VIP Synthetic Methods

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Facile Catalytic Hydrosilylation of Pyridines**

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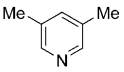
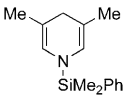
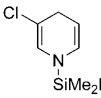
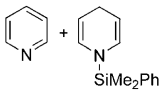
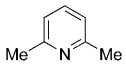
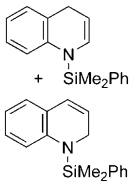
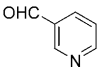
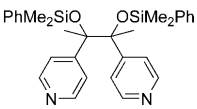
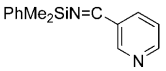
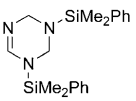
Dedicated to Professor Dmitry A. Lemenovskii on the occasion of his 65th birthday

The catalytic hydrosilylation of imines has emerged as an important method for the preparation of amines, whereas the hydrosilylation of other nitrogen-containing substrates remains a significant synthetic challenge.[1,2] Only a handful of catalytic methods for the hydrosilylation of nitriles to amines,[3] nitriles to imines,[3b,4,5] amides to amines,[6,7] and nitroarenes to anilines[8] are known. The addition of silanes to pyridines is even rarer. The synthesis of silylated 1,2- and/or 1,4-dihydropyridines is of importance as a potential method for the preparation of partially reduced pyridines, which are often used as selective reducing agents[9] and could be valuable building blocks for organic synthesis.[10] Harrod and co-workers reported the only example to date of a homogeneous hydrosilylation of pyridines.[11,12] The use of a titanium catalyst at 80 °C gave silylated dihydropyridines; however, these reactions were compromised by the concomitant hydrogenation of the products to tetrahydropyridines. In related studies, Crabtree and co-workers developed a reduction of quinolines by silanes in the presence of $[Rh(nbd)(PPh_3)_2]PF_6$ (nbd = norbornadiene), which catalyzes the generation of the highly active product SiH_4 from H_3SiPh.[13] The stoichiometric insertion of pyridine into an Fe–Si bond to give an η^3-1-silyl-1,4-dihydropyridinyl complex was described by Tobita and co-workers.[14]

Herein, we report a surprisingly facile catalytic hydrosilylation of pyridines with the additional advantages that it is 1) 1,4-regioselective and 2) reversible. We also report the coupling of the reaction products with organic substrates, including the preparation of amides from acid chlorides and a novel zinc-mediated hydrosilylation of imines.

We reported previously that the cationic ruthenium complex $[Cp(iPr_3P)Ru(NCCH_3)_2]^+$ (**1**) catalyzes a variety of hydrosilylation reactions,[15] including the first chemoselective monohydrosilylation of nitriles.[5c] Encouraged by this success, we chose to investigate the addition of silanes to pyridines. Simple pyridines were subjected to catalytic hydrosilylation by $HSiMe_2Ph$ in dichloromethane in the presence of **1** (5% mol; Table 1). The special feature of this reaction is that it occurs rapidly even at room temperature and, unlike

Table 1: Catalytic hydrosilylation of pyridines with $HSiMe_2Ph$.[a]

Entry	Substrate	Conv. [%][b]	*t* [h]	Product(s)
1		86[c]	0.5	 **2**
2		82	3	
3		100	0.25	
4		47	3	
5		0	3	–
6		0	24	–
7		0	24	–
8		50[d]	0.5	
9[e]		100	0.5	Mixture of partially reduced pyridines
10[e]		100	0.5	Mixture of partially reduced pyridines
11		50	0.25	
12[5c]		68	14	
13[e]		98	3.5	

[a] General procedure: **1** (5% mol) was added to a solution of the substrate and the silane in CH_2Cl_2. [b] Conversion was determined on the basis of ^1H NMR spectroscopy. [c] The conversion was 96% when the reaction was carried out under solvent-free conditions. [d] The conversion was 70% when the reaction was carried out under solvent-free conditions. [e] The reaction was carried out with 2 equivalents of the silane.

