# Silane Alcoholysis by a Nickel(II) Complex in an N, O, S Ligand Environment

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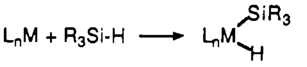
Transition metal catalyzed activation of silanes[1] can occur by oxidative addition (eq 1) or by formation of a $\sigma$ complex (eq 2).[2]


(1)


(2)

Oxidative addition appears to be required for the catalysis of alkene hydrosilation, because the key step is insertion of the unsaturated substrate into the M–H or M–Si bond.[3] Silane alcoholysis (eq 3),[4] a reaction we have previously studied in detail

$$R_3SiH + R'OH \rightleftharpoons R_3SiOR' + H_2 \qquad (3)$$

using iridium catalysts,[5] is thought to be catalyzed most efficiently by formation of an intermediate $\sigma$ complex. The metal is believed to polarize the Si–H bond and so favor nucleophilic attack by ROH. Unfortunately, it is difficult to eliminate Si–H oxidative addition as the true pathway, since a $\sigma$ complex can be in equilibrium with the corresponding oxidative addition product.[6] Few catalysts for this reaction at room temperature have been reported previously, namely $[IrH_2(THF)_2(PPh_3)_2]SbF_6$,[5] $Ru(PMe_3)_2(CO)_2Cl_2$,[7] $Co_2(CO)_8$,[8] and $IrX(CO)L_2$ and $[IrCl(C_8H_{14})_2]_2$.[9] In this paper, we report the first nickel catalyst and the first non-organometallic catalyst for this reaction.

The Si–H bond chemically resembles H–H, and systems which bind silanes as a $\sigma$ complex also seem to bind $H_2$ in the same way.[2] Since silane alcoholysis is a heterolytic reaction of Si–H, we hope that studying it will also allow us to understand $D_2/H^+$ exchange (eq 4), a heterolytic activation of $H_2$ that is observed both for

$$D_2 + H_2O \rightleftharpoons HD + HOD \qquad (4)$$

authentic $H_2$ $\sigma$ complexes[5] and in hydrogenase. Hydrogen is believed to be activated by the [Ni, Fe] hydrogenases[10] by binding of $H_2$ to the essential Ni ion. The coordination environment and oxidation states involved are controversial, but it is clear that both O or N and S donor atoms are in the coordination sphere. The coordination number for Ni is probably 5–6, and oxidation states from Ni(I) to Ni(III) have been proposed for various states of the enzyme. In prior work we have reported some functional models for hydrogenase reactions, such as $D_2/H^+$ exchange[11] and $H^+$ reduction to $H_2$.[12] In an attempt to understand the factors that lead to H–H activation, we now look at the related reaction of Si–H activation.

## Experimental Section

Nickel(II) acetate tetrahydrate ($Ni(OAc)_2{\cdot}4H_2O$), salicylaldehyde, thiosemicarbazide, and triethylsilane ($Et_3SiH$) were purchased from Aldrich. Spectrochemical grade solvents were used without further purification. Salicylaldehyde thiosemicarbazone ($tssH_2$) was prepared by reaction of thiosemicarbazide and salicylaldehyde in refluxing EtOH as reported previously.[13] In all kinetic experiments, the solutions were degassed by purging with $N_2$ and the reactions were performed anaerobically.

**Bis[(salicylaldehyde thiosemicarbazonato)nickel(II)], $[Ni(tss)]_2$.** To a solution of $Ni(OAc)_2{\cdot}4H_2O$ (0.249 g, 1 mmol) in ca. 20 mL of hot (70 °C) absolute ethanol (EtOH) was added a hot ethanolic solution of $tssH_2$ (0.195 g, 1 mmol) to give an orange-brown precipitate, which was filtered hot, washed with EtOH and acetone, and dried in air. Yield: 0.24 g (ca. 98%). Anal. Calcd (found) for $NiC_8H_7N_3OS$: C, 37.77 (38.14); H, 3.19 (2.78); N, 15.92 (16.68); S, 12.82 (12.71). IR (Nujol mull on NaCl plates), cm$^{-1}$: 3400 (w), 3253 (w, br), 3160 (w, br), 1601 (s), 1516 (s).

