(16) *tert*-Butoxyhydridodisilane, $HSiMe_2SiMe_2O^tBu$, was synthesized by modification of the reported method.[15] A 5 mm Pyrex NMR tube was charged with 0.61 g (3.2 mmol) of $HSiMe_2SiMe_2NEt_2$[15b] and 0.5 g (6.75 mmol) of ^tBuOH in 1 mL of C_6D_6 at 0 °C. The NMR tube was sealed under vacuum and heated at 80 °C for 2 h in an oven. After 2 h, ^{29}Si NMR spectroscopy showed the disappearance of resonances at −2.8 and −42.4 ppm due to the aminohydridodisilane and the appearance of two new resonances at 3.7 and −41.3 ppm due to the formation of *tert*-butoxyhydridodisilane, $HSiMe_2SiMe_2O^tBu$. Distillation through a small column at 98−100 °C gave the title compound (0.15 g, 36% yield). ^1H NMR (ppm, 300 MHz, C_6D_6): 0.17 (d, 6H, J = 4.5 Hz, $SiMe_2$), 0.29 (s, 6H, $SiMe_2$), 1.20 (s, 9H, ^tBu), 3.95 (m, 1H, J = 4.5 Hz, Si−H). ^{13}C NMR (ppm, 75.5 MHz, C_6D_6): −6.35 ($SiMe_2$), 2.66 ($SiMe_2$), 32.20 (CMe_3), 72.49 (CMe_3). ^{29}Si NMR (59.6 MHz, C_6D_6): 3.7, −41.3 ($SiMe_2H$). IR (hexane, cm^{-1}): 2095.6 (Si−H).