Hydrosilane Synthesis by Catalytic Hydrogenolysis of Chlorosilanes and Silyl Triflates

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ABSTRACT: Hydrogenolysis of the chlorosilanes and silyl triflates (triflate = trifluoromethanesulfonate, OTf) $\text{Me}_{3-n}\text{SiX}_{n+1}$ ($\text{X} = \text{Cl}, \text{OTf}; n = 0, 1$) to hydrosilanes at mild conditions (4 bar H_2 , room temperature) is reported using low loadings (1 mol-%) of the bifunctional catalyst $[\text{Ru}(\text{H})_2\text{CO}(\text{HPNP}^{\text{IPr}})]$ ($\text{HPNP}^{\text{IPr}} = \text{HN}(\text{CH}_2\text{CH}_2\text{P}(\text{iPr})_2)_2$). Endergonic chlorosilane hydrogenolysis can be driven by chloride removal, e.g. with $\text{NaBAR}_4^{\text{F}}$ ($\text{BAR}_4^{\text{F}} = \text{B}(\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2)^-$). Alternatively, conversion to silyl triflates enables facile hydrogenolysis with NEt_3 as base, giving Me_3SiH , Me_2SiH_2 and Me_2SiHOTf , respectively, in high yields. An outer-sphere mechanism for silyl triflate hydrogenolysis is supported by DFT computations. These protocols provide key steps for the synthesis of the valuable hydrochlorosilane Me_2SiClH , which can also be directly obtained in yields over 50% by hydrogenolysis of chlorosilane/silyl triflate mixtures.

INTRODUCTION

Organohydrosilanes are important reagents for olefin hydrosilylation¹ and other applications such as C-H bond silylation,² desulfurization of fuels,³ or dehydrogenative oligo/polysilane formation.⁴ (Organo)hydrochlorosilane building blocks $\text{SiH}_x\text{Cl}_y\text{R}_z$ enable the orthogonal synthesis of branched polysiloxanes and self-healing silicones by sequential polycondensation and cross-linking via hydrosilylation as used e.g. for the fabrication of release coatings, moldings and adhesives.⁵

a) Müller-Rochow Process:

b) Reduction with LiAlH_4 :

c) (Partial) Chlorination of Hydrosilanes:

d) Hydrogenolysis of Chlorosilanes:

e) Hydrogenolysis of Silyl Triflates:

Scheme 1. Synthetic routes to hydro(chloro)silanes.

Some of these precursors, like MeSiCl_2H , are conveniently obtained as a byproduct of the Müller-Rochow process. In contrast, Me_2SiClH synthesis suffers from low crude yields (0.01-0.5%, Scheme 1a) and challenging separation procedures, necessitating alternative synthetic routes to hydro(chloro)silanes from chlorosilanes.⁶ Hydrosilanes can be prepared by salt metathesis from chlorosilanes with LiAlH_4 (Scheme 1b). Besides the low atom economy that is associated with the use of complex hydride reagents, this approach is not commonly applicable for the synthesis of hydrochlorosilanes due to overreduction. Alternatively, partial chlorination of hydrosilanes,⁷ e.g. selective $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed hydrosilane acidolysis serves as a versatile route to organohydrochlorosilanes (Scheme 1c).⁸ However, direct organochlorosilane hydrogenolysis as a source of hydrosilanes remains elusive due to the unfavorable thermochemistry ($\text{Me}_3\text{SiCl} + \text{H}_2 \rightarrow \text{Me}_3\text{SiH} + \text{HCl}$; $\Delta G^\circ = +22.2 \text{ kcal mol}^{-1}$).⁸

Very recently, Shimada and co-workers pioneered⁹ the hydrogenolysis of silyl triflates and halides $\text{R}_{3-n}\text{SiX}_{n+1}$ with iridium catalysts (Scheme 1d/e).¹⁰ With relatively high catalyst loadings (5-10 mol-%) and long reaction times (2-7 days), moderate yields around 50-60 % in Me_2SiH_2 and Me_2SiHCl could be obtained upon hydrogenolysis of $\text{Me}_2\text{SiOTf}_2$ or *in situ* prepared Me_2SiI_2 and Me_2SiICl , respectively. Guided by our recent work on de-/hydrogenation with bifunctional catalysts,¹¹ we here report ruthenium

catalyzed hydrogenolysis of chlorosilanes and silyl triflates with low catalyst loadings.