**Triethylsilane Alcoholysis.** Rates of ethanolysis of $Et_3SiH$ in 50% (v/v) DMSO–benzene solutions at 23 °C with various catalyst preparations (Table I) were measured manometrically by the method of Luo and Crabtree.[5] For the experiments of Figure 1, the reaction of equimolar amounts of $Ni(OAc)_2{\cdot}4H_2O$ and $tssH_2$ with 0.8 mmol of $Et_3SiH$ and 0.8 mmol of MeOH in 1.5 mL of 50% (v/v) DMSO-$d_6$–$C_6D_6$ was followed while purging with $N_2$ to remove the $H_2$. At 5-min intervals, ca. 0.3-mL aliquots of the reaction mixture were removed and added to NMR tubes containing 0.8 mmol of pyridine to quench the reaction. The amount of product formed was determined by comparison of the integrals of the ($CH_3CH_2$) resonances in the $^1H$ NMR of the product $Et_3SiOMe$ versus those of the reactant $Et_3SiH$, and rates were determined from these data. The experiments in Figure 3 were also performed by this NMR method using 0.01 mmol each of $Ni(OAc)_2{\cdot}4H_2O$ and $tssH_2$ either with or without an $N_2$ purge.

## Results

The salicylaldehyde thiosemicarbazone ligand ($tssH_2$, $o$-OH-$C_6H_4CH{=}NNHC(S)NH_2$)[13] contains both O and N donor groups as well as a semicarbazide sulfur that has strong thiolate character because the canonical form $S^-{-}C{=}NHR^+$ is the predominant contributor.[11a] Reaction of a 1:1 ratio of $tssH_2$ and $Ni(OAc)_2{\cdot}4H_2O$ in refluxing ethanol produced a deep orange solid in 98% yield. The infrared spectrum and elemental analysis were consistent with formulation of the product as $[Ni(tss)]_2$ (**1**), in which the ligand must be doubly deprotonated to maintain electroneutrality, and we propose the dimeric O-bridged **1** structure below by analogy with the structure of the tetramethyl derivative, determined by X-ray crystallography.[14] Compound **1** is soluble only in DMSO or DMF, and the insolubility of the complex has frustrated our crystallization attempts to date. The $^1H$ NMR of an orange DMSO-$d_6$ solution of **1** shows extremely broad peaks ($\omega_{1/2}$ ca. 150 Hz) at 11.9 ppm, exchangeable with $D_2O$ and therefore assigned to N–H protons, and at 6.2–8.3 ppm assigned to –CHO and aromatic protons. Solutions of **1** are diamagnetic as indicated by the Evans method for magnetic

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**Table I.** Activity of Silane Alcoholysis Catalysts

| catalyst precursor | rate[a] |
|---|---|
| (1) $[\mathrm{Ni(tss)}]_2$ | 45 |
| (2) $\mathrm{Ni(OAc)_2{\cdot}4H_2O + tssH_2}$ | 40 |
| (3) $\mathrm{Ni(OAc)_2{\cdot}4H_2O + tssH_2 + 2Et_3N}$ | 22 |
| (4) $\mathrm{Ni(OAc)_2{\cdot}4H_2O + tssH_2 + CO}$ (1 atm) | 21 |
| (5) $\mathrm{NiCl_2{\cdot}6H_2O + tssH_2}$ | 0 |
| (6) $[\mathrm{Ni(tssH_2)_2]Cl_2}$ | 0 |
| (7) $\mathrm{NiCl_2{\cdot}6H_2O + tssH_2 + Et_3N}$ | 27 |
| (8) $[\mathrm{Ni(tssH_2)_2]Cl_2 + Et_3N}$ | 15 |
| (9) $\mathrm{Ni(OAc)_2{\cdot}4H_2O}$ | 0 |
| (10) $\mathrm{tssH_2}$ | 0 |
| (11) $\mathrm{Cu(OAc)_2{\cdot}H_2O + tssH_2}$ | 0 |
| (12) $\mathrm{Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O + tssH_2 + Et_3N}$ | 0 |

[a] Rate in millimoles of $H_2$ produced per hour per millimole of Ni (=turnovers/hr).

