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## Hydrogenolysis of Polysilanes Catalyzed by Low Valent Nickel Complexes

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*Dedicated to Prof. Dr. José Manuel González Díaz on the occasion of his 60<sup>th</sup> birthday*

### Abstract

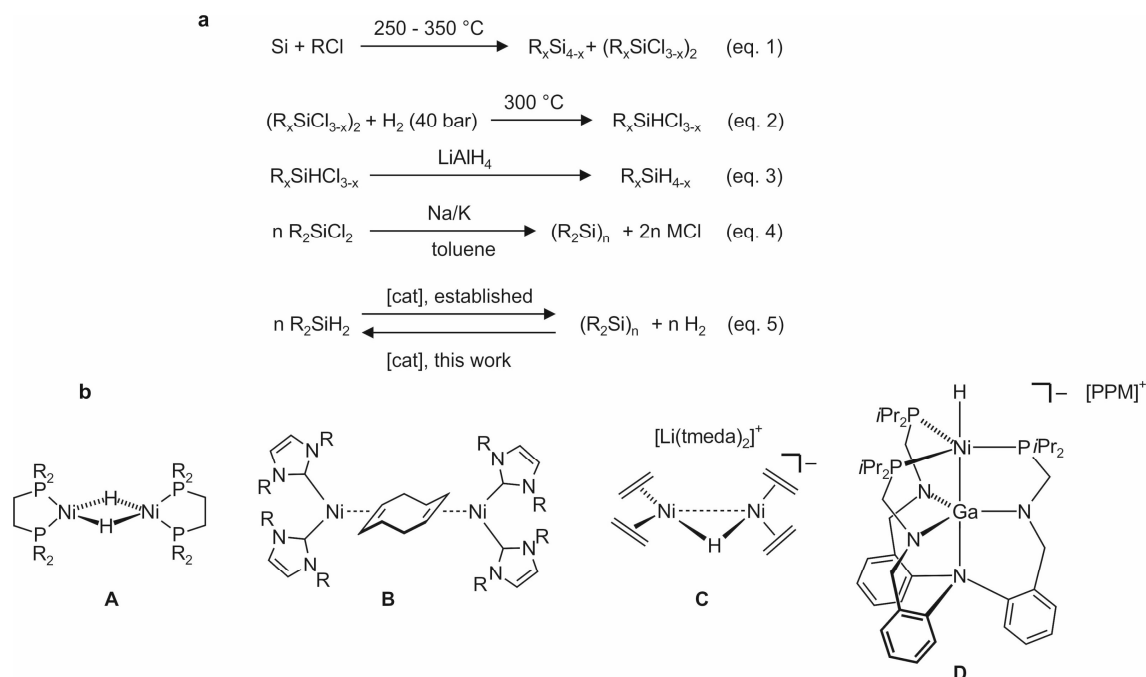
*The dehydrogenation of organosilanes ( $R_xSiH_{4-x}$ ) under formation of Si–Si bonds is an intensively investigated process leading to oligo- or polysilanes. The reverse reaction is little studied. Up to date, the hydrogenolysis of Si–Si bonds requires very harsh conditions and is very unselective leading to multiple side products. Here we describe a new catalytic hydrogenation of oligo- and polysilanes, which is highly selective and proceeds under mild conditions. New low valent nickel hydride complexes are used as catalysts and secondary silanes,  $RR'SiH_2$ , are obtained as products in high purity.*

### Introduction

Hydrosilanes are widely used reagents in the hydrosilylation of unsaturated molecules to give organosilanes<sup>1,2</sup> and are crucial components in CVD (chemical vapor deposition) processes.<sup>3,4</sup> Elegant methods for the use of surrogates for flammable hydrosilanes were developed recently,<sup>5</sup> but these are not atom efficient and require additional synthetic steps. A clean simple *in situ* method for especially the preparation of the very reactive hydrosilanes remains therefore desirable.

Organohydrosilanes are commonly produced by halide/hydride exchange reactions from organohalosilanes,  $R_xSiX_{4-x}$ . The latter are produced in the Müller<sup>6</sup>-Rochow<sup>7</sup> process (Figure 1a, eq. 1), the Barry process,<sup>8</sup> hydrosilylation reactions,<sup>9</sup> and Grignard-type reactions.<sup>10</sup> The cleavage of Si–Si bonds is used to break down the “high-boiling” residues from the Müller-Rochow process (mostly chlorodisilanes  $R_{6-x}Si_2Cl_x$ ) to monomers  $R_xSiHCl_{3-x}$ , either under harsh conditions (HCl gas, up to 900°C)<sup>11</sup> or using dihydrogen and expensive precious metals as catalysts (eq. 2).<sup>12</sup> Subsequently, the partially hydrogenated compounds  $R_xSiHCl_{3-x}$  are reacted again with costly metal hydrides ( $LiAlH_4$ ) in classical salt metathesis reactions to form the corresponding hydrosilanes (eq. 3).<sup>13</sup> The products are

often absorbed to the complex mixture of metal hydride chloride salts as side products and consequently difficult to purify. Polysilanes, on the other hand, are easily prepared via a Wurtz-type reductive coupling of chlorosilanes in high yield (eq. 4).<sup>14</sup>



**Figure 1.** **a**) Industrial Müller-Rochow process for the synthesis of organochlorosilanes (eq. 1). Hydrogenation of the “high-boiling residue” (eq. 2). Synthesis of hydrosilanes by a classical hydride transfer reaction (eq. 3). Wurtz-type dehalogenation of chlorosilanes to polysilanes (eq. 4). Hydrogenation/dehydrogenation equilibrium proposed syntheses of hydrosilanes (eq. 5). **b**) Selected examples of low valent nickel olefin and nickel hydride complexes relevant to this work.

