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Characterization of Strongly Bound Transition-Metal–Molecular Silane Cationic Complexes in the Gas Phase

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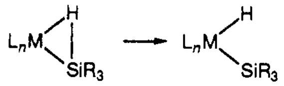
Summary: Formation and characterization of strongly bound molecular silane–Fe$^+$ complexes are described in the gas phase by using Fourier transform mass spectrometry (FTMS). The relative order of silane binding energies is Me$_2$SiH$_2$ > Me$_3$SiH > MeSiH$_3$ > Me$_4$Si > SiH$_4$. The binding energy of SiH$_4$ exceeds 31.3 ± 1.8 kcal/mol, and the binding energy of Me$_2$SiH$_2$ is ca. 39.9 ± 1.4 kcal/mol.

The oxidative addition of a Si–H bond to a transition-metal center is an obligatory step in many transition-metal-mediated transformations of organosilanes, including hydrosilation[1] and silane alcoholysis.[2] Formation of an η^2-Si–H coordination complex (three-center–two-electron bond; 1) is a prerequisite step for formal oxidative addition to yield 2. Recently, several examples of coordination complexes of 1 have been generated and characterized.[3–9] 1 is important because it is intermediate toward formal Si–H oxidative addition and is related to the corresponding H–H and C–H three-center–two-electron bond complexes.[10] The most intensely studied system has been the interaction of Si–H with CpMn(CO)$_2$, where electron-withdrawing substituents on the silane favor formal oxidative addition.[4] Photoelectron spectroscopy[4] has provided information on the extent of electron density donation to or from a metal center or bound silane; however, there is little information concerning binding energies.[11] In this communication we describe the formation of *strongly* bound molecular silane–Fe$^+$ coordination complexes in the gas phase. Methylsilanes, Me$_x$SiH$_{4-x}$ (x = 0–4), were studied; all yielded formation of molecular coordination complexes with Fe$^+$, and their binding energies were bracketed by ion/molecule displacement reactions.



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Experiments were performed by using a modified Nicolet FTMS-1000 Fourier transform mass spectrometer.[12–14] FeCO$^+$ was generated by electron impact ionization of Fe(CO)$_5$, and Fe(CH$_2$CH$_2$)$^+$ was produced by reaction of Fe$^+$ (laser desorption/ionization)[15] with n-butane (reaction 1).[16] Precursor reagents were admitted into the vacuum chamber *via* a pulsed solenoid inlet valve.[17] A 1-s delay follows the opening of the pulsed valve to allow the pulsed reagents to be removed from the vacuum chamber. Then, the desired ion is isolated by swept ejection pulses[12,13] and allowed to react with a static pressure ((2–6) × 10^{-8} Torr) of a neutral reagent.[18] A static argon pressure of 1 × 10^{-5} Torr was maintained throughout these experiments and served both to facilitate ion thermalization prior to reaction and to act as the target for collision-activated dissociation (CAD).[19,20]

$$\mathrm{Fe^+} + n\text{-}\mathrm{C_4H_{10}} \rightarrow \mathrm{Fe(CH_2CH_2)^+} + \mathrm{C_2H_6} \qquad (1)$$

Silanes (Me$_x$SiH$_{4-x}$, x = 0–4) react rapidly with FeCO$^+$ to yield exclusive displacement of CO (reaction 2). **3** may exist either as a molecularly bound silane–Fe$^+$ complex or

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$$FeCO^+ + Me_xSiH_{4-x} \rightarrow \underset{\mathbf{3}}{(FeMe_xSiH_{4-x})^+} + CO \qquad (2)$$

as an insertion species (e.g., $HFe(SiMe_2H)^+$ or $(H)_2Fe(SiMe_2)^+$ for Me_2SiH_2). Insight into the structure of **3** can be obtained by studying specific reactivity and by a consideration of how Fe^+ reacts with silanes. Fe^+ is inert with SiH_4 and forms exclusive adducts with $MeSiH_3$ and Me_4Si (eff = 0.001 and 0.27, respectively).[21] These adducts are presumably stabilized by infrared radiative emission.[22] In contrast, Fe^+ reacts with Me_2SiH_2 and Me_3SiH by reactions 3 and 4 with rate constants (k) of (2.0 ± 1.0) ×