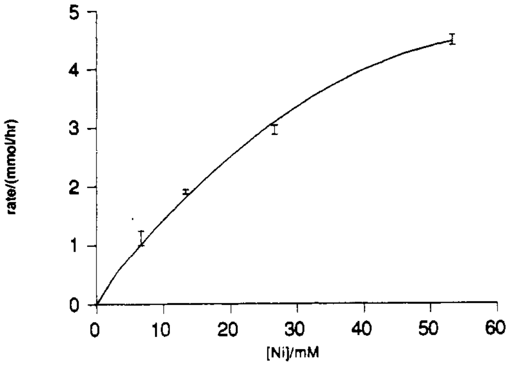
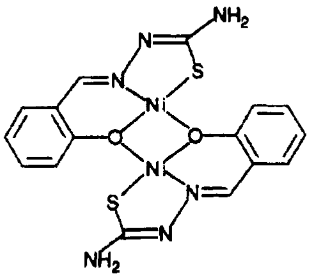


**Figure 1.** Reaction rate (millimoles of $\mathrm{Et_3SiOEt}$ produced per hour) vs total Ni concentration (based on amount of $\mathrm{Ni(Oac)_2{\cdot}4H_2O}$ added). Each data point is the average of three runs, and the error bars indicate the precision of the data.



**1**

susceptibility,[15] and integration with respect to an internal standard ($\mathrm{CH_2Cl_2}$) shows that at least 95% of the complex is in a diamagnetic form. The spectral broadening may be due either to a small amount of a five- or six-coordinate paramagnetic species with solvent in the axial positions[16] or to a monomer–dimer equilibrium (see below). Cyclic voltammetry of **1** (in DMF, 0.1 M $\mathrm{(Bu_4N)(ClO_4)}$ backing electrolyte, at glassy carbon electrode vs SCE) reveals only poorly defined oxidations and reductions at $E_0 > +0.5$ V and $E_0 < -1.4$ V, respectively.

Compound **1** was found to catalyze silane alcoholysis at room temperature in 50% DMSO–benzene with EtOH or MeOH as substrate. We have also found that 1:1 mixtures of $\mathrm{Ni(OAc)_2{\cdot}4H_2O}$ and $\mathrm{tssH_2}$ have properties and catalytic activities essentially identical to those of isolated **1**. The catalytic activity of various complexes and catalyst preparations is shown in Table I. Both the known[11,13] $[\mathrm{Ni(tssH_2)_2}]^{2+}$ and 2:1 (mol/mol) mixtures of $\mathrm{tssH_2}$ and $\mathrm{NiCl_2{\cdot}6H_2O}$ give yellow solutions that are catalytically inactive and identical by $^1$H NMR. Activity and the orange color can be restored in both cases by addition of $\mathrm{Et_3N}$, and the resulting NMR spectrum is a superposition of those of **1** and the free ligand. These observations indicate that deprotonation of the ligand favors formation of the 1:1 L:Ni complex as shown in eq 5. When nickel acetate is used, the basic acetate ions are

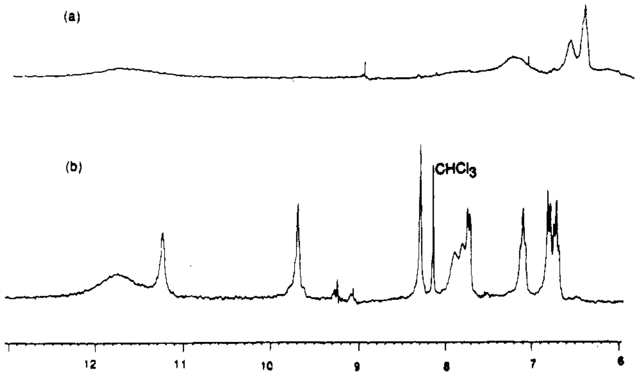


**Figure 2.** $^1$H NMR spectra: (a) 0.01 mmol of **1**/**1a** in 50% (v/v) DMSO-$d_6$–$\mathrm{CCl_4}$ + 0.8 mmol of MeOH; (b) same sample as part a after a 1.5-h reaction with 0.8 mmol of $\mathrm{Et_3SiH}$.

$$[\mathrm{Ni(tssH_2)_2}]^{2+} \underset{2\mathrm{H}^+}{\overset{2\mathrm{Et_3N}}{\rightleftharpoons}} {}^1/_2[\mathrm{Ni(tss)}]_2 + \mathrm{tssH_2} \qquad (5)$$

sufficient and no extra base is necessary to deprotonate the ligand, but with nickel chloride added base is required for activity.