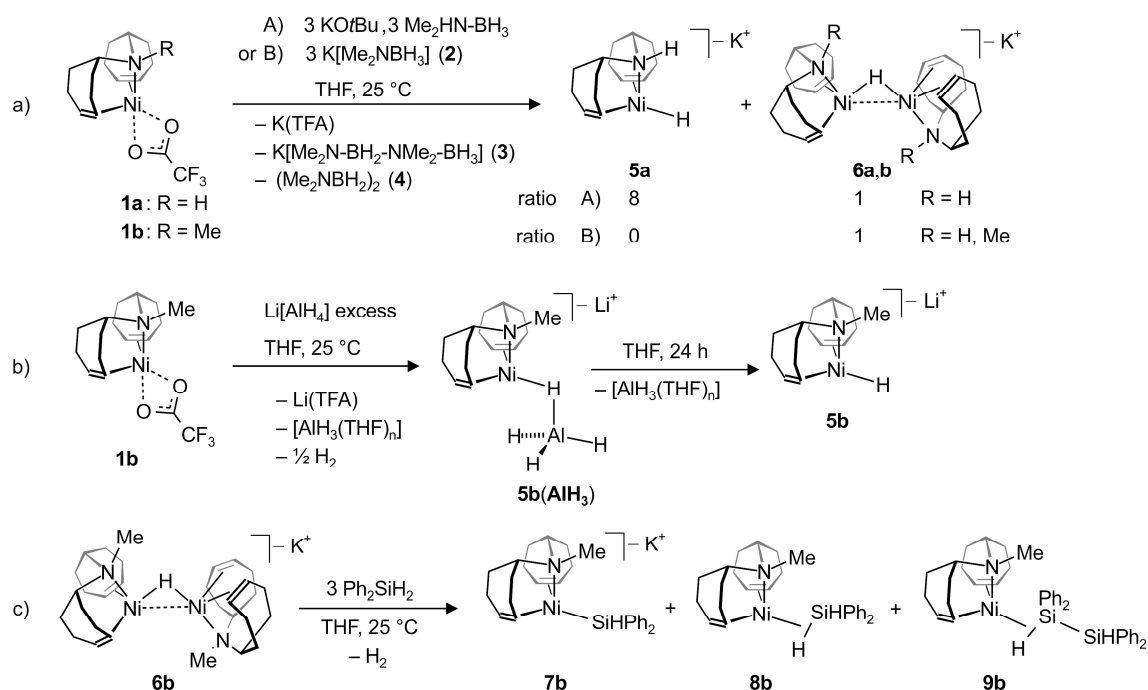
The dehydrogenation of silanes,  $\text{R}_2\text{SiH}_2$ , to oligo- and polysilanes has been intensively investigated (Figure 1a, eq. 5 left to right)<sup>15,16</sup> and both  $\sigma$ -bond metathesis according to  $2 \text{Si-H} \rightarrow \text{Si-Si} + \text{H-H}$  (metallocene catalysts) or a sequence of oxidative/reductive eliminations (catalysts with late transition metals)<sup>17,18</sup> are accepted mechanisms. Silane dehydrogenation is also promoted by low-valent nickel catalysts,<sup>19</sup> where Ni hydride species are proposed as intermediates. Notably, the dinuclear nickel(I) hydride **A** (Figure 1b) dehydrogenates primary silanes to give polysilanes.<sup>20</sup> Also the related zerovalent  $[\text{Ni}(\text{dmpe})_2]$  [dmpe = 1,2-bis(dimethylphosphino)ethane] produces linear polysilanes selectively.<sup>21</sup> The principle of microscopic reversibility suggests that the opposite reaction, namely the catalytic hydrogenation of Si-Si bonds, may be possible (Figure 1a, eq. 5 right to left). Based on experimentally determined bond energies, we estimate that the hydrogenation of Si-Si

bonds [ $\Delta H_{\text{diss}}(\text{Si-Si}) = 73.1 - 88.0 \text{ kcal mol}^{-1}$ ] is a thermodynamically allowed process [ $\Delta H_{\text{diss}}(\text{Si-H}) > 90 \text{ kcal mol}^{-1}$ ].<sup>22</sup> Indeed, Rosenberg *et al.*<sup>23</sup> determined an equilibrium constant of  $K_c = 10^4$  for  $\text{Ph}_2\text{HSi-SiHPh}_2 + \text{H}_2 \rightleftharpoons 2 \text{Ph}_2\text{SiH}_2$  at room temperature, which bolsters our expectation that the hydrogenation of Si-Si bonds is exergonic.<sup>24</sup> Yet, the hydrogenation of Si-Si bonds is very rare and only disilanes with one Si-Si bond were successfully converted as was reported independently by Braun<sup>25,26</sup> and Radius<sup>27</sup> using either a Pt complex or the binuclear Ni(0) complex **B** (Figure 1b) as catalysts achieving turn over numbers (TON's) of up to 20. The hydrogenation of higher oligo- or polysilanes is unknown.

Nickel hydride complexes<sup>28</sup> have been frequently proposed as intermediates in reactions where hydrogen is used to cleave chemical bonds (hydrogenolysis)<sup>29</sup> and have demonstrated high efficiency in the electrocatalytic production of  $\text{H}_2$ .<sup>30</sup> Moreover, in the recent years the interests in this class of compounds have been primarily determined by the development of synthetic models of the active sites of nickel-containing hydrogenases and methyl-coenzyme M reductase.<sup>31</sup> Inclusion of cooperative ligands and reactivity studies of well-defined hydride nickel complexes have provide important advances in these catalytic processes. In contrast to divalent and monovalent nickel hydride species, very few zero-valent Ni hydrides were described such as: (i) the binuclear olefin Ni(0) complex **C** which is only stable at temperatures below  $-20^\circ\text{C}$ ;<sup>32</sup> (ii) the anionic carbonyl complex  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ni}_2(\text{CO})_6\text{H}]$ ,<sup>33</sup> and (iii) complex **D** containing a Ga(III) center which stabilizes the electron rich Ni center by a Ni→Ga interaction.<sup>34</sup>

## Results and Discussion

We reported that the monovalent nickel complex  $[\text{Ni}(\text{TFA})(\text{trop}_2\text{NH})]$  **1a** ( $\text{trop}_2\text{NH} = \text{bis}(5H\text{-dibenzo}[a,d]\text{cyclohepten-5-yl})\text{amine}$ ; TFA = trifluoroacetate) is a particularly active catalyst in the dehydrogenation of amino boranes under mild conditions.<sup>35</sup> Spectroscopic studies suggested that two diamagnetic hydrido Ni complexes **5a** and **6a** participate in the catalytic cycle. Both contain the diolefine-amine  $\text{trop}_2\text{NH}$  which has remarkable properties as stabilizing ligand for low-valent metal complexes.<sup>36, 37</sup> We could now isolate such low-valent nickel hydrides and characterize them structurally.