RESULTS AND DISCUSSION

The considerably higher Si–Cl (~100 kcal mol⁻¹) vs. Si–H (~69 kcal mol⁻¹) bond dissociation energy renders hydride vs. chloride metathesis a thermochemically challenging step.¹² Therefore, a transition metal catalyst with low M–H hydricity^{13,14} was targeted, as indicated e.g. by the capability to catalyze the hydrogenation of CO₂ to formate ($\Delta G^\circ_{\text{H}}(\text{HCO}_2^-) = 44$ kcal/mol in MeCN). Ruthenium MACHO-type catalysts, i.e. [RuCl(H)CO(HPNP^R)] (HPNP^R = HN(CH₂CH₂PR₂)₂), show high activities in CO₂ hydrogenation.¹⁵ A stoichiometric control experiment confirmed that the *trans*-dihydride complex [Ru(H)₂(CO)(HPNP^{iPr})] (**1**) readily reacts with Me₃SiCl to the corresponding hydrosilane in almost quantitative spectroscopic yield (Scheme 2). This observation also demonstrates favorable kinetics for hydride transfer to chlorosilanes with this catalyst class. However, HCl elimination and H₂ heterolysis from the resulting ruthenium chloro complex **2** requires strong bases like alkaline metal hydroxides, alkoxides or amides, which all proved incompatible with chlorosilane substrates. Accordingly, attempts for catalytic hydrogenolysis of Me₃SiCl in THF with NEt₃ as base were unsuccessful. Computational evaluation confirmed endergonic hydrogenolysis with model base NMe₃ (Me₃SiCl + H₂ + NMe₃ → Me₃SiH + [HNMe₃]Cl; $\Delta G^\circ = 11.9$ kcal/mol), suggesting the requirement of additional driving force to achieve turnover.

Scheme 2. Stoichiometric hydride transfer of **1** with Me₃SiCl.

In situ chloride precipitation was therefore evaluated as a synthetic strategy. Addition of NaBAR^F₄ (BAR^F₄⁻ = B(C₆H₃-3,5-(CF₃)₂)₂⁻) to complex **2** in PhF as solvent results in the formation of new species by NMR spectroscopy accompanied by NaCl precipitation (see Electronic Supporting Information, ESI). The ³¹P and ¹H spectroscopic and mass spectrometric data closely resemble the reported values for [Ru(H)CO(HPNP^{iPr})]BF₄.¹⁶ Exchange of the solvent with THF-d₈ restores **2**, indicating a strong solvent dependence of the chloride abstraction equilibrium.

Chlorosilane hydrogenolysis (4 bar H₂, r.t.) with **1** (1 mol-%) as catalyst was therefore examined in the presence of stoichiometric amounts of NaBAR^F₄ and excess NEt₃ as base in PhF. Trimethylchlorosilane as substrate (Table 1, Entry 1) requires relatively long reaction times giving spectroscopic yields in Me₃SiH around 50 % after about a week. In contrast, hydrogenolysis of Me₂SiCl₂ (with 2 eq. NaBAR^F₄) to Me₂SiH₂ proceeds at a much faster rate within a day in yields up to around 80 %¹⁷ under otherwise identical conditions (Entry 2), presumably due to the higher

electrophilicity of the substrate. With only 1 eq. NaBAR^F₄ (Entry 3), Me₂SiH₂ remains the preferred product, leaving almost half of the substrate unreacted. Replacing NEt₃ by 2,6-lutidine as base did not give any hydrogenolysis product even after several days under otherwise identical conditions.

