

Catalytic silane alcoholysis based on the $C_5H_5(CO)(PPh_3)Fe^+$ moiety. NMR spectroscopic identification of key intermediates

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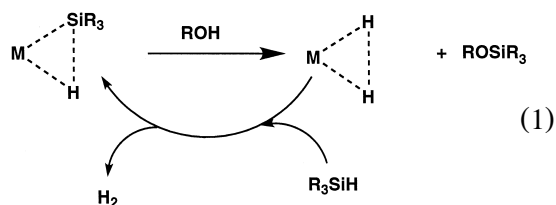
Abstract

The $Cp(CO)(PPh_3)Fe^+$ fragment has been shown to catalyze silane alcoholysis in the presence of the non-coordinating counterion, $B Ar'_4^-$ ($Ar' = 3,5-(CF_3)_2C_6H_3$). When ethanol is used, catalyst deactivation rapidly occurs. However, when phenol is utilized, catalytic activity continues until all of the phenol has been consumed. In each case, key intermediates in the catalytic cycle, including resting states, have been observed using low temperature NMR spectroscopy. The modes of catalyst deactivation when ethanol is used have also been determined. © 1998 Elsevier Science B.V.

1. Introduction

In an attempt to find new methods to selectively protect alcohols, a variety of silane alcoholysis catalysts have been investigated² [3–10]. Wilkinson's catalyst ($Rh(PPh_3)_3Cl$) has been shown to carry out this type of reaction by Ojima [11] and Corriu [12–14]. However, tertiary silanes do not react and competitive hydrosilation is a problem if an alcohol possessing a double bond is utilized. Singer has had good success using $(CO)_2(PPh_3)_2RuCl_2$ as a catalyst as it is very active and no competing hydrosilation is observed [15]. Other catalysts that are similarly selective include $Rh_2(pfb)_4$ ($pfb =$ perfluorobutyrate), and $((CO)_4MnBr)_2$ [16,17]. In all of the above cases, the catalysis is pre-

sumed to occur through the reaction of an alcohol with either a silyl hydride complex or an η^2 -silane complex which leads to the formation of a silyl ether and a dihydride complex or an η^2 - H_2 complex. H_2 is then displaced by silane to close the catalytic cycle (Eq. (1)).



While all of the catalysts described above are neutral metal complexes, Crabtree has reported extraordinary rates of silane alcoholysis (ca. $50,000 \text{ h}^{-1}$) using the cationic complex, $[IrH_2(THF)_2(PPh_3)_2]SbF_6$ [18]. The tremendous activity has been ascribed to the fact that two solvent molecules can dissociate from the metal

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² For reviews of silane alcoholysis see Refs. [1,2].

center allowing both alcohol and silane to coordinate simultaneously which then react in an intramolecular fashion. Attempts to detect intermediates in the catalytic cycle were unsuccessful; however, Crabtree was able to synthesize a model compound in which the silane molecule was bound to the metal center in a non-classical fashion.

We have recently reported the generation and characterization of cationic iron η^2 -silane complexes of the type $\text{Cp}(\text{CO})(\text{PR}_3)\text{Fe}(\text{HSiEt}_3)^+$ [19] which are rapidly hydrolyzed by water. For example, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{HSiEt}_3)^+$, **1**, is formed upon protonation of the neutral iron silyl complex with $\text{H}(\text{OEt}_2)_2\text{BAr}'_4$ ($\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$). Complex **1** reacts rapidly with water to give a cationic iron $\eta^2\text{-H}_2$ complex, **2**. If excess silane is present, H_2 is displaced at room temperature by Et_3SiH which reforms the silane complex. This species is stable after the solution has been 'dried' by this combination of reactions (Scheme 1).

This sequence of steps is similar to those proposed for systems known to carry out catalytic silane alcoholysis and we therefore chose to investigate the catalytic activity of these iron systems in this regard. We report here the first example of a silane alcoholysis catalyst in which all of the intermediates in the cycle have been detected by variable temperature NMR spectroscopy and modes of catalyst deactivation have been identified.

2. Results and discussion

2.1. Preliminary observations

Preliminary experiments were carried out to test the catalytic activity of the iron triethylsilane complex, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{HSiEt}_3)^+$, **1**, in the alcoholysis of Et_3SiH . A solution of **1** was treated with 1000 equivalents of Et_3SiH and 200 equivalents of ethanol. Et_3SiOEt and H_2 were formed, and the course of the catalysis could be qualitatively monitored by measuring

H_2 evolution. The rate of evolution of H_2 gas at 20 s corresponded to 7.8 TO/min. However, activity rapidly dropped and at 12 min, the rate of H_2 evolution corresponded to only 1 TO/min even though only ca. 50 equivalents of silane had been consumed. After 20 min, no further activity could be measured. The system underwent a noticeable color change during the course of the reaction. The solution was initially a yellow-orange color, but after 5 min it turned light green. To probe the details of this catalysis, a series of variable temperature NMR experiments were carried out as described below.

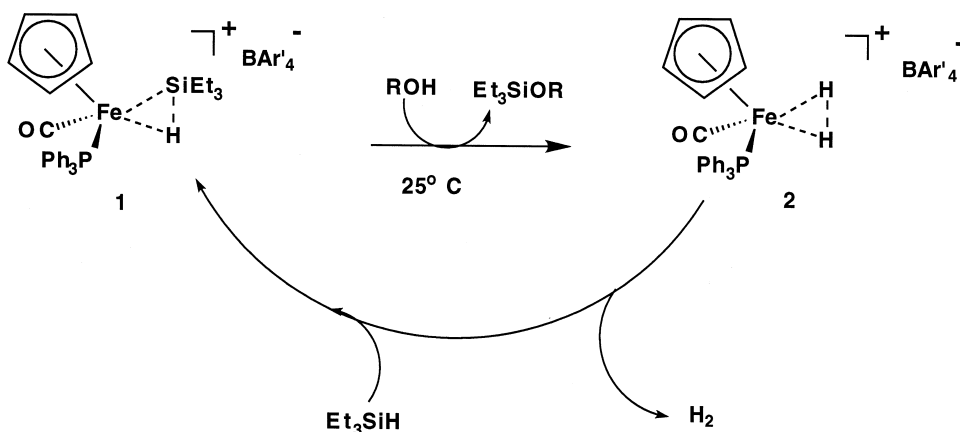
2.2. Variable temperature NMR studies of the catalytic system