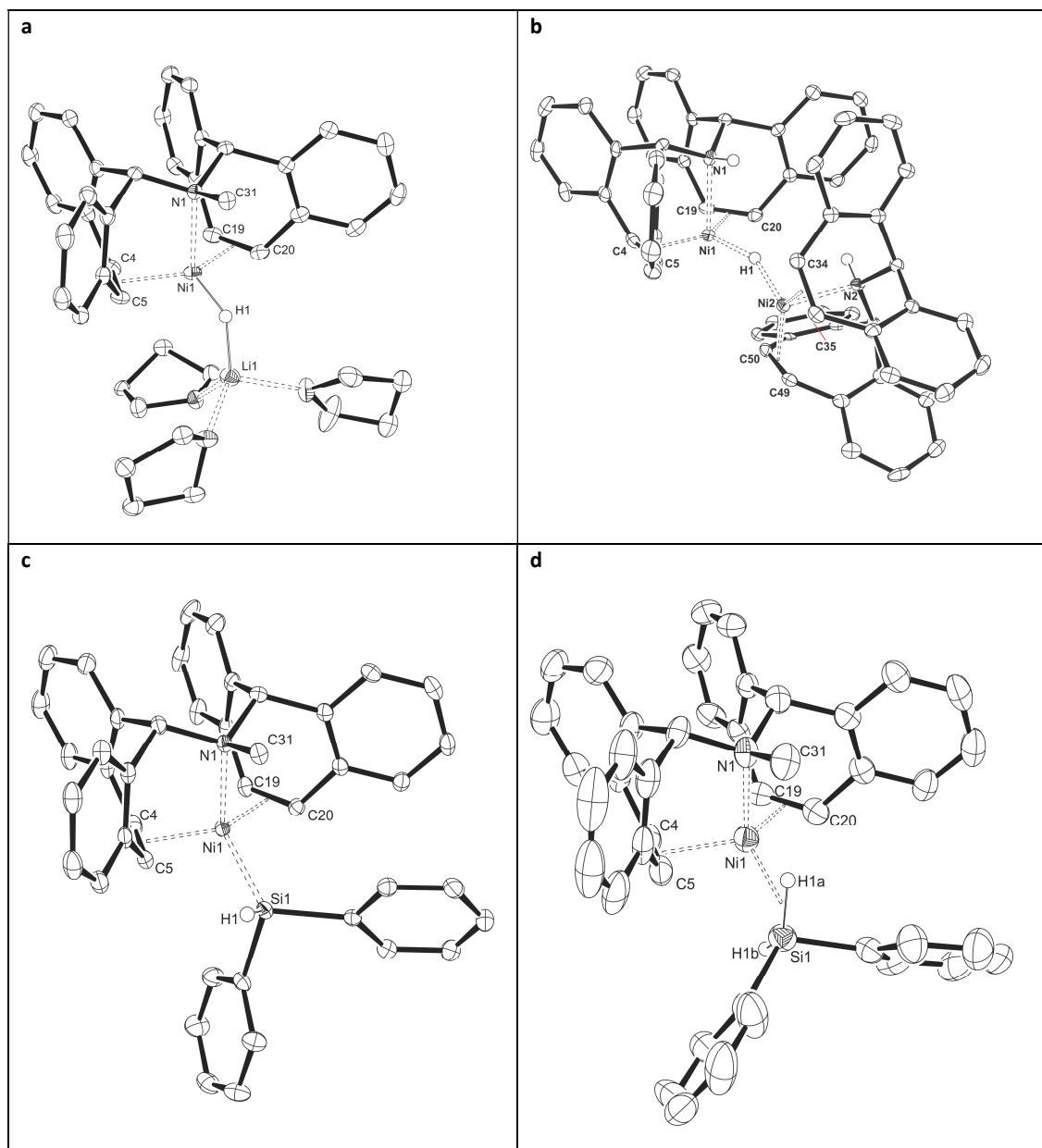


**Scheme 1. a, b)** Synthesis of terminal anionic Ni(0) hydride complexes **5a,b** and bridging dinuclear Ni(0) complexes **6b** and **6b**. **c)** Synthesis of potassium salts with terminal anionic Ni(0) silyl complexes **7a,b** and neutral Ni(0) silane complexes **8b** and **9b**.

When [Ni(TFA)(trop<sub>2</sub>NH)] **1a** reacts with dimethylaminoborane and KOtBu in THF for 30 minutes at room temperature (r.t.), a 8 : 1 ratio of the mononuclear Ni(0) hydride complex K[NiH(trop<sub>2</sub>NH)] **5a** and the dinuclear [Ni(0)<sub>2</sub>(μ-H)(trop<sub>2</sub>NH)<sub>2</sub>] **6a** is obtained (Scheme 1a) together with a mixture of the linear amido borane **3** and cyclic aminoborane (Me<sub>2</sub>NBH<sub>2</sub>)<sub>2</sub> (**4**).<sup>35</sup> When the amidoborane salt K[Me<sub>2</sub>NBH<sub>3</sub>] (**2**) was reacted with **1a** or **1b**, the dinuclear bridging hydride complexes **6a** or **6b** were formed selectively. The *N*-methylated derivative **5b** could be obtained as stable Li salt in 56% yield (Scheme 1b) using Li[AlH<sub>4</sub>] as reductant and hydride transfer reagent. When this reaction is carried out rapidly with an excess of Li[AlH<sub>4</sub>], hydrogen evolution is observed and beside hydride **5b**, pale red crystals of Li[Ni(AlH<sub>4</sub>)(trop<sub>2</sub>NMe)] [**5b**(AlH<sub>3</sub>)] were isolated at -30 °C. In THF solution, [**5b**(AlH<sub>3</sub>)] completely converts to hydride **5b** (r. t., 24 h). The terminal hydride ligand in **5a, b** shows a <sup>1</sup>H NMR resonance at δ = -4.75 and -4.59 ppm while the chemical shifts for the bridging hydride in **6a** and **6b** are observed at lower frequencies at δ = -8.12 and -6.06 ppm, respectively.<sup>28, 38</sup> In order to probe the dehydrogenation activity vis-a-vis silanes, the dinuclear complex K[Ni<sub>2</sub>(μ-H)(trop<sub>2</sub>NMe)<sub>2</sub>] **6b** was reacted with three equivalents of Ph<sub>2</sub>SiH<sub>2</sub>. Within five minutes, the silyl nickelate **7b** and the Ni(0) silane complex [Ni(trop<sub>2</sub>NMe)(*η*<sup>2</sup>-HSiHPh<sub>2</sub>)] (**8b**) are formed as 1 : 1 mixture (Scheme 1c). Addition of