Table 1. Hydrogenolysis of chlorosilanes with catalyst **1**.^[a]

$$\text{Me}_{3-n}\text{SiCl}_{n+1} + (n+1) \text{NaBAR}^{\text{F}}_4 \xrightarrow[\text{- [HNEt}_3\text{] [BAR}^{\text{F}}_4\text{] - NaCl}]{\text{H}_2 \text{ (4 bar), NEt}_3, \text{PhF, r.t., [1] (1 mol-\%)}} \text{Me}_{4-n}\text{SiH}_n$$

$n = 0, 1$

Entry	Substrate	NaBAR ^F ₄ (eq.)	Conv. ^[b]	Product (Yield ^[b])	Rxn. time
1	Me ₃ SiCl	1.1	77 % ^[c]	Me ₃ SiH (51 %)	195h
2	Me ₂ SiCl ₂	2.0	100 %	Me ₂ SiH ₂ (75 %)	24h
3	Me ₂ SiCl ₂	1.1	59 %	Me ₂ SiH ₂ (37 %)	20h

[a] General conditions: 0.027 mmol chlorosilane, 0.03 or 0.054 mmol NaBAR^F₄, 0.26 μmol **1**, 0.36 mmol NEt₃, 0.5 mL PhF, 4 bar H₂, r.t. [b] Conversions/Yields were determined by ¹H NMR integration of all signals in the Me₃Si region around 0 ppm vs. an internal standard (1,2,4,5-tetramethylbenzene). [c] Conversion of [Me₃SiNEt₃][BAR^F₄] is given.

Catalytic attempts with other alkaline metal salts of weakly coordinating anions (WCA), such as NaOTf, KPF₆, NaBPh₄, NaSbF₆ or NaBF₄, only gave (sub-)stoichiometric hydrosilane yields with respect to catalyst loading even at high substrate conversion (see ESI). To clarify the role of the WCA, the catalytic reaction with NaBAR^F₄ was monitored by NMR spectroscopy. The experiment revealed the presence of an intermediate with a ²⁹Si resonance of 47.4 ppm, i.e. characteristic for base stabilized silyl cations.¹⁸ The same species is obtained upon mixing Me₃SiCl with NaBAR^F₄ and NEt₃ in PhF in the absence of catalyst. Furthermore, NEt₃ coordination to silicon is evidenced by a cross peak of the amine methylene protons with the ²⁹Si resonance in the ¹H-²⁹Si HMBC spectrum (Figure 1). These results suggest that *in situ* formed [Me₃SiNEt₃]⁺ is the actual substrate, which is sufficiently stabilized by the BAR^F₄⁻ anion under catalytic conditions.¹⁹

Figure 1. ¹H-²⁹Si HMBC spectrum of the product from the reaction of Me₃SiCl with NaBAR^F₄ and NEt₃.

Table 2. Hydrogenolysis of silyl triflates with catalyst **1**.^[a]

$\text{Me}_{3-n}\text{SiOTf}_{n+1} \xrightarrow[\text{- [HNEt}_3\text{][OTf]}]{\text{H}_2 \text{ (1-4 bar), NEt}_3, \text{C}_6\text{D}_6, \text{r.t., [1] (0.1 - 1 mol-\%)}} \text{Me}_{3-n}\text{SiH}_{n+1}$ $n = 0, 1$					
Entry	Substrate	Base (eq.)	Conv. [b]	Product (Yield ^[b])	Rxn. time
1	Me ₃ SiOTf	NEt ₃ (1.1)	99 %	Me ₃ SiH (85 %)	18h
2 ^[c]	Me ₃ SiOTf	NEt ₃ (1.1)	92 %	Me ₃ SiH (82 %)	46h
3 ^[d]	Me ₃ SiOTf	NEt ₃ (1.0)	90 %	Me ₃ SiH (85 %)	26h
4 ^[d]	<i>t</i> BuMe ₂ SiOTf	NEt ₃ (1.1)	3 %	< 1 %	7d
5	Me ₂ SiOTf ₂	NEt ₃ (2.2)	100 %	Me ₂ SiH ₂ (82 %)	1h
6	Me ₂ SiOTf ₂	NEt ₃ (1.0)	99 %	Me ₂ SiHOTf (82 %) Me ₂ SiH ₂ (4 %)	1h