The following series of reactions were carried out and monitored by variable temperature NMR spectroscopy in an attempt to observe catalytic intermediates and understand how catalyst deactivation was occurring. During the catalytic runs, there was an excess of triethylsilane present as well as numerous species bearing a triethylsilyl substituent, most of which possessed overlapping resonances in this region. Nevertheless, the catalysis was monitored using other resonances of the key intermediates and these are shown in Table 1. All of the intermediates were independently prepared (see Section 3) and the resonances listed in Table 1 were unique to these species and allowed their unambiguous identification.

The sequence of reactions described below is summarized in Scheme 2.

(1) $\text{Cp}(\text{PPh}_3)(\text{CO})\text{FeCH}_3$, **3**, was protonated in an NMR tube in CD_2Cl_2 using $\text{H}(\text{OEt}_2)_2\text{BAr}'_4$ at -78°C which gave both the iron ether complex, **4**, (identified by a Cp resonance at 4.72 ppm), as well as the aquo complex, **5**, (Cp resonance at 4.62 ppm) which is formed by reaction of the cationic iron fragment with trace water present in the solution. The two species were present in a 1:2 ratio.

(2) At -80°C , 20 equivalents of Et_3SiH were added to the sample. Observation at -60°C



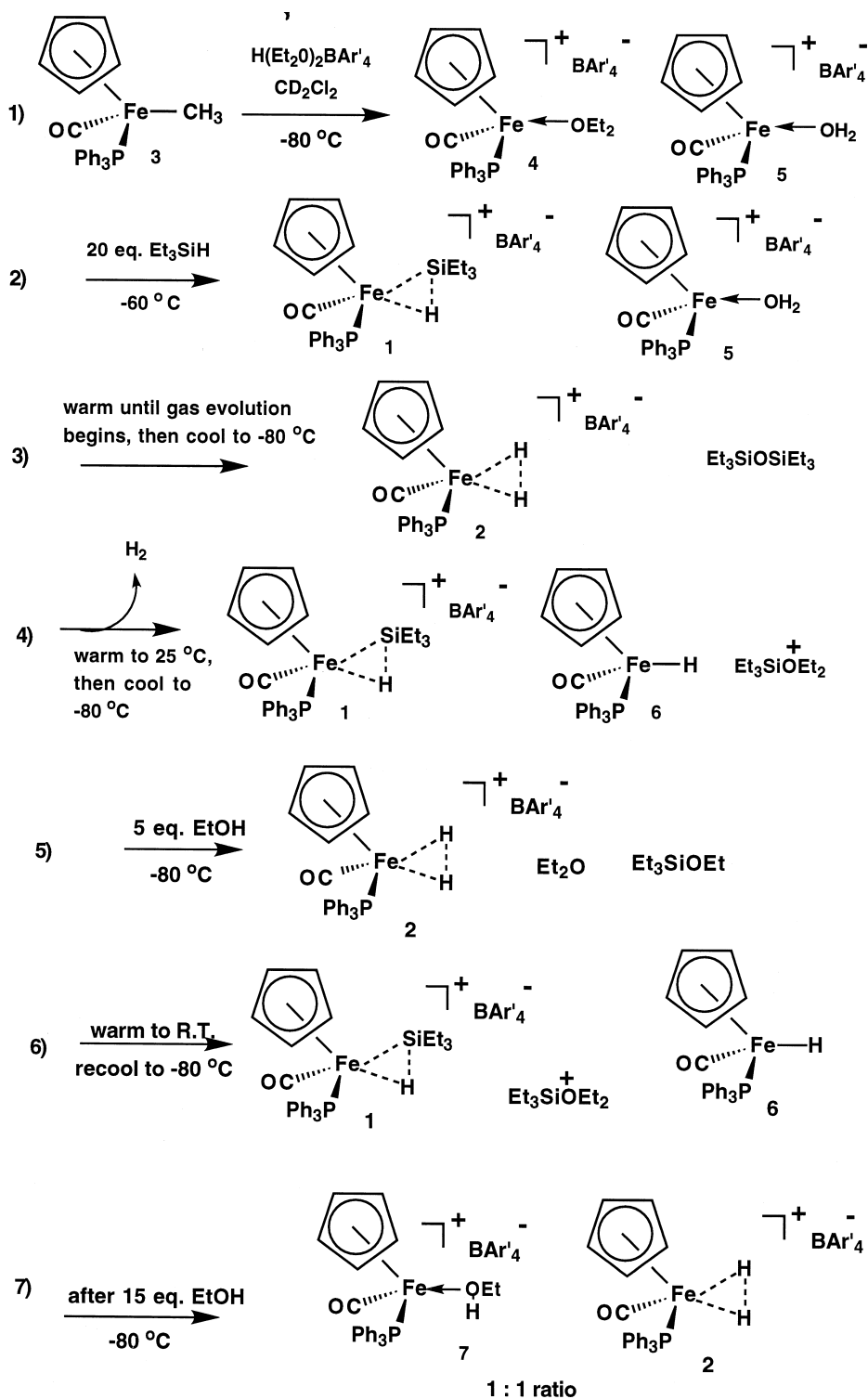
indicated that the silane had displaced the Et_2O from the iron center to give the cationic silane complex, **1**. This species was identified by a doublet at -16.6 ppm for the hydride reso-

nance and a Cp resonance at 4.76 ppm [19]. The aquo complex remained present.