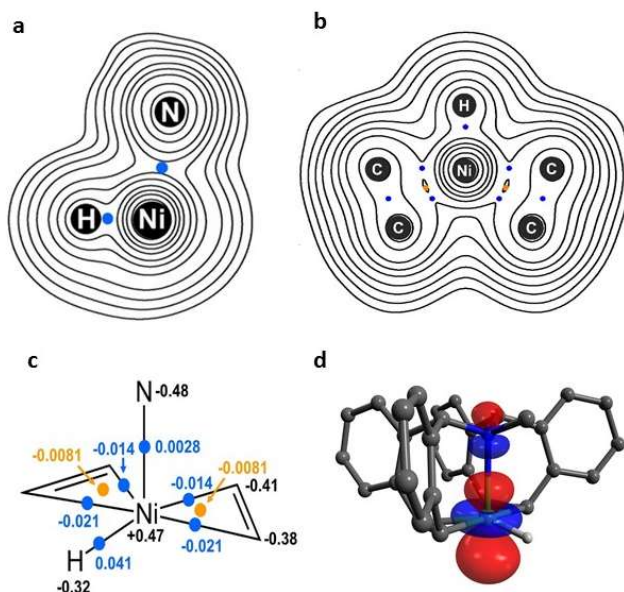
K[Me<sub>2</sub>NBH<sub>3</sub>] (**2**) immediately converts the silane complex **8b** to the silyl complex **7b** under concomitant liberation of H<sub>2</sub> and formation of the cyclic amino borane **4**. If the reaction mixture containing **7b**, **8b**, and Ph<sub>2</sub>SiH<sub>2</sub> is kept for longer time in a closed reaction vessel at room temperature, the slow formation of the disilane complex [Ni(trop<sub>2</sub>NMe)( $\eta^2$ -HSiPh<sub>2</sub>-SiPh<sub>2</sub>H)] (**9b**) is observed (for alternative selective methods to prepare salts **7a,b** with Ni(0) silyl anions in high yields directly from **1a,b**, see Supp. Information). The silyl complexes **7a,b** and silane complexes **8b** and **9b** were characterized by <sup>1</sup>H-, <sup>29</sup>Si-NMR and two-dimensional <sup>29</sup>Si-<sup>1</sup>H HMQC NMR spectroscopy (See Supp. Information for details).

Single crystals of the terminal hydrido complex [Li(thf)<sub>3</sub>][NiH(trop<sub>2</sub>NMe)] **5b** and its AlH<sub>3</sub> adduct [Li(THF)<sub>3</sub>][Ni(AlH<sub>4</sub>)(trop<sub>2</sub>NMe)] **5b(AlH<sub>3</sub>)**, the bridging hydrido complexes **6a,b**, the silyl complexes **7a,b**, the silane complex [Ni(trop<sub>2</sub>NMe)( $\eta^2$ -HSiHPh<sub>2</sub>)] **8b**, and the disilane complex [Ni(trop<sub>2</sub>NMe)( $\eta^2$ -HSiPh<sub>2</sub>-SiPh<sub>2</sub>H)] **9b** were isolated and investigated via X-ray diffraction analysis. Plots of the structures of **5b**, **6a**, **7b** and **8b** are shown in Figure 2 (for a complete set of data on all structures see Supp. Information). The structures show two remarkable features: (i) With exception of **7b**, the coordination sphere around the Ni(0) center in all complexes is trigonal pyramidal. The sum of angles defined by the hydride ligand and the centroids (ct) of both coordinated C=C<sub>trop</sub> units is close to 360 ° and the Ni center deviates only little from the best plane through the centroids (ct's) of the coordinated C=C<sub>trop</sub> units and the hydride (0.1 – 0.2 Å). In the sterically more encumbered silyl complex **7b** with the trop<sub>2</sub>NMe ligand, the deviation of the Ni center from the Si, ct1, ct2 plane is larger (0.31 Å). (ii) The Ni-N bonds are remarkably long exceeding by far 2.2 Å. For comparison, the Ni-N bond in the Ni(I) complex **1a** is much shorter (2.061 Å). The coordinated olefinic bonds trans to the hydride are long (> 1.42 Å) indicating efficient electron donation from the d<sup>10</sup>-Ni(0) center to the (pp)π\* orbitals of the C=C<sub>trop</sub> units. In the bridging hydride complexes **6a,b**, the Ni-H-Ni angles vary significantly [**6a**: 151(3)°; **6b**: 121(3)°] which goes hand in hand with a variation of the Ni-Ni distance: **6a**: 3.041(1) Å; **6b**: 2.760(1) Å. Both are longer than in [Ni<sub>2</sub>(μ-H)(C<sub>2</sub>H<sub>4</sub>)<sub>4</sub>]<sup>-</sup> (**C**) - the only other known anionic dinuclear Ni(0) hydride complex – showing a short Ni-Ni distance at 2.596(1) (Ni-H-N 125°) which was attributed to a weak non-covalent interaction between the d<sup>10</sup> valence electron configured Ni(0) centers.<sup>32, 39</sup>



**Figure 2.** Molecular structures of **5b**, **6a**, **7b** and **8b**.

The Ni–Si bond lengths in **6a,b** [2.247(1) Å, 2.229(1) Å] are comparable to other nickel silyl complexes.<sup>40,41</sup> The isolation of the rare  $d^{10}$   $\eta^2$ -(Si–H)Ni(0) complexes **7b** and **8b** is noteworthy. Obviously the back donation of electron density from Ni(0) into the C=C<sub>trop</sub> units is sufficiently strong to prevent oxidative cleavage under insertion of the Ni center into the Si–H bond.<sup>42</sup>



**Figure 3.** **a)** Electron density contour map of complex **5b** in the N–Ni–H plane. **b)** Electron density contour map of complex **5b** in the trigonal plane with the two C=C<sub>trop</sub> units, the Ni, and the H center. **c)** Energy densities and NPA charges (black) at the bond, BCPs (blue), and ring critical points, RCPs (orange). **d)** HOMO of **5b** at a surface isovalue = 0.055. ● = bond critical point, ● = ring critical point.