The reaction rate is *not* directly proportional to catalyst concentration. As shown in Figure 1, the reaction rate displays a negative deviation from ideal linear behavior as the total concentration of nickel is increased. We attribute this behavior to an equilibrium (eq 6) between dimeric **1** and a solvated,

$$\underset{\mathbf{1}}{[\mathrm{Ni(tss)}]_2} + 2\mathrm{DMSO} \rightleftharpoons \underset{\mathbf{1a}}{2[\mathrm{Ni(tss)(DMSO)}]} \qquad (6)$$

monomeric form **1a** in which the monomer is the active catalyst. At lower nickel concentrations, monomeric **1a** is favored and the activity consequently is higher. The insolubility of the compound in volatile solvents has precluded our attempts to obtain a solution molecular weight by the vapor diffusion method,[17] but the spectroscopic behavior of solutions of **1**/**1a** in the presence of inhibitors has provided further evidence for the monomeric nature of the catalyst. In the presence of excess lutidine (=lut, 2,6-dimethylpyridine), catalysis is completely inhibited, and the ligand peaks in the aromatic region, broad in the absence of lutidine, become well resolved, allowing identification of the resonances due to the CH═N proton at 8.12 ppm and the aromatic protons at 6.61, 6.80, 6.98, and 7.12 ppm. These observations are consistent with formation of a catalytically inactive species of the form Ni(tss)(lut).

Since metal hydrides are known to react with $\mathrm{CCl_4}$ to yield $\mathrm{CHCl_3}$,[18] we carried out the reaction in the presence of $\mathrm{CCl_4}$ to see if we could trap any intermediate hydride. We do indeed find $\mathrm{CHCl_3}$ as a product when the reaction of alcohol with silane is carried out in 50% (v/v) DMSO–$\mathrm{CCl_4}$ catalytic systems, which is evidence for an intermediate Ni–H. These solutions become pale yellow within ca. 10 minutes and clearly display $^1$H NMR peaks of the $[\mathrm{Ni(tssH_2)_2}]^{2+}$ species (see Figure 2); in the presence of excess $\mathrm{Et_3N}$, the solution remains orange, the spectrum of $[\mathrm{Ni(tssH_2)_2}]^{2+}$ does not appear, and crystalline $\mathrm{Et_3NHCl}$ precipitates (eq 7). The appearance of $[\mathrm{Ni(tssH_2)_2}]^{2+}$ is due to the buildup of $\mathrm{H^+}$ (according to eq 5) that results from interception of the intermediate Ni–H by $\mathrm{CCl_4}$; excess $\mathrm{Et_3N}$ removes $\mathrm{H^+}$ as $\mathrm{Et_3NHCl}$, so no $[\mathrm{Ni(tssH_2)_2}]^{2+}$ species is observed in this case.

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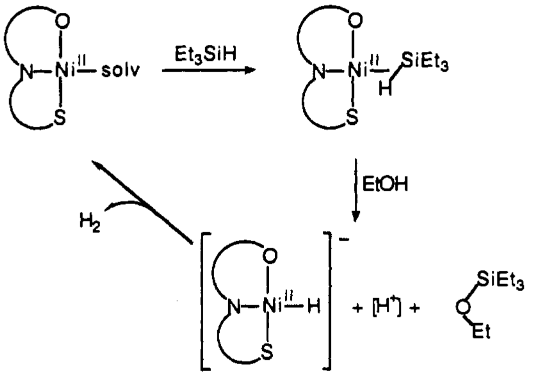
$$CCl_4 + R_3SiH + R'OH + Et_3N \rightarrow CHCl_3 + R_3SiOR' + [Et_3NH]Cl \quad (7)$$

Control experiments confirm that reaction 7 does not proceed in the absence of catalyst.