(3) The NMR tube was removed from the probe and warmed briefly to room temperature.

Table 1
Characteristic ^1H NMR shifts used to identify key species in the catalytic cycle

<p>1</p>	<p>Cp 4.76 ppm Fe(Si-H) -16.6 (d)</p>	<p>2</p>	<p>Cp 4.90 ppm Fe(H)$_2$ -10.8 (broad)</p>
<p>4</p>	<p>Cp 4.72 ppm OCHHCH$_3$ 3.3 (mult) 3.1 (mult)</p>	<p>5</p>	<p>Cp 4.62 ppm</p>
<p>6</p>	<p>Cp 4.40 ppm Fe-H -13.6 ppm (d)</p>	<p>7</p>	<p>Cp 4.66 ppm CH$_2$ 2.74 (mult) CH$_3$ 0.54 (t)</p>
<p>$\text{Et}_3\text{Si}^+\text{OEt}_2$</p>	<p>OCH$_2$ 4.46 ppm (q) OCH$_2$CH$_3$ 1.48 (t)</p>		



Scheme 2.

Evolution of H_2 was observed. This occurs via the reaction of the water with the silane complex. Hydrolysis of the silane complex is presumed to give initially the protonated silanol and the neutral iron hydride, neither of which is observed. Rapid proton transfer gives the dihydrogen complex, **2**, which loses H_2 at room temperature. If the sample is recooled to -80°C as soon as gas evolution begins, then the iron dihydrogen complex, **2**, is the only organometallic species observed in solution (Cp, 4.90 ppm, $\text{Fe}(\text{H}_2)$, -10.8 ppm). It is important to note that for each equivalent of water present, 2 equivalents of silane are consumed since the initial hydrolysis product, Et_3SiOH , can react with another equivalent of silane complex to give hexaethyldisiloxane (vide infra).

(4) If the tube is rewarmed to 25°C until all the H_2 has evolved and then recooled to -80°C , three species are present in a 1:1:1 ratio: the silane complex, **1**, the neutral iron hydride complex, **6**, (Cp, 4.40 ppm, H, -13.6 ppm) and triethylsilyldiethyloxonium BAR'_4^- (OCH_2 , 4.46 ppm (q), OCH_2CH_3 , 1.48 (t)). The latter two species are formed upon reaction of Et_2O with the silane complex.

(5) At -80°C , 5 equivalents of ethanol were added to the NMR tube. Observation at this temperature indicated that the dihydrogen complex, **2**, was the only organometallic species present. The ethanol reacts rapidly with the silane complex giving a transient protonated silyl ether and the neutral iron hydride complex. Rapid proton transfer leads to formation of the dihydrogen complex. Ethanol also reacts with the triethylsilyldiethyloxonium tetraarylborate to give Et_2O and the protonated silyl ether which can also protonate the iron hydride complex.

(6) If the sample is warmed to room temperature, gas evolution occurs as Et_3SiH displaces H_2 . Upon recooling to -80°C , the silane complex, **1**, triethylsilyldiethyloxonium tetraarylborate, and the iron hydride complex, **6**, are present as observed previously.

(7) The same sequence of events is repeated upon addition of another 5 equivalents of ethanol

(10 equivalents total). However, upon addition of 5 more equivalents of ethanol at -80°C , followed by warming to room temperature, some gas evolution is evident and the solution turns green. Observation at -80°C indicates that no Et_3SiH remains; the iron dihydrogen complex, **2**, was found to be present in a 1:1 ratio with another organometallic species which was determined to be the iron ethanol complex, **7**, (Cp, 4.66 ppm). The latter species is presumed to be formed by displacement of H_2 by ethanol. Clearly, if ethanol is able to displace H_2 from the metal center, this provides a pathway for catalyst deactivation.

Given the potential importance of the previous result, we next examined the interaction of the iron dihydrogen complex, **2**, with ethanol more closely. The neutral iron hydride complex, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}$, **6**, was protonated at -80°C with $\text{H}(\text{OEt}_2)_2\text{BAR}'_4$. Observation at -80°C showed that the iron dihydrogen complex, **2**, was the predominant species. However, a small amount of the neutral iron hydride, **6**, still remained (10:1 ratio). Upon addition of 5 equivalents of ethanol at -80°C , the Cp resonances and the hydride resonances broadened significantly which is suggestive of exchange between the iron hydride and the dihydrogen complex. Confirmation of this hypothesis was obtained by cooling the sample to -110°C . At this temperature, the exchange process was frozen out and both Cp and hydride resonances for each complex were observed. The dihydrogen complex was the major species, but there was a significant amount of the iron hydride complex present (2:1 ratio). Upon addition of 5 more equivalents of ethanol to the NMR tube and observation at -110°C the iron hydride complex became the predominant species (3:2 ratio). Warming the solution to -100°C led to line broadening and further warming led to coalescence at ca. -95°C . Warming to 20°C led to formation of the ethanol complex, **7**, as the only observable organometallic species (Scheme 3).

This experiment provides evidence that ethanol can disrupt the catalytic cycle in two

ways. It can deprotonate the iron dihydrogen complex in a reversible fashion to give the iron hydride complex and EtOH_2^+ . However, ethanol also displaces H_2 from the metal center to give the ethanol complex.