In order to gain some insight into the electronic structure of the anionic low-valent Ni hydride and silyl complexes, DFT calculations were performed for **5b** [B3LYP with mixed basis sets 6-31g(d) for C and N atoms and 6 31g(d,p) for H atoms, as well as effective core potential LANL2DZ for the nickel metal center]. Specifically, the Atoms-in-Molecule (AIM) theory of Bader<sup>43</sup> allows to identify bond critical points (bcp = ●) and ring critical points (rcp = ●).<sup>44</sup> As Figure 3a and 3b clearly show, there are bcp's between Ni and N, Ni and the C centers of the C=C<sub>trop</sub> units, and Ni and H. Furthermore, rcp's indicate metallacyclopropane character of the Ni and C=C<sub>trop</sub> interaction as a result of significant ligand-to-metal donation,  $\pi(\text{C}=\text{C})\rightarrow\text{Ni}$ , and metal-to-ligand back-donation,  $\text{Ni}\rightarrow\pi^*(\text{C}=\text{C})$ . The Ni atom carries a positive partial NPA charge of +0.47 e while all surrounding atoms are negatively charged. Figure 3c gives the energy densities at these critical points.<sup>45</sup> The negative values at the bcp's between Ni and all C atoms indicate polar but covalent interactions. The positive value at the bcp between Ni and H indicates a predominantly ionic interaction Ni<sup>+</sup>, H<sup>-</sup>. The bcp between Ni and N has a small positive value, which is indicative of a very weak interaction as also seen for van-der-Waals contacts or hydrogen-bridges. The HOMO of complex **5b** is displayed in Figure 3d and shows the anti-bonding interaction between the occupied  $d_{z^2}$ -orbital at Ni(0) and the lone pair at N. Based on these data, the extraordinarily long Ni–N bond in **5b** and all other complexes listed here are best described as a



structurally and electrostatically enforced anti-bonding interaction. This is in stark contrast to the Ni–Ga interaction in complex **D** (Figure 1b) which corresponds to a  $dz^2(\text{Ni}) \rightarrow p(\text{Ga})$  two electron donor-acceptor-interaction.<sup>34</sup>

The isolation of the disilane complex **9b** suggests that the low-valent Ni hydride or silyl complexes may be catalysts for the dehydrogenation of silanes. This is indeed the case. Either the hydride complexes **5b**, **6a,b**, the silyl complexes **7a,b**, or the precursor complexes **1a,b** in combination with amidoborane **2**, catalyze the dehydrogenation of  $\text{Ph}_2\text{SiH}_2$  at room temperature. With 1 – 5 mol% of the nickel complexes, a mixture of oligosilanes  $\text{H}(\text{Ph}_2\text{Si})_n\text{H}$  ( $n \leq 4$ ) was obtained (see Table S1 in Supp. Information for details). The principle of micro reversibility implies that the low valent Ni complexes should also catalyze the hydrogenation of oligo- and polysilanes. Attempts to convert tertiary disilanes such as  $\text{Me}_3\text{Si-SiMe}_3$ ,  $\text{Ph}_3\text{Si-SiPh}_3$ ,  $\text{Me}_2\text{PhSi-SiPhMe}_2$ , or  $\text{Me}_3\text{Si-SiPh}_3$  to the corresponding tertiary silanes using **6b** as catalyst,  $\text{KO}^t\text{Bu}$  as activator, and 1 bar  $\text{H}_2$  were little encouraging. The first two silanes did not react because of low solubility ( $\text{Ph}_3\text{Si-SiPh}_3$ ) and lack of interaction with the activator while  $\text{Me}_2\text{PhSi-SiPhMe}_2$  was converted in 53% yield, with significant scrambling to  $\text{Me}_2\text{SiH}_2$  and  $\text{Me}_2\text{SiPh}_2$  after extended reaction times (see Table S3). The asymmetric disilane  $\text{Me}_3\text{Si-SiPh}_3$  was hydrogenated to the expected products  $\text{Ph}_3\text{SiH}$  and  $\text{Me}_3\text{SiH}$  but in low yield (< 20%). However, the hydrogenolysis of the oligosilanes  $\text{H}(\text{SiPh}_2)_n\text{H}$  using isolated pure Ni(0) hydrides **5b** or **6a,b** as catalysts at room temperature under 1 bar of hydrogen was highly successful (entry 1, Table 1). This reaction is the direct reverse of the above reported dehydrogenation of  $\text{Ph}_2\text{SiH}_2$ . The optimal conditions for this and all other oligo- and polysilane hydrogenation reactions are listed in Table 1 (for an extended set of data on catalyst screening and optimization, see Tables S2 – S7 in Supp. Information). The reaction can be effectively extended to cyclic silanes, as  $\text{Si}_5\text{Ph}_{10}$  in which case the easily accessible Ni(I) complex **1b** was employed as catalyst precursor. Note that  $\text{Ph}_2\text{SiH}_2$  is slowly reconverted to the initial mixture of oligosilanes  $\text{H}(\text{SiPh}_2)_n\text{H}$  ( $n = 2 - 4$ ) when the Ni catalyst is not separated from the reaction mixture and hydrogen release is permitted.