$$Fe^+ + Me_2SiH_2 \xrightarrow{0.10} (FeMe_2SiH_2)^+ \qquad (3a)$$

$$\xrightarrow{0.90} FeSiC_2H_6^+ + H_2 \qquad (3b)$$

$$Fe^+ + Me_3SiH \xrightarrow{0.10} (FeMe_3SiH)^+ \qquad (4a)$$

$$\xrightarrow{0.35} FeSiC_3H_8^+ + H_2 \qquad (4b)$$

$$\xrightarrow{0.55} FeSiC_2H_6^+ + CH_4 \qquad (4c)$$

10^{-10} (eff = 0.18) and (6.1 ± 3.0) × 10^{-10} cm^3 molecule^{-1} s^{-1} (eff = 0.65), respectively.[23,24] Fe^+ reacts with $(CH_3)_2SiD_2$ to yield dehydrogenation exclusively as D_2 loss, and $(CH_3)_3SiD$ yields demethanation exclusively as CH_3D and dehydrogenation predominantly as HD (a trace of H_2 loss is also observed). Reactions 3 and 4 combined with isotopic labeling suggest that Fe^+ initially inserts into a Si–H bond followed by elimination of H_2 or CH_4.

Ethene and ethene-d_4 react with the silane adducts ($(FeSiH_4)^+$, $(FeMeSiH_3)^+$, and $(FeMe_4Si)^+$) formed in reaction 2 to yield exclusive silane displacement, with *no* H/D scrambling observed with ethene-d_4. The silane adduct $(FeMe_2SiH_2)^+$, formed by reaction 2, yields both adduct formation and silane displacement with ethene (reaction 5; k = (7.7 ± 2.3) × 10^{-10} cm^3 molecule^{-1} s^{-1}, eff

$$(FeMe_2SiH_2)^+ + C_2H_4 \xrightarrow{0.10} (FeMe_2SiH_2)C_2H_4^+ \qquad (5a)$$

$$\xrightarrow{0.90} FeC_2H_4^+ + Me_2SiH_2 \qquad (5b)$$

= 0.76). Similar results were obtained for reaction with ethene-d_4, with *no* H/D exchange observed. Me_2SiH_2 reacts with $Fe(CH_2CH_2)^+$ to yield both ethene displacement (0.57) and adduct formation (0.43). CAD of the adduct, $(FeMe_2SiH_2)C_2H_4^+$, yields competitive Me_2SiH_2 (0.78) and ethene (0.22) losses at low collision energy. In contrast to the above silane displacement reactions, the $(FeMe_3SiH)^+$ adduct reacts with ethene to yield both silane displacement and formation of $FeSiC_3H_8^+$ (formally a dehydrogenation process) (reaction 6; k = (6.6 ± 2.0) ×

$$(FeMe_3SiH)^+ + C_2H_4 \xrightarrow{0.74} FeC_2H_4^+ + Me_3SiH \qquad (6a)$$

$$\xrightarrow{0.23} FeSiC_3H_8^+ + (C_2H_6) \qquad (6b)$$

$$\xrightarrow{0.03} (FeMe_3SiH)C_2H_4^+ \qquad (6c)$$

10^{-10} cm^3 molecule^{-1} s^{-1}, eff = 0.65). A consideration of thermodynamics strongly suggests that the neutral species lost in reaction 6b is ethane and *not* C_2H_4/H_2 losses (ca. 33 kcal/mol less favorable).[25] Ethene-d_4 yields similar results, with ethane loss exclusively as $C_2D_4H_2$. Reaction of Me_3SiH with $FeC_2H_4^+$ yields competitive adduct formation (0.33) and ethane loss (0.67). Ethane loss as $C_2D_4H_2$ (0.38) is observed for reaction of $FeC_2D_4^+$ with Me_3SiH, as well as adduct formation (0.62).