During an actual catalytic run, bulk quantities of silane and ethanol are added to the reaction mixture and we sought to examine which species were predominant under these conditions. The catalyst system was prepared as before by protonation of $\text{Cp}(\text{PPh}_3)(\text{CO})\text{FeCH}_3$ with $\text{H}(\text{OEt}_2)_2\text{BAR}'_4$ followed by addition of 50 equivalents of Et_3SiH which gave the species described earlier (Scheme 4). At -80°C , 30 equivalents of ethanol were added giving a very pale green solution. Observation at -80°C indicated that the neutral iron hydride, **6**, was the major organometallic species present along with a small amount of the ethanol complex, **7**, (6:1 ratio). Presumably at this temperature, the acid/base reaction is the predominant reaction pathway and the presence of a large excess of ethanol favors the formation of the iron hydride complex via deprotonation of the dihydrogen complex. Upon briefly warming the tube to room temperature, the solution turned a dark green color. Reobservation at -80°C indicated that the ethanol complex, **7**, was now the major

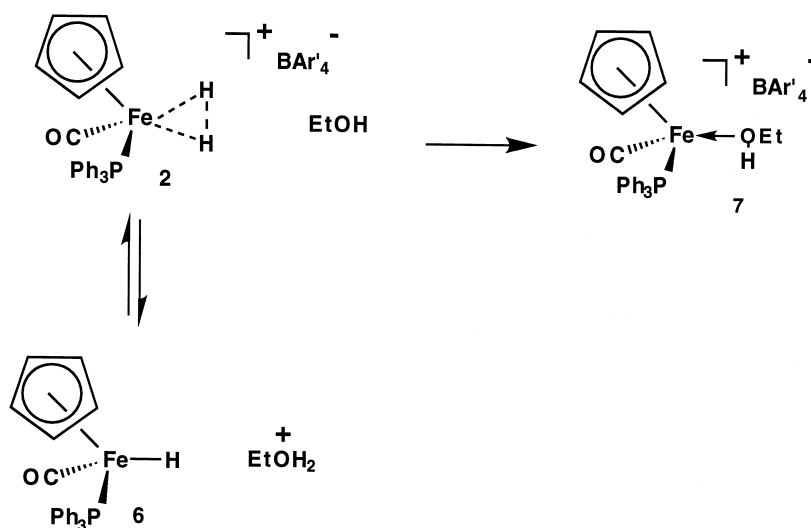
species present (ca. 2:1 ratio with respect to the iron hydride). H_2 was also evident in solution. When the sample was warmed to 20°C , complete conversion to the ethanol complex occurred. Although no iron dihydrogen complex was observed, it is clear that the conversion of the iron hydride to the ethanol complex must occur through loss of H_2 from the dihydrogen complex.

This result suggests that at 25°C in this catalytic cycle, the iron hydride complex, **6**, is the resting state. Conversion to the dihydrogen complex, **2**, must occur followed by displacement by silane in order to reenter the catalytic cycle. It appears that once the ethanol complex is formed, the catalyst is 'dead' as no further reaction occurs.

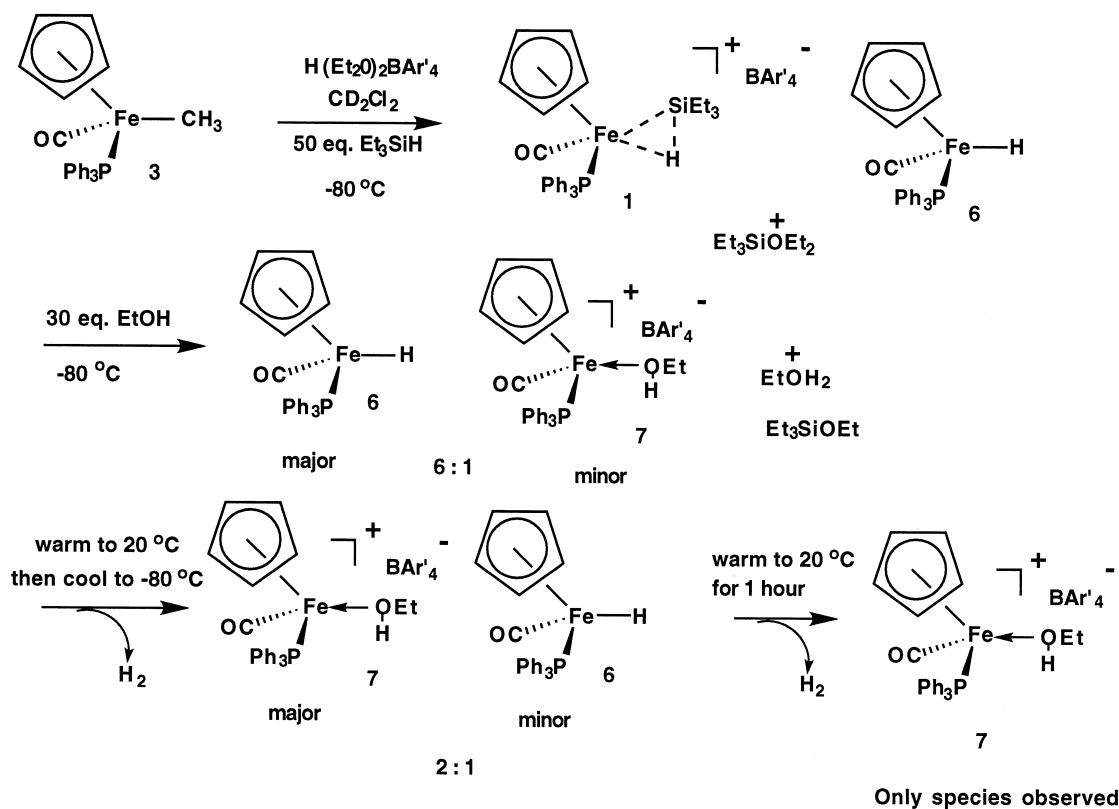
From these results, we concluded that both the basicity and the nucleophilicity of the alcohol are potentially important in deactivation processes. In an effort to extend catalyst lifetimes and improve activity phenol was examined.