[a] General conditions: 0.1 mmol substrate, 1 μmol **1**, 4 bar H₂, 0.5 ml C₆D₆, r.t. [b] Conversions/Yields were determined by ¹H NMR integration of all signals in the Me_xSi region around 0 ppm vs. an internal standard (1,2,4,5-tetramethylbenzene)). [c] 0.1 μmol **1** (0.1 mol-%). [d] 1.2 bar H₂ was used.

Alternative hydrogenolysis strategies were examined to avoid the stoichiometric use of expensive NaBAR₄ as chloride scavenger. Silyl triflates can be easily obtained from organochlorosilanes and HOTf with HCl as the only by-product,²⁰ possibly providing a better leaving group for catalysis. Reaction of **1** with Me₃SiOTf (1 eq.) in C₆D₆ selectively gives Me₃SiH and [RuH(OTf)CO(HPNP^{iPr})] (**3**) by NMR spectroscopy. Complex **3** was independently prepared from **1** with HOTf and fully characterized including single-crystal X-ray diffraction (Figure 2). Importantly, Me₃SiOTf is hydrogenated (1-4 bar H₂, r.t.) to trimethylsilane in benzene with high yield (> 80 %) using NEt₃ as base (Table 2, Entries 1-3). Full conversion is obtained overnight with 4 bar H₂ and 1 mol-% catalyst. Almost the same yield is achieved after 46 h with loadings as low as 0.1 mol-% **1** (Entry 2). Reduction of the H₂ pressure (1.2 bar) gives the same yield with only slightly longer reaction times (Entry 3). Hydrogenolysis of *t*BuMe₂SiOTf was not successful (Entry 4) presumably due to steric shielding.

In comparison, double hydrogenolysis of the bistriflate substrate Me₂SiOTf₂ to Me₂SiH₂ is remarkably facile and far more rapid than with the previously reported iridium catalyst (5 mol-% [Ir], 7 days, 53% yield).¹⁰ Full conversion and 82 % yield in dihydrosilane is obtained within only 1 h (1 mol-% **1**, Entry 5). Furthermore, highly selective

semihydrogenolysis is obtained within the same time (Entry 6) using one eq. of base to give Me₂SiHOTf in 82 % yield.

During the course of catalysis, **3** is the only ruthenium species observed by ¹H and ³¹P NMR spectroscopy. After some time, the conjugate acid [HNEt₃][OTf] forms a separate ionic liquid phase, which might be beneficial to drive the reaction (see below). Importantly, the substrate, base and catalyst remain dissolved in the benzene layer.

Figure 2. Molecular structure of **3** from single-crystal X-ray diffraction (ellipsoids set at 30% probability, hydrogen atoms except H111 and H112 omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ru1-C17 1.8320(16), Ru1-N1 2.1969(13), Ru1-O2 2.2957(11), Ru1-P1 2.3195(4), Ru1-P2 2.3276(5), Ru1-H112 1.52(2), C(17)-Ru(1)-N(1) 175.11(6), N(1)-Ru(1)-O(2) 90.82(4), P(1)-Ru(1)-P(2) 164.903(14), O(2)-Ru(1)-H(112) 178.3(8).