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the previously reported titanium-catalyzed hydrosilylation, affords selectively the product of 1,4-addition, the *N*-silyl dihydropyridine **2** (Table 1, entry 1). The selective formation of this product is of significance, as conventional reduction methods usually give mixtures of 1,2- and 1,4-dehydropyridines.[10]

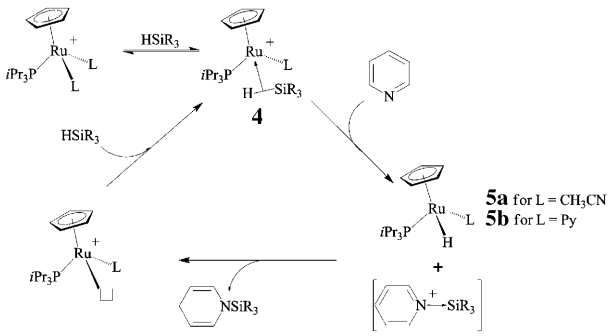
Substitution in the 3- and 5-positions had no effect on the success of this reaction (Table 1, entry 2), and a halogen in the 3-position was tolerated (entry 3). In contrast, attempted hydrosilylation of 2-bromopyridine afforded a mixture of pyridine and the silylated 1,4-dihydropyridine with low overall conversion (Table 1, entry 4). This product composition suggests that the substrate initially undergoes dehalogenation, which is followed by hydrosilylation. In general, substitution in the 2-, 4-, and 6-positions inhibited the reaction completely (Table 1, entries 5–7). These results suggest that the steric accessibility of the nitrogen center and the 4-position is important. The lack of reactivity observed for 4-methylpyridine (Table 1, entry 7) also highlights the preference of this system for 1,4-reduction over the common 1,2-reduction. The challenging substrate quinoline was successfully converted into a mixture of 1,4- and 1,2-hydrosilylated products in moderate yield (Table 1, entry 8). This reaction proceeded in better yield (70%) when it was carried out under solvent-free conditions.

To check the compatibility of this reaction with the presence of functional groups, we attempted the hydrosilylation of 3-acetyl- and 3-formylpyridine; however, a mixture of products was observed in both cases (Table 1, entries 9 and 10). In contrast, the hydrosilylation of 4-acetylpyridine cleanly gave a pinacol derivative (Table 1, entry 11). This result suggests the possibility of a radical pathway. A cyano group was hydrosilylated preferentially to give the corresponding 3-silyliminoformyl pyridine in high yield (Table 1, entry 12). Finally, the bishydrosilylation of triazine provided a 1,2,3,4-tetrahydro derivative in high yield (Table 1, entry 13).

Even more surprisingly, we discovered that the hydrosilylation is reversible. In the presence of catalyst **1**, compound **2** transferred the silane moiety to benzonitrile to give pyridine and the imine $PhHC{=}NSiMe_2Ph$. With 3,5-lutidine, an equilibrium mixture of 1,4-hydrosilylated pyridine derivatives was formed. The treatment of compound **2** with $DSiMe_2Ph$ in the presence of **1** (5 mol%) resulted in deuteration exclusively at the 4-position. To the best of our knowledge, these reactions are the first examples of a reversible hydrosilylation.[16]

Compound **2** also underwent dehydrosilylation in benzene upon the addition of $B(C_6F_5)_3$, which abstracted hydride from the 4-position with the precipitation of the pyridinium salt $[C_5H_5N{\cdot}SiMe_2Ph]HB(C_6F_5)_3$. This salt decomposed slowly (in 24 h) in dichloromethane with the formation of $C_5H_5N{\cdot}B(C_6F_5)_3$ and $HSiMe_2Ph$.

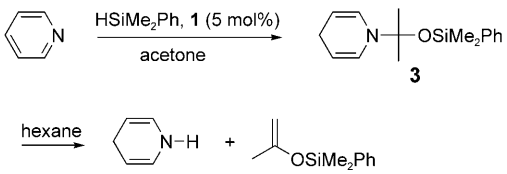
For the addition of silanes to carbonyl compounds and nitriles under the catalysis of **1**, we previously suggested an ionic hydrosilylation mechanism based on the formation of cationic silane σ complexes **4** and nucleophilic abstraction of a silylium ion by the substrate, followed by hydride transfer from the ruthenium hydride **5** (Scheme 1).[5c,15] We proved previously the formation of silane σ-complexes **4** as intermediates in these reactions.[15] To underpin the feasibility of the hydride-transfer step, we prepared a neutral pyridine-stabilized hydride complex **5b** by the treatment of **1** with *t*BuOK in *i*PrOH in the presence of excess pyridine. Complex **5b** was characterized by NMR spectroscopy. As expected, the reaction of **5b** with the readily available pyridinium salt $[(Et_3Si)(Py)][B(C_6F_5)_4]^-$ (Py = pyridine) yielded the 1,4-hydrosilylated pyridine. The catalytic hydrosilylation of pyridine with the deuterated silane $DSiMe_2Ph$ provided further evidence for the suggested mechanism. The deuterium atoms were found exclusively in the 4-position of the product. In contrast, Harrod and co-workers postulated that in the titanium-catalyzed hydrosilylation of pyridines, the products of 1,4-addition stem from the kinetic products of 1,2-addition.[11]



Scheme 1. Proposed mechanism for the hydrosilylation of pyridines.