2.3. Triethylsilane alcoholysis with phenol

$\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCH}_3$, **3**, was protonated with $\text{H}(\text{OEt}_2)_2\text{BAR}'_4$ at 0°C in CH_2Cl_2 and 2500



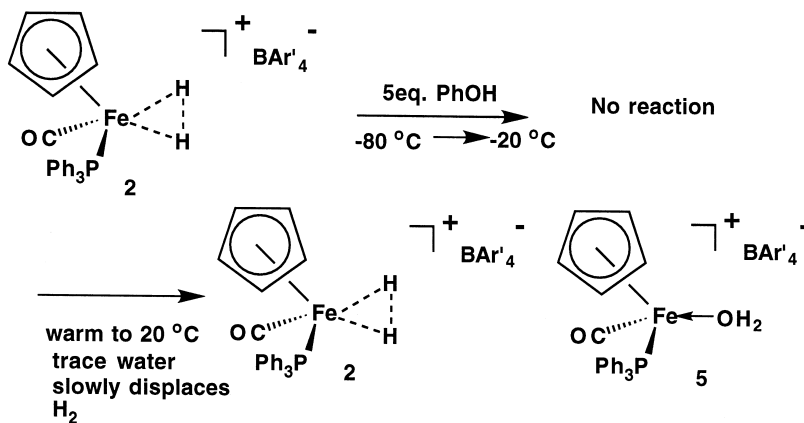
Scheme 3.



Scheme 4.

equivalents of Et_3SiH were added. The solution was warmed to room temperature and H_2 evolution occurred upon reaction of trace water with the silane complex. Next, 2000 equivalents of PhOH were added to the solution followed by

10,000 equivalents of both PhOH and Et_3SiH which led to vigorous gas evolution. Gas evolution was reasonably constant over the entire course of the reaction. After 30 min, measurement of H_2 evolution yielded a rate of 80

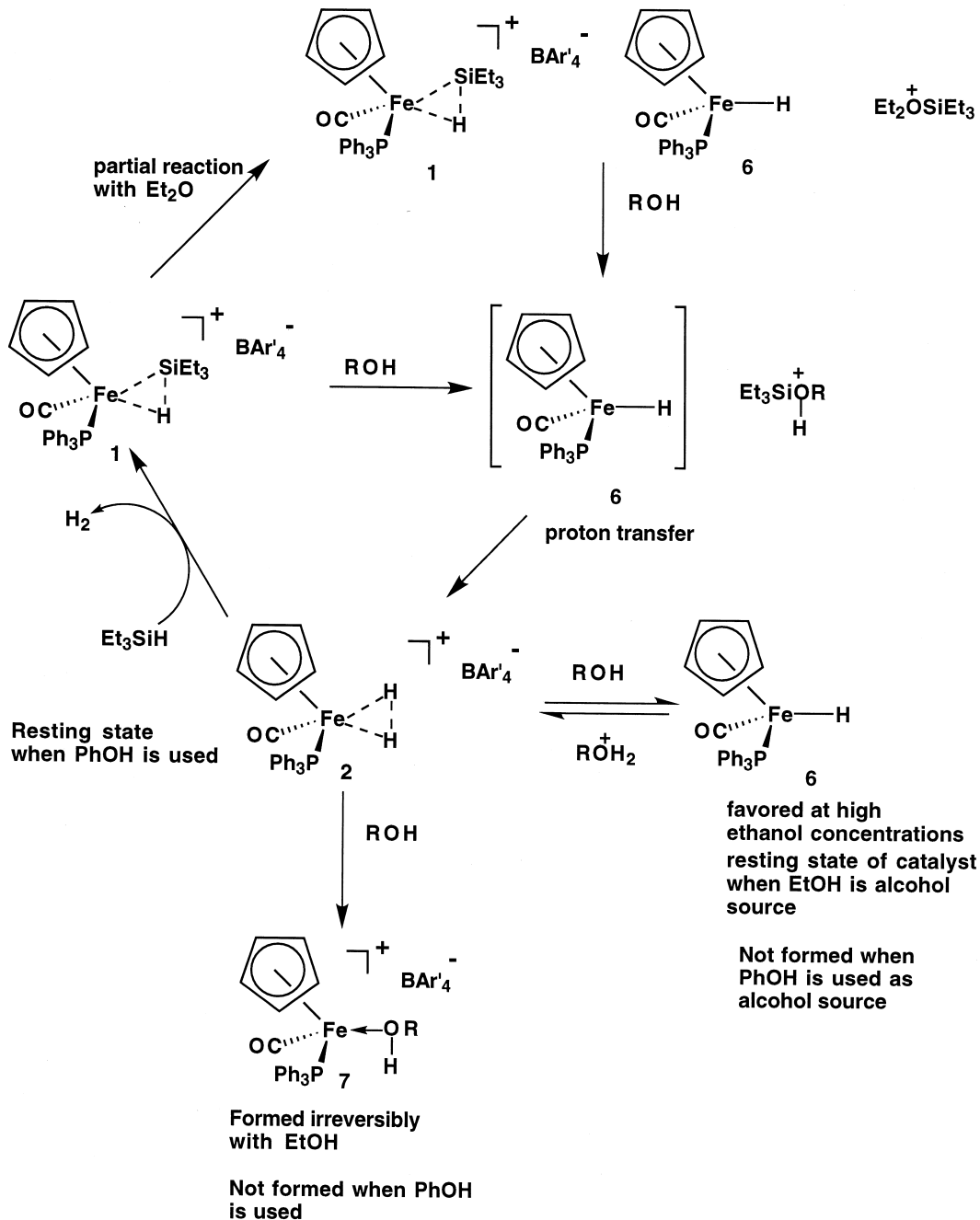


Scheme 5.

TO/min. The reaction was complete (no gas evolution) after 2 h and 40 min with an average rate of 75 TO/min over the entire reaction. No phenol remained and Et_3SiOPh was isolated in high yields. It is clear from this result that the

phenol does not deactivate the catalyst system as was the case with ethanol.