The *complete* absence of H/D exchange for reaction of the (Fe–silane)$^+$ adducts with ethene-d_4 suggests that insertion into the Si–H bond has *not* occurred. H/D exchange by reversible ethene insertion/β-hydrogen elimination would be expected for a Si–H insertion species.[26,27] Consequently, the (Fe–silane)$^+$ adducts are believed to consist of molecular silane bound to Fe^+. The displacement of CO from $FeCO^+$ combined with silane displacement from the (Fe–silane)$^+$ adducts by ethene indicates that $D^0(Fe^+–CO)$ = 31.3 ± 1.8 kcal/mol[28] $< D^0(Fe^+–(Me_xSiH_{4-x})) \leq D^0(Fe^+–CH_2CH_2)$ = 39.9 ± 1.4 kcal/mol.[29] Observation that Me_2SiH_2 displaces ethene from $FeC_2H_4^+$ and that ethene displaces Me_2SiH_2 from $(FeMe_2SiH_2)^+$ suggests that $D^0(Fe^+–Me_2SiH_2) \approx D^0(Fe^+–C_2H_4)$. Hence, Fe^+ forms *strongly* bound molecular silane complexes! The relative binding energy of the silanes to Fe^+ was determined by silane/silane displacement reactions (e.g., reaction 7).

$$Fe(Me_3SiH)^+ + Me_2SiH_2 \rightarrow Fe(Me_2SiH_2)^+ + Me_3SiH \qquad (7)$$

These results reveal the following order of relative silane binding energies:

$$Me_2SiH_2 > Me_3SiH > MeSiH_3 > Me_4Si > SiH_4$$

Reaction with mixed deuterated silanes (e.g., $Fe(Me_3SiH)^+$ with Me_2SiD_2) revealed *no* H/D exchange, again consistent with formation of molecular silane–Fe^+ complexes. The bis(silane) adduct $Fe(Me_4Si)_2^+$ is readily formed by reaction 8. Me_4Si is readily displaced by the silanes

$$Fe^+ + 2Me_4Si \rightarrow Fe(Me_4Si)_2^+ \qquad (8)$$

Me_3SiH, Me_2SiH_2, and $MeSiH_3$ to produce mixed bis(silane) adducts. For example, $Fe(Me_3SiH)(Me_2SiH_2)^+$ is formed by reaction of $Fe(Me_4Si)_2^+$ with a mixture of

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Me_3SiH and Me_2SiH_2. SORI-CAD[30] of these mixed bis(silane) adducts yields initial, exclusive loss of the more weakly bound silane consistent with the above relative order of binding energies.

We now consider the structure of the $Fe(silane)^+$ adducts. The binding energy of Fe^+ to propane has recently been found to be 19 ± 2 kcal/mol.[31] This binding energy is significantly less than that for the above silanes (>31 kcal/mol). The strong binding energy coupled with the specific dehydrogenation of Me_2SiH_2 strongly suggests that Fe^+ interacts with a Si–H bond instead of a C–H bond of methylsilanes. It has been found that metals which display a weak interaction with C–H bonds may display strong interactions with Si–H bonds.[4] This interaction could be in the form of a nearly linear Fe^+–H–Si bond angle[32] or in the form of a three-center–two-electron bond complex similar to 1.

We believe that structure 1 is more likely for the $Fe(silane)^+$ adducts on the basis of the numerous examples of 1 in the literature.[3–9] If the nature of the interaction of the silane with Fe^+ is purely electrostatic, then the binding energy should follow silane polarizability with Me_4Si, the most strongly bound silane. The above relative order of silane binding energies clearly indicates that the interaction is more complicated than that of a simple ion–dipole model. The general electronic features of 1 involve donation of electron density from a Si–H σ bond to an empty metal orbital (σ interaction) and back-donation of electron density from filled metal orbitals to the Si–H σ^* orbital (σ^* interaction).[3,33] The extent of this electron donation should be reflected in the binding energy. The relative order of silane binding energies may be accounted for by considering both of these factors (polarizability and σ/σ^* electron donation). Me_4Si is unique in that it does not contain a Si–H bond. In this case, the bonding could be dominated by an ion–dipole interaction with some Si–C or C–H σ/σ^* interaction.

It is interesting that the two silanes that are reactive with Fe^+ are the two most strongly bound molecular species. Surprisingly, Me_2SiH_2 reacts ca. 3 times slower with Fe^+ than with Me_3SiH. This suggests that there is a lower barrier for insertion into the Si–H bond of Me_3SiH than for Me_2SiH_2 (assuming that initial bond insertion is the rate-limiting step). We are currently studying the interaction of silanes with a variety of metal ion complexes, in order to more fully understand the factors affecting bond activation, and probing the reaction mechanism.

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