Although we believe that the hydride is predominantly transferred to the pyridinium cation in a single step (a two-electron process), we cannot exclude the possibility of a sequence of one-electron processes. For the closely related system $RO_2C{-}NC_5H_5^+/[Cp(dppe)RuH]$ (dppe = 1,2-bis(diphenylphosphanyl)ethane), Norton and co-workers found that both pathways are feasible.[17] In fact, the mechanism of single-electron transfer (SET) can operate preferentially for substrates with substituents in the 4-position. For example, the SET mechanism can account for the formation of the pinacol product in the hydrosilylation of 4-acetylpyridine (Table 1, entry 11). We indeed observed the EPR spectrum of a ruthenium-centered paramagnetic species in a frozen reaction mixture of pyridine, $HSiMe_2Ph$, and complex **1** (20%).[18]

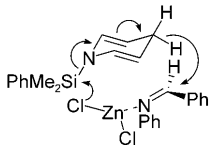
To check further the compatibility of pyridine hydrosilylation with the presence of a carbonyl functionality, we studied silane addition to a 1:1 mixture of pyridine and acetone. Unexpectedly, we observed a mixture of **2** and the product **3** of its formal N–Si addition across the C=O bond. The attempted hydrosilylation of pyridine in acetone as the solvent afforded **3** as the only product [Eq. (1)]. However, extraction of the product with hexane resulted in a formal



(1)

dehydroamination reaction with the formation of 1,4-dihydropyridine and a silylated enol.

The reaction of **2** with acid chlorides afforded the corresponding amide and $ClSiMe_2Ph$. In contrast, **2** did not react with ethyl acetate even at elevated temperatures (up to 100 °C) and in the presence of catalyst **1** (5 mol %). Compound **2** did not react with aldimines, even when complex **1** was used as an activator. However, we found that **2** slowly (50 % conversion after 2 days, as determined by NMR spectroscopy) hydrosilylated the aldimine PhN=CHPh in ether in the presence of $ZnCl_2$ (1 equiv). No reaction between **2** and PhN=CHPh or between **2** and $ZnCl_2$ was observed; nor did $HSiMe_2Ph$ react with PhN=CHPh in the presence of $ZnCl_2$ under these conditions. We believe that $ZnCl_2$ effectively plays the same role in this reaction as a phosphoric acid in the reduction of imines by 1,4-dihydropyridines;[19] that is, it promotes the formation of a cyclic transition state (Scheme 2). The requirement of very high temperatures (150–200 °C) for previously reported $ZnCl_2$-mediated hydrosilylation reactions further supports this hypothesis.[4a,20]

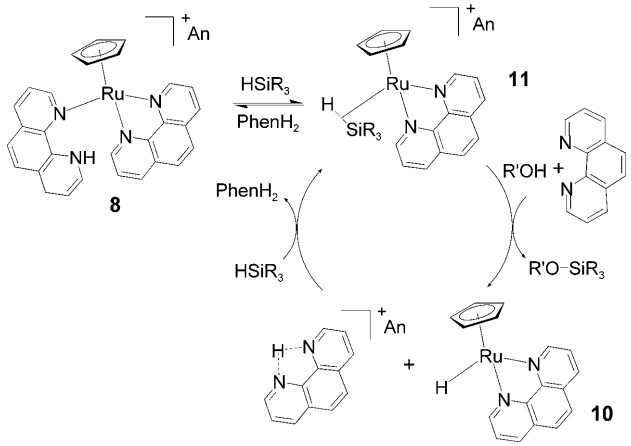


Scheme 2. Synchronized reaction of **2**, PhN=CHPh, and $ZnCl_2$.

Although quinoline underwent hydrosilylation (Table 1, entry 8), its chelating analogue, phenanthroline, poisoned the catalyst by forming the very stable complex $[Cp(iPr_3P)Ru(\kappa^2\text{-phen})]^+$ (**6**). To free up a reaction site in the catalyst, we attempted the hydrosilylation of phenanthroline in the presence of $[CpRu(NCCH_3)_3]^+$, which contains three potentially labile ligands. However, only very low conversion was observed. Accidentally, we discovered that adventitious water triggers a different catalytic process: in the presence of water, the compound $[Cp(NCCH_3)Ru(\kappa^2\text{-phen})]^+$ (**7**) formed in situ catalyzed the reduction of phenanthroline by excess $HSiMe_2Ph$ to 1,4-dihydrophenanthroline. An analogous process occurred in the presence of an alcohol as the proton source. The reaction was accompanied by intensive evolution of dihydrogen as a result of concomitant silane hydrolysis (alcoholysis). However, independent experiments showed that no hydrogenation of phenanthroline by gaseous hydrogen occurred under these conditions in the absence of the silane.