To probe the reasons for the drastic differences between ethanol and phenol, the reaction of the dihydrogen complex, **2**, with phenol was



Scheme 6.

examined (Scheme 5). The dihydrogen complex was prepared from protonation of the neutral iron hydride and observed by ^1H NMR spectroscopy at -80°C . Addition of 5 equivalents of PhOH at -80°C produced no change in the spectrum. It was clear that no deprotonation, reprotonation was occurring. No change in the system was observed up to -20°C , but at 0°C , a small resonance appeared at 4.62 ppm which is the Cp resonance for the aquo complex, **5**, (8:1 ratio). After 30 min at 20°C , the conversion of the dihydrogen complex to the aquo complex had progressed (3:1 ratio), and after 1 h, the aquo complex was the predominant species in solution. This experiment showed that phenol does not interact with the dihydrogen complex in the same manner as ethanol; it does not deprotonate the dihydrogen complex and it does not displace H_2 from the metal center. Since neither of the deactivation pathways is available, high turnover numbers can be achieved without catalyst deactivation. During a catalytic run, all traces of water would be consumed by reaction with the silane complex to form siloxanes.

For comparative purposes, the silane alcoholysis using phenol was examined by variable temperature NMR spectroscopy. In order to confirm that the above result was consistent with the presence of a large excess of phenol, the dihydrogen complex, **2**, was first generated and observed at -80°C . Next, 50 equivalents of PhOH were added. Observations were identical to those made above. No deprotonation of the dihydrogen complex occurred and upon warming to 20°C , only a small amount of the aquo complex formed. No phenol complex was observed. The sample was next cooled to -80°C and 60 equivalents of Et_3SiH were added. It was allowed to warm until catalysis began (gas evolution observed) and was then recooled to -80°C . NMR observation at this temperature showed only the iron dihydrogen complex, **2**, to be present which indicates that this species is the resting state of the catalytic cycle when phenol is used. The catalysis was allowed to run

to completion. Subsequent NMR observation showed the silane complex, **1**, the neutral iron hydride complex, **6**, and the triethylsilyloxonium species to be present.

Scheme 6 summarizes the silane alcoholysis activity of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{HSiEt}_3)^+$. When ethanol is used, catalytic activity rapidly diminishes, however when phenol is used, catalyst turnover rates are constant until all of the phenol has been consumed. It has been demonstrated by using low temperature NMR spectroscopy that, upon treatment of the iron silane complex with an alcohol, the silyl ether and the $\eta^2\text{-H}_2$ complex are formed. However, the next step in the reaction pathway is clearly dependent on the alcohol that is utilized (Scheme 6). When ethanol is used, the dihydrogen complex, **2**, is readily deprotonated to give the neutral iron hydride complex, **6**, which is the catalyst resting state in the presence of excess ethanol. When this species is reprotonated to give the H_2 complex, displacement of H_2 by ethanol ultimately occurs and effectively terminates the catalytic cycle. On the other hand, when phenol, which is both less basic and less nucleophilic than ethanol, is utilized, the activity of the catalyst is high with no termination pathways evident. Phenol neither deprotonates the dihydrogen complex, **2**, nor displaces H_2 from the metal center. Under these conditions, the H_2 complex is the resting state in the catalytic cycle and in this case, the rate-determining step appears to be displacement of H_2 by Et_3SiH .

3. Experimental section

3.1. General

All manipulations were performed under an atmosphere of dry, deoxygenated nitrogen using Schlenk techniques with a double manifold vacuum line, or in a vacuum atmosphere dry box, unless otherwise noted. Nitrogen gas was purified by passage through a column of BASF catalyst (R3-11) heated to 130°C followed by a column of activated molecular sieves. ^1H chem-

ical shifts were referenced to residual protio solvent peaks (CHDCl_2 δ 5.32). ^{13}C chemical shifts were referenced to ^{13}C solvent signals (CD_2Cl_2 δ 53.8). Methylene chloride was purified and rendered oxygen-free by distillation under a nitrogen atmosphere using P_2O_5 . CD_2Cl_2 was dried over CaH_2 and vacuum transferred to a Kontes flask. Et_3SiH was purchased from Aldrich and stored over 4 Å molecular sieves followed by degassing. $\text{H}(\text{OEt}_2)_2^+\text{BAR}_4'^-$ [20,21], $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{CH}_3)$ [22], $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}^3$, and $\text{Ph}_3\text{C}^+\text{BAR}_4'^-$ [24] were prepared according to published procedures. $\text{Et}_3\text{SiOEt}_2^+\text{BAR}_4'^-$ was generated in situ using the procedure of Kira [25].

3.2. Generation of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{HOEt})^+\text{BAR}_4'^-$

$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{CH}_3)$ (10 mg, 0.023 mmol) and $(\text{Et}_2\text{O})_2\text{H}^+\text{BAR}_4'^-$ (1.1 eq., 26.2 mg, 0.026 mmol) were added to an NMR tube and kept in a -78°C bath. CD_2Cl_2 (0.7 ml) was added at -78°C . ^1H NMR observation at -40°C showed that $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{OEt}_2)^+$ was present. Ethanol (5 eq., 6.9 μl , 0.12 mmol) was added at -78°C and the tube was warmed to 0°C . Observation at this temperature showed that the ethanol complex had formed. At -80°C , the two diastereotopic methylene protons exhibit unique resonances as multiplets at 2.93 and 2.85 ppm. Upon warming to 0°C , the two sets of resonances overlap and are observed as a broad multiplet at 2.74 ppm. ^1H NMR (CD_2Cl_2 , 0°C) δ 4.66 ppm (s, C_5H_5), 2.74 (m, 2H, CH_2), 0.54 (t, 3H, $J = 7.0$ Hz, CH_3).