In addition to the experiments shown in Scheme 1a, we have verified that the trifluoroacetate complex **1b** is converted to the hydride complex **6b** using  $\text{KO}^t\text{Bu}$  in the presence of  $\text{H}_2$ . This nucleophilic additive is also needed to activate the cyclic oligosilanes (entries 2 and 3) or polymeric silanes (entry 4). This is especially important in reactions with the highly insoluble dimethylpolysilane which upon addition of small amounts of  $\text{KO}^t\text{Bu}$  is first converted to soluble  $(\text{Me}_2\text{Si})_6$  and silyl anions before the hydrogenation proceeds.<sup>46</sup> The THF solutions of the methylated silanes and  $\text{KO}^t\text{Bu}$  as activator must be saturated with  $\text{H}_2$  before the nickel catalyst is added, otherwise no conversion is observed. In all cases, good to

excellent yields of  $\text{Me}_2\text{SiH}_2$  were obtained in NMR experiments (up to 92%). The reaction can be easily scaled up and  $\text{Me}_2\text{SiH}_2$  was isolated by distillation from the reaction mixture in 80% yield.

**Table 1.** Hydrogenation of oligo- and polysilanes catalyzed by nickel complexes.<sup>[a]</sup>

$$(\text{SiRR}')_n + n \text{H}_2 \xrightarrow[\text{THF}]{[\text{cat}], \text{Additive}} n \text{RR}'\text{SiH}_2$$

Entry	Substrate	cat (mol%)	Additive (equiv)	H <sub>2</sub> (bar)	Reaction time (h)	Monomer yield (%)
1 <sup>[b]</sup>		<b>6a</b> (1)	KAB (0.03)	1	48	>99
2		<b>1b</b> (0.6)	KO <sup>t</sup> Bu (0.03)	5	48	79
3		<b>5b</b> (0.8)	KO <sup>t</sup> Bu (0.05)	2	24	92
4 <sup>[c]</sup>		<b>5b</b> (0.2)	KO <sup>t</sup> Bu (0.01)	2	24	90
5 <sup>[d]</sup>		<b>1b</b> (1)	LiAlH <sub>4</sub> (0.1)	5	18	79

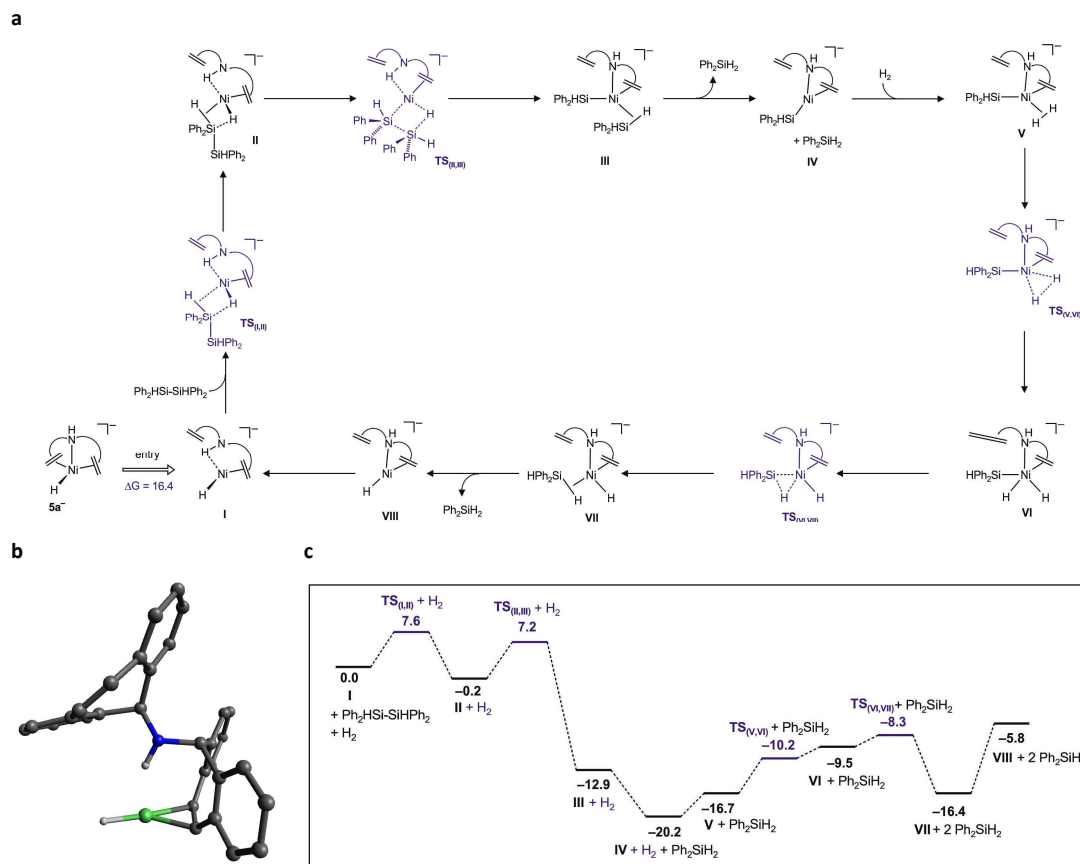
[a] Reaction conditions: Silane (0.34 -1.72 mmol Si units) in THF, additive (0.01 – 0.1 equiv, respect to Si units), [Ni] catalyst (0.2 - 1 mol%) was added and reacted with H<sub>2</sub> (1 - 5 bar) at ambient temperature. [b] Substrate is a mixture of trisilane and tetrasilane in a 2:1 ratio. [c] Polydimethylsilane Mw = 1100 - 1700. [d] Polymethylphenylsilane Mn (g mol<sup>-1</sup>) = 28'500,  $\bar{D}$  = 1.22.