DFT calculations were performed for the PMe₂-truncated model system **1**^{Me} with NMe₃ as model base to obtain further insight into the hydrogenolysis mechanism (Scheme 3). Geometry optimizations were performed at the RI-PBE-D3/def2-SVP level of theory. Improved energies were obtained from subsequent SMD-PBEo-D3/def2-TZVP single-point calculations validated against explicitly correlated coupled-cluster energies.²¹ The lowest energy pathway commences with a barrierless endergonic adduct formation between **1**^{Me} and Me₃SiOTf to yield intermediate **1**^{Me}. Si-O-bond heterolysis proceeds via **ts1**^{Me} as the turnover limiting transition state of the overall process. This leads to exergonic formation of **1**^{Me}, which is stabilized by hydrogen bonding of the OTf⁻ anion to the HPNP ligand. Subsequent displacement of Me₃SiH by the triflate anion exhibits a small activation barrier (10 kcal mol⁻¹ via **ts2**^{Me}). The resulting triflate complex **3**^{Me} represents the thermodynamic resting state (ΔG° = -10.4 kcal mol⁻¹), in line with the experimental observations (see above). Regeneration of **1**^{Me} proceeds without significant barriers and involves H₂-binding to **1**^{Me} followed by base assisted heterolysis via **ts4**^{Me}. Overall, hydrogenolysis of Me₃SiOTf and regeneration of the catalyst is computed to be slightly endergonic. This result suggests that the reaction is partially driven by the [HNMe₃][OTf] ionic liquid phase separation, which was approximated as an isolated contact ion pair in the

computational approach. The effective activation barrier of

could be increased only to 12 % using a $\text{Me}_2\text{SiCl}_2\text{:Me}_2\text{SiOTf}_2$

Scheme 3. Computed pathway for the hydrogenolysis of Me_3SiOTf using **1**^{Me}; ΔG° in kcal mol⁻¹ (SMD-PBEo-D3/def2-TZVP//RI-PBE-D3/def2-SVP).

25 kcal mol⁻¹ is therefore estimated from the energy interval between the resting state **3**^{Me} and the rate-limiting **ts1**^{Me}. This value is in agreement with a reaction that proceeds at room temperature.²²

Resting state **3**^{Me} is stabilized by N–H⋯OTf hydrogen bonding, as confirmed by the experimental structure of **3** (Figure 2). The *N*-methylated catalyst [RuH(OTf)CO(MePNP^{iPr})] (**4**, MePNP^{iPr} = MeN(CH₂CH₂Pr)₂) was therefore employed to probe for rate acceleration by resting state destabilization. The hydrogenolysis rate of Me_3SiOTf with NEt₃ as base is, in fact, slightly increased (91 % conversion after 130 min) with respect to **3** (81 % conversion after 135 min) under identical conditions.

Scheme 4. Redistribution of chlorosilanes and silyl triflates.

The hydrogenolysis protocols outlined above provide key precursors for facile organohydrochlorosilane synthesis in high yield at mild conditions with low catalyst loadings. Chlorosilyl triflate semihydrogenolysis could be an alternative route for direct synthesis. $\text{Me}_2\text{SiClOTf}$ can be obtained from Me_2SiCl_2 with 1 eq. HOTf as main product according to *in situ* NMR examination. However, isolation attempts by distillation lead to chloride/triflate dismutation (Scheme 4). At r.t. equilibration is slow (ca. 4 d), but considerably accelerated upon addition of amines (e.g. NEt₃ or 2,6-lutidine) or **1** (ca. 1 h).²³ Consequently, mixtures of Me_2SiCl_2 and $\text{Me}_2\text{SiOTf}_2$ might be directly used after equilibration under catalytic conditions. Rapid (< 5 h), full conversion with respect to triflate is obtained with NEt₃ as base (1 mol-% **1**). However, Me_2SiH_2 is the main hydrogenolysis product (36 %).²⁴ The desirable hydrochlorosilane Me_2SiClH is observed only in 5 %²⁴ spectroscopic yield, which

ratio of 5:1 to reduce the $\text{Me}_2\text{SiOTf}_2$ equilibrium concentration.

Scheme 5. Hydrogenolysis of a mixture of Me_2SiCl_2 and $\text{Me}_2\text{SiOTf}_2$ with catalyst **1**.²⁴

Screening of other ruthenium, iron and iridium pincer catalysts (see ESI) gave slightly varying dihydrochlorosilane yields. We therefore anticipate kinetic control of the selectivity. Computational evaluation of the $\