3.3. Catalysis of Et_3SiH alcoholysis using $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{HSiEt}_3)^+\text{BAR}_4'^-$

3.3.1. $\text{ROH} = \text{PhOH}$

A Schlenk flask charged with $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCH}_3$ (12 mg, 0.028 mmol) and

$\text{H}(\text{OEt}_2)_2^+\text{BAR}_4'^-$ (57.2 mg, 0.046 mmol) was placed in an ice bath. This mixture was dissolved in 3 ml of CH_2Cl_2 to give a green solution. Et_3SiH (2500 equivalents, 11.2 ml) was syringed into the solution. When the ice bath was replaced with a 25°C water bath the silane solution immediately became yellow and vigorous evolution of H_2 gas was observed. PhOH (2000 equivalents, 5.6 ml of a 10 M CH_2Cl_2 solution) was syringed into the flask. Then 10,000 equivalents (44.8 ml) of Et_3SiH and 10,000 equivalents (28.2 ml of a 10 M CH_2Cl_2 solution) of PhOH was added to the solution. Evolution of H_2 was monitored and at 30 min the rate of H_2 evolution corresponded to 80 TO/min. After 2 h and 40 min, H_2 evolution ceased and upon workup, PhOSiEt_3 was obtained in a 99% yield. The average rate of the catalysis over the entire reaction was 75 TO min^{-1} . ^1H NMR (CD_2Cl_2) δ 7.26 ppm (t, 2H, meta), 6.96 (t, 1H, para), 6.88 (d, 2H, ortho), 1.02 (t, 9H, $J_{\text{HH}} = 7.0$ Hz, SiCH_2CH_3), 0.78 (q, 6H, $J_{\text{HH}} = 7.0$ Hz).

3.3.2. $\text{ROH} = \text{ethanol}$

Et_3SiH (600 eq., 2.7 ml) was added to a CH_2Cl_2 or chlorobenzene (5 ml) solution of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCH}_3$ (12 mg, 0.028 mmol) and $\text{H}(\text{OEt}_2)_2^+\text{BAR}_4'^-$ (57.2 mg, 0.046 mmol) as above. Then ethanol (500 equivalents, 0.8 ml) was syringed into the flask and evolution of H_2 was monitored. At 20 s, the rate of evolution corresponded to 8 TO/min. The solution took on a green color within 5 min after the ethanol was added and the rate of H_2 evolution decreased over time. At 20 min, no measurable activity was observed.

3.4. Reaction of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{H}_2)^+$ with ethanol

$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe-H}$ (10 mg, 0.024 mmol) was added to an NMR tube and dissolved in 0.4 ml CD_2Cl_2 . The solution was cooled to -78°C and a solution of $\text{H}(\text{OEt})_2^+\text{BAR}_4'^-$ (2 equivalents, 48.6 mg, 0.048 mmol) in 0.4 ml CD_2Cl_2 was added to the tube. Observation at -80°C

³ $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}$ was prepared by methods described in Ref. [19]. An alternate route has been published previously: see Ref. [23].

showed that the dihydrogen complex was present in a 10:1 ratio with respect to the iron hydride complex. Addition of ethanol (5 equivalents, 7.0 μ l, 0.12 mmol) at -78°C led to the observation of broadened Cp and hydride resonances. Upon cooling to -110°C , the exchange process was frozen out and the dihydrogen complex was present in a 2:1 ratio with respect to the iron hydride complex. Addition of 5 more equivalents of ethanol shifted the equilibrium in favor of the hydride complex which was now the predominant species (3:2 ratio). Upon warming the tube, the Cp resonances broadened with coalescence at ca. -95°C . Warming to 20°C led to the formation of the ethanol complex as the exclusive species.

3.5. ^1H NMR studies of working catalyst solutions

The working catalyst system was examined by ^1H NMR spectroscopy. A series of reagents were added and spectra recorded at various times and temperatures to detect intermediates present in solution. Key intermediates, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{H}_2)^+$, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{OEt}_2)^+$, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{HSiEt}_3)^+$, and $\text{Et}_3\text{SiOEt}_2^+\text{BAR}_4'^-$ have been independently generated and are described below or elsewhere [19,25]. In the first experiment, ethanol is added stepwise to the NMR tube after an excess of Et_3SiH has been added. In the second experiment, after addition of 50 eq. of Et_3SiH , 30 eq. of ethanol is added at one time. In the third experiment, silane alcoholysis using PhOH is examined.

3.5.1. (I)

(a) $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}-\text{CH}_3$ (10 mg, 0.023 mmol) and $\text{H}(\text{OEt}_2)_2^+\text{BAR}_4'^-$ (2 equivalents, 48 mg, 0.046 mmol) were transferred to a 5 mm NMR tube and kept in a -78°C bath. CD_2Cl_2 (0.7 ml) was added at -78°C and the tube was warmed to -40°C until the solution turned green. ^1H NMR analysis at -40°C showed formation of the ether coordinated iron complex ($\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{OEt}_2)^+$) and the aquo complex $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{OH}_2)^+$ (Cp, 4.62 ppm)

(1:2 ratio). A sharp singlet at 0.18 ppm (CH_4) was also observed.

$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{OEt}_2)^+$: ^1H NMR (CD_2Cl_2 , -40°C) δ 7.7–7.0 ppm (m, aryl), 4.72 (s, C_5H_5), 3.30 (mult., 2H, $\text{Fe}(\text{O}(\text{C}H'H\text{CH}_3)_2)$), 3.11 (mult., 2H, $\text{Fe}(\text{O}(\text{C}H'H\text{CH}_3)_2)$), 0.67 (t, 6H, $J = 7.0$ Hz, $\text{C}H_3$).

(b) Next Et_3SiH (20 equivalents, 74.4 μ l, 0.46 mmol) was added via a syringe to the septum-capped tube at -78°C and the tube was warmed to -60°C . The solution turned yellow. Et_3SiH displaces Et_2O from the metal center to give the silane complex, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{HSiEt}_3)^+$. The aquo complex is still present.

$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{HSiEt}_3)^+$ (pertinent resonances): ^1H NMR (CD_2Cl_2 , -80°C) δ 4.76 ppm (s, C_5H_5), -16.6 (d, 1H, $J_{\text{PH}} = 29$ Hz, $J_{\text{SiH}} = 67.3$ Hz, $\text{Fe}(\text{SiH})$).