In additional experiments, the homogeneity of the reaction mixture was investigated. When the hydrogenolysis of  $\text{Si}_6\text{Me}_{12}$  was performed in the presence of an excess of Hg, no inhibition of the catalytic reaction was observed. High resolution transmission electron microscopy (HRTEM) gives no evidence for crystalline metallic nickel particles. A second recharge of substrate (for example  $\text{Si}_5\text{Ph}_{10}$ )

to the reaction mixture results in little loss of activity (75% yield  $\text{Ph}_2\text{SiH}_2$  vs. 79% in the first run, see Table 1, entry 2). However, addition of an excess of triphenylphosphine (3 equivalents with respect to **1b**) added to a reaction mixture which had reached about 30% conversion of  $\text{Si}_5\text{Ph}_{10}$  (after ca. 6h) provokes a considerable decrease in the catalytic activity (45% NMR yield  $\text{Ph}_2\text{SiH}_2$  after 48h). These experiments indicate that very likely nickel complexes in homogeneous solution are the active species.

The direct conversion of the *in situ* generated  $\text{Me}_2\text{SiH}_2$  - in pure form a highly flammable gas at room temperature (b.p. =  $-20\text{ }^\circ\text{C}$ ) with a flash point below  $-40\text{ }^\circ\text{C}$  - to siloxanes by reaction with water or anhydrous ethanol according to  $\text{Me}_2\text{SiH}_2 + 2\text{ ROH} \rightarrow \text{Me}_2\text{Si(OR)}_2 + 2\text{ H}_2$  was tested. The addition of water to a cooled ( $-40\text{ }^\circ\text{C}$ ) reaction mixture containing the silane leads to the quantitative formation of a mixture of cyclic and linear silicone oligomers. The corresponding reaction with EtOH affords cleanly  $\text{Me}_2\text{Si(OEt)}_2$  and hydrogen gas as by product (see Supp. Information for details).

In order to gain some insight into a possible mechanism of the hydrogenolysis of Si-Si bonds, DFT calculations [B3LYP with 6-31g(d) for C and N atoms, 6-31g(d,p) for H atoms, LANL2DZ for the nickel center] were carried out for the hydrogenolysis of a disilane. We chose  $\text{HPh}_2\text{Si-SiPh}_2\text{H}$  as substrate and  $[\text{Ni(H)(trop}_2\text{NH)}]^-$  (**5a**<sup>-</sup>) as Ni species (for calculations with complex **5b**<sup>-</sup>, see Supp. Information). The calculated reaction energy for  $\text{HPh}_2\text{Si-SiPh}_2\text{H} + \text{H}_2 \rightarrow 2\text{ Ph}_2\text{SiH}_2$  is  $\Delta G_{\text{R}} = -9.3\text{ kcal mol}^{-1}$ . The free Gibbs energies ( $\text{kcal mol}^{-1}$ ) for the individual reaction steps are listed in Figure 4 with respect to the catalytically active complex **I** ( $0.0\text{ kcal mol}^{-1}$ ). The calculations indicate a very similar Minimum Energy Reaction Path (MERP) for  $[\text{Ni(H)(trop}_2\text{NMe)}]^-$  (**5b**<sup>-</sup>) with the only difference that intermediates which show a Ni...HN interactions have a Ni...HC interaction between Ni and the N-methyl group instead. Inclusion of solvent effects do not significantly alter the energy profile (see Figure S18-S21 in Supp. Information). The calculations indicate that the hydrido nickelate **5a**<sup>-</sup> is only a pre-catalyst, which leads to the active catalyst **I**. A possible MERP from **5a**<sup>-</sup> to **I** shows a rather shallow energy profile and involves first a weakly endergonic cleavage of the Ni-N interaction ( $3.0\text{ kcal mol}^{-1}$ ) proceeding via a low barrier ( $2.8\text{ kcal mol}^{-1}$ ). In the next step, the  $\text{C}=\text{C}_{\text{trop}}$  unit is de-coordinated, which proceeds via a sizable barrier of  $19.5\text{ kcal mol}^{-1}$ , to give the complex **I** in an overall endergonic reaction  $\Delta G_{(\text{5a} \rightarrow \text{I})} = 16.4\text{ kcal mol}^{-1}$  (Figure S17 in Supp. Information). This anionic  $d^{10}$ -Ni complex **I** serves as entry point into the catalytic cycle (Figure 4a) and can be viewed as almost linear 14 electron Ni(0) complex ( $\text{H-Ni-ct} = 158.4\text{ }^\circ$ ; ct = centroid of the  $\text{C}=\text{C}_{\text{trop}}$  bond) where the electron rich basic Ni center is internally protonated by the NH group ( $\text{Ni}\cdots\text{H} = 2.184\text{ \AA}$ ; see Figure 4b for a plot of the calculated structure).



**Figure 4.** **a**) Proposed mechanism (DFT; B3LYP, 6-31g(d) for C,N atoms; 6-31g(d,p) for H, LANL2DZ for Ni) of the hydrogenolysis of oligosilanes catalyzed by **5a<sup>-</sup>**. Activated complexes at transition states are shown in blue. Ni...N distances (Å): **I**: 3.142; **TS<sub>(II,III)</sub>**: 3.140; **II**: 3.004; **TS<sub>(II,III)</sub>**: 2.692; **III**: 2.322; **IV**: 2.263; **V**: 2.587; **TS<sub>(V,VI)</sub>**: 2.677; **VI**: 2.636; **TS<sub>(VI,VII)</sub>**: 2.510; **VII**: 2.278; **VIII**: 2.363; **TS<sub>(VII,I)</sub>**: 2.974. **b**) Calculated structure of **I**: Ni-H 1.569 Å, Ni-H 1.569 Å, Ni-ct: 1.965 Å, Ni...H 2.184 Å, C=C<sub>trop</sub> 1.439 Å. **c**) Energy profile for the reaction  $\text{Ph}_2\text{HSi-SiHPh}_2 + \text{H}_2 \rightarrow 2 \text{Ph}_2\text{SiH}_2$  catalyzed by **I**; free Gibbs energies,  $\Delta G$ , are given in kcal mol<sup>-1</sup>.