On the basis of the above evidence, and by analogy to the mechanism previously proposed for our Ir catalyst,[5] we propose the following catalytic scheme:



Alkylsilane binds as a $\sigma$ complex to the equatorial Ni site and is activated toward nucleophilic attack of the alcohol at silicon, yielding the product silyl ether as well as an intermediate Ni(II)–H species and $H^+$. Protonation of the nickel hydride produces $H_2$ and regenerates the catalyst. In this system, we believe that oxidative addition of $Et_3SiH$ to give a Ni(IV) species is highly unlikely, since Ni(IV) is only known to be stable in the presence of strongly donating ligands and ligands which allow partial delocalization of the high charge on the metal, such as oximes and dithiocarbamates.[19] Our electrochemical studies show that $[tss]^{2-}$ provides no significant stabilization for higher nickel oxidation states. In addition, no hydrosilation of styrene was observed in this system, a reaction that normally requires oxidative addition of silane to the metal.[3] None of the postulated intermediates has yet been observed spectroscopically, but they are probably short-lived.

Nickel is required for activity. Copper(II) has the same tendency to form square planar complexes of the type we propose,[20] yet entry 11 (Table I) shows that the corresponding in situ catalyst derived from $Cu(OAc)_2$ is inactive. Similarly, an equimolar mixture of ferrous ammonium sulfate and $tssH_2$ in the presence of excess $Et_3N$ shows no activity. Thus, nickel appears unique in its ability to catalyze this reaction, at least with $[tss]^{2-}$ as a ligand. One of the key questions concerning hydrogenase is why nickel is the metal involved, rather than the more common biologically significant redox-active elements, Cu or Fe.

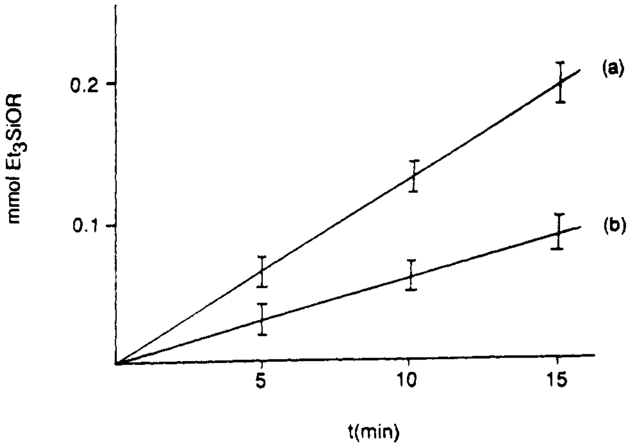


**Figure 3.** Catalytic formation of $Et_3SiOMe$ vs. time (a) under $N_2$-purged conditions and (b) in a closed system. Each data point is the average of three runs, and the error bars indicate the precision of the data.

The reaction is inhibited by donor ligands such as $Cl^-$, $AcO^-$, and pyridine, all of which presumably compete for the silane binding site. Inhibition by 1 atm CO is also observed (see Table I, entry 4); $H_2$ase itself also shows CO inhibition. We have as yet been unable to observe any Ni–CO intermediate, however, so binding seems to be weak.

Catalysis is also inhibited by $H_2$. As shown in Figure 3, if the $H_2$ product is allowed to build up in the system, the rate of alcoholysis is ca. 50% slower than when $H_2$ is continuously removed by $N_2$ purge. The rate determined in this way under $N_2$ purge is ca. 70 turnovers per hour, which is significantly higher than that determined from manometric measurements (40 turnovers per hour; see Table I, entry 2). This indicates inhibition of the reaction by $H_2$ in a closed system in which the $H_2$ can build up, which we ascribe to competitive binding of $H_2$ at the reactive site on the metal. This suggests that $H_2$ can indeed bind to Ni(II) in an N, O, S environment. We have not been able to observe this binding or that of $Et_3SiH$ directly by NMR, and so it must again be weak. In no case do we observe $D_2/H^+$ exchange under the conditions described here. Many other complexes studied fail to catalyze silane alcoholysis; initial work on the 1:1 complex of Ni(II) and *N*-(2-mercaptophenyl)salicylaldimine shows comparable silane alcoholysis but no $D_2/H^+$ exchange activity.

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