(c) The sample was then warmed to room temperature which leads to hydrolysis of the silane complex by water and subsequent loss of H_2 . After gas evolution had stopped, NMR analysis at -80°C showed the presence of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}$, $\text{Et}_2\text{OSiEt}_3^+\text{BAR}_4'^-$, and the silane complex in a 1:1:1 ratio.

$\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}$ (pertinent resonances): ^1H NMR (CD_2Cl_2 , -80°C) δ 7.7–7.0 ppm (m, aryl), 4.40 (s, C_5H_5), -13.6 (d, $J_{\text{HP}} = 74.1$ Hz, 1H, $\text{Fe}-\text{H}$).

$\text{Et}_2\text{OSiEt}_3+\text{BAR}_4'^-$ (pertinent resonances): ^1H NMR (CD_2Cl_2 , -80°C) δ 4.46 ppm (q, 4H, $J_{\text{HH}} = 7.1$ Hz, $(\text{CH}_3\text{C}H_2)_2\text{O}^+\text{SiEt}_3$), 1.48 ppm (t, 6H, $J_{\text{HH}} = 7.1$ Hz, $(\text{C}H_3\text{C}H_2)_2\text{O}^+\text{SiEt}_3$).

(d) H_2 pressure in the tube was released. The tube was cooled to -80°C and ethanol (5 equivalents, 6.9 μ l, 0.12 mmol) was added at this temperature. Warming the sample to room temperature until evolution of H_2 started, followed by immediate cooling at -80°C led to the observation of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{H}_2)^+$ as the only organometallic species. A sharp singlet at 4.55 ppm was observed for H_2 .

$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{H}_2)^+$ (pertinent resonances): ^1H NMR (CD_2Cl_2 , -80°C) δ 4.90

ppm (s, C_5H_5), -10.71 (br, $Fe(H_2)$).

(e) Warming the tube back to room temperature resulted in vigorous evolution of H_2 . H_2 pressure in the tube was released and when no further gas evolution was observed, the tube was recooled to $-80^\circ C$. The 1H NMR spectrum at $-80^\circ C$ showed $Cp(CO)(PPh_3)FeH$, $Et_2OSiEt_3^+BAR_4'^-$, $Cp(CO)(PPh_3)Fe(HSiEt_3)^+$ to be present.

(f) Repeating the same procedure using another 5 equivalents of ethanol gave the same result as above. After a total of ca. 15 equivalents of ethanol had been added, the solution turned green and the 1H NMR spectrum recorded at $-80^\circ C$ showed that the SiH resonance of Et_3SiH had disappeared indicating that all the silane had been consumed. (The water present in solution accounts for the consumption of the other 5 equivalents of silane.) $Cp(CO)(PPh_3)Fe(HOEt)^+$ and $Cp(CO)(PPh_3)Fe(H_2)^+$ were present in a 1:1 ratio.

3.5.2. (2)

An NMR tube was charged with $Cp(CO)(PPh_3)Fe-CH_3$ (10 mg, 0.024 mmol) and $H(OEt_2)_2^+BAR_4'^-$ (2 equivalents, 48.5 mg, 0.048 mmol) and cooled to $-80^\circ C$. CD_2Cl_2 (0.7 ml) was added followed by 50 equivalents of Et_3SiH (186 μl , 1.2 mmol). The tube was warmed to allow all of the trace moisture to react with the silane complex after which the species described earlier ($Cp(CO)(PPh_3)FeH$, $Et_2OSiEt_3^+BAR_4'^-$, $Cp(CO)(PPh_3)Fe(HSiEt_3)^+$) were found to be present. The tube was recooled to $-80^\circ C$ and 30 eq. of ethanol (42.7 μl , 0.73 mmol) were added which gave a light green solution. Observation at this temperature showed that the neutral iron hydride complex was present along with the iron ethanol complex (6:1 ratio). Upon warming the tube to room temperature, the solution took on a dark green color. Observation upon recooling to $-80^\circ C$ indicated that the iron ethanol complex was now the major species present (2:1 ratio with respect to the iron hydride complex). After 1 h at $20^\circ C$,

complete conversion to the iron ethanol complex had occurred.

3.5.3. (3)

$Cp(CO)(PPh_3)FeH$ (10 mg, 0.024 mmol) was weighed in an NMR tube in the dry box. The tube was cooled to $-80^\circ C$ and 0.3 ml of CD_2Cl_2 was added. $H(OEt_2)_2^+BAR_4'^-$ (2 equivalents, 49.3 mg, 0.049 mmol) was dissolved in 0.4 ml of CD_2Cl_2 and this was added via syringe to the NMR tube. Observation at $-80^\circ C$ showed $Cp(CO)(PPh_3)Fe(H_2)^+$ to be the only organometallic species present. $PhOH$ (50 equivalents, 1.2 mmol, 121 μl of a 10 M CH_2Cl_2 solution) was added to the tube. No reaction was observed to occur at $-80^\circ C$, but upon warming to $20^\circ C$, the aquo complex was observed as a minor species (1:8 ratio). The NMR tube was recooled to $-80^\circ C$ and Et_3SiH (60 equivalents, 1.4 mmol, 230 μl) was added. Upon warming the solution to $20^\circ C$, silane alcoholysis commenced and vigorous gas evolution was observed. The tube was returned to the probe at $-80^\circ C$ and observation at this temperature showed that $Cp(CO)(PPh_3)Fe(H_2)^+$ was the only organometallic species present. The tube was removed from the probe and the catalysis was allowed to continue. When gas evolution had stopped, NMR observation indicated that $Cp(CO)(PPh_3)FeH$, $Et_2OSiEt_3^+BAR_4'^-$, $Cp(CO)(PPh_3)Fe(HSiEt_3)^+$ were present.

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