Monitoring of the course of phenanthroline reduction by NMR spectroscopy revealed that the complex $[Cp(\kappa^2\text{-phen})Ru(\kappa^1\text{-phenH}_2)]^+$ (**8**) with a partially reduced phenanthroline ligand was the predominant ruthenium species in the reaction mixture. At the end of reduction, **8** was slowly converted into the hydride-bridged dimer $[\{Cp(\kappa^2\text{-phen})Ru\}_2(\mu\text{-H})]^+$ (**9**). Although complex **9** itself is not an active catalyst, its formation provides some evidence for the intermediacy of a neutral ruthenium hydride, [Cp(phen)RuH] (**10**). Unfortunately, numerous attempts to prepare compound **10** from the precursor **7** have been unsuccessful so far. In all cases, the complex **9** was observed as the major product.

The postulated catalytic cycle of phenanthroline reduction starts with the displacement of a labile ligand L in $[Cp(\kappa^2\text{-phen})RuL]^+$ ($L = NCCH_3$, $phenH_2$) by the silane to give the silane σ complex **11** (Scheme 3). This complex is probably too sterically loaded to react with phenanthroline but can react with water to furnish the hydride **10** and the protonated



Scheme 3. Catalytic hydrogenation of phenanthroline. $An = PF_6^-$.

silanol $[PhMe_2SiOH_2]^+$, which is then deprotonated by phenanthroline to give $[H\text{-phen}]^+$. Hydride transfer from **10** to the 4-position of $[H\text{-phen}]^+$ affords the two-hydrogen-atom-reduced phenanthroline, which coordinates to ruthenium to give a latent form of the catalyst, the observed complex **8**.

In summary, we have discovered unprecedented catalytic activity and 1,4-selectivity in the hydrosilylation of pyridines by complex **1** and the catalytic reduction of phenanthroline by $HSiMe_2Ph$ in the presence of the complex $[Cp(H_3CCN)Ru(\kappa^2\text{-phen})]^+$ (**7**).

Experimental Section

For general reaction conditions, see the Supporting Information.

Synthesis of **2**: $[CpRu(PiPr_3)(CH_3CN)_2]PF_6$ (0.20 g, 3 mol %) was added to a solution of pyridine (1.00 mL, 12.3 mmol) and $HSiMe_2Ph$ (2.00 mL, 13.0 mmol) in CH_2Cl_2 (20 mL), and the resulting mixture was stirred for 6 h at ambient temperature. The removal of all volatiles under vacuum and distillation of the resulting oil under reduced pressure then gave **2** (1.97 g, 74 %) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.58$–7.52 (m, 2H, Ph), 7.42–7.32 (m, 3H, Ph), 5.89 (d, $J_{H,H} = 8.3$ Hz, 2H, NC*H*=CH), 4.45 (dt, $J_{H,H} = 8.3$, 3.2 Hz, 2H, NCH=C*H*CH_2), 2.95 (m, 2H, CH_2), 0.42 ppm (s, 6H, SiMe); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 136.5$, 133.8, 129.8, 128.7, 128.1, 100.1, 22.5, −2.4 ppm; ^1H–^{29}Si HSQC ($CDCl_3$): $\delta = 1.1$ ppm.

Dehydrosilylation of **2** with benzonitrile: $[CpRu(PiPr_3)(CH_3CN)_2]PF_6$ (0.002 g, 2 mol %) was added to a solution of **2** (30 μL, 0.14 mmol) and PhCN (14 μL, 0.14 mmol) in [D6]acetone (0.6 mL), and the resulting mixture was stirred at ambient temperature. After 24 h, 40 % conversion of **2** into $PhCH{=}NSiMe_2Ph$ and pyridine was observed. Conversion was complete after 18 days at ambient temperature.

Exchange reaction of **2** with $DSiMe_2Ph$: $[CpRu(PiPr_3)(CH_3CN)_2]BAF$ (0.005 g, 5 mol %) was added to a solution of **2** (20 μL, 0.09 mmol) and $DSiMe_2Ph$ (14.3 μL, 0.09 mmol) in CH_2Cl_2 (0.6 mL), and the resulting mixture was stirred at ambient temperature. After 24 h, 25 % deuteration of the 4-position of **2** was

observed. According to ^{2}H NMR spectroscopy, no deuterium incorporation at other positions of **2** occurred.

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