In the first step of the catalytic cycle, complex **I** reacts with disilane via a barrier of 7.6 kcal mol<sup>-1</sup> to give the  $\eta^2$ -Si-H disilane complex **II** ( $\Delta G^1 = -0.2$  kcal mol<sup>-1</sup>) which rearranges to the activated complex **TS<sub>(II,III)</sub>** (7.2 kcal mol<sup>-1</sup>) in which the Si-Si bond is co-planar with the Ni-H bond. A  $\sigma$ -bond metathesis occurs in which a new Ni-Si and Si-H bond are formed at the expense of cleaving the Si-Si and Ni-H bond. The Ni silyl complex **III** formed in that second reaction step loses immediately in step 3 the  $\eta^2$ -coordinated  $\text{H}_2\text{SiPh}_2$  ligand as first product molecule to give the 16 electron Ni(0) silyl amino olefin complex **IV**. Overall, the reaction  $\text{II} \rightarrow \text{IV}$  is exergonic by  $\Delta G^{2+3} = -20.0$  kcal mol<sup>-1</sup>. In the next step 4,  $\text{H}_2$  is added in a weakly endergonic reaction ( $\Delta G_{(\text{IV,V})} = 3.5$  kcal mol<sup>-1</sup>) to yield the  $\text{H}_2$  complex **V**. The

$\eta^2$ -bonded  $H_2$  ligand is then oxidatively cleaved in step 5 to give the Ni(II) silyl dihydride **VI** in a further mildly endergonic reaction, ( $\Delta G^5 = 7.2 \text{ kcal mol}^{-1}$ ). In step 6, complex **VI** decomposes via a very small barrier ( $1.2 \text{ kcal mol}^{-1}$ ) to give the  $\eta^2\text{-H}_2\text{SiPh}_2$  complex **VII** in an exergonic reaction ( $\Delta G^6 = -6.9 \text{ kcal mol}^{-1}$ ). Finally, the second equivalent  $\text{Ph}_2\text{SiH}_2$  is released in an endergonic reaction step 7 ( $\Delta G^7 = 10.6 \text{ kcal mol}^{-1}$ ) to give the nickel hydrido amine olefin complex **VIII**. This complex immediately rearranges to give **I**, which is  $3.5 \text{ kcal mol}^{-1}$  more stable and shows a diminished anti-bonding interaction between the lone-pair at N and the occupied  $d_{z^2}$  orbital at Ni. This final step 8 turns the catalytic cycle over. Overall, this reaction mechanism involves classical intermediates which undergo  $\sigma$ -bond metatheses. Only modest activation barriers below  $8 \text{ kcal mol}^{-1}$  are encountered along the MERP. In agreement with the proposed mechanism, no significant kinetic isotope effect was observed when  $D_2$  was used instead of  $H_2$ . A notable feature of the intermediates and activated complexes involved in the catalytic cycle is the wide range of Ni–N distances. Only the Ni silyl intermediates **III** and **IV**, the  $\eta^2\text{-H}_2\text{SiPh}_2$  complex **VII**, and the hydride **VIII** show Ni–N bond lengths below  $2.4 \text{ \AA}$ . All other species have very long Ni–N distances which exceed in some cases even  $3 \text{ \AA}$  (see Supp. Information for details).

### Conclusion

A new class of low-valent  $d^{10}\text{-Ni(0)}$  hydride and silyl complexes was synthesized which contain stabilizing amino bis(olefin) ligands. These complexes are remarkably effective in the hydrogenation of all Si–Si bonds in oligo- and polysilanes. Some reactions require small amounts of a nucleophilic additive which is needed to break-up a Si–Si bond according to:  $(R_2Si)_x + Nuc^- \rightarrow (Nuc)R_2Si\text{-}(SiR_2)_{x-2}\text{-}SiR_2^-$ . This activation is not necessary when the substrate contains already one Si–H bond which allows binding to the metal center to give a  $\eta^2\text{-Si-H}$  complex. The almost quantitative formation of  $\text{Me}_2\text{SiH}_2$  from  $(\text{Me}_2\text{Si})_6$  and  $(\text{Me}_2\text{Si})_x$  is especially noteworthy. These experimental findings and DFT calculations give some first insights for further catalyst design and improvement. Key-features of the  $d^{10}\text{-}[Ni(X)(trop_2NR)]^-$  ( $R=H, Me; X=H, SiR_3$ ) complexes are: (i) a low-valent electron rich metal center which promotes both,  $\sigma$ -bond metathesis and oxidative additions; (ii) a double hemi-labile tripodal ligand which is achieved by an electrostatically enforced anti-bonding interaction between the Ni and N center and the intrinsically low binding energy of olefins to metal centers. These special features allow accessing low-coordinated 14 and 16 electron  $d^{10}\text{-Ni}$  hydrides and silyl complexes, which readily interact with Si–H and H–H bonds. At the same time, the rigidity of the central seven-membered cycloheptatriene-ring of the trop ligand platform ensures sufficient kinetic stabilization of all intermediates within the catalytic cycle. Future work will seek to enhance the catalytic activity of the complexes by structural modification of the ligand in such a way that the liberation of one coordination site is even more facilitated. Additionally, catalytic hydrogenation of Si–Si bonds and transfer of the transiently formed Si–H to an organic molecule, according to:  $(SiR_2)_x + x H_2 + 2x A=B \rightarrow$

x  $R_2Si(A-BH)_2$  may be realized which is a highly atom efficient process that employs only relatively harmless chemicals.

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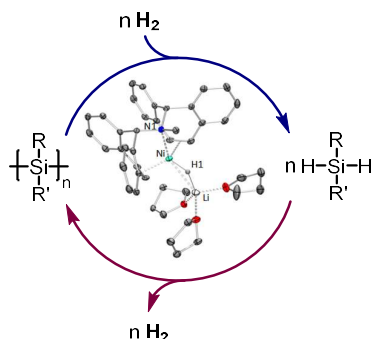
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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** Nickel hydride – polysilanes – hydrogenolysis – hydrosilanes – olefin ligands – silyl complexes – silane complexes

## Table of Contents



The Si–Si bonds in polysilanes are converted to Si–H bonds under mild conditions using low-valent anionic Ni(0) hydride catalysts. The reaction is reversible and dehydrogenative coupling of hydrosilanes is likewise possible. Experiments and DFT calculations indicate that low-coordinated 14 and 16 electron  $d^{10}$ -Ni hydrides, silyl and silane intermediates are involved in the catalytic cycle which likely consists of sequential  $\sigma$ -metathesis and OA/RE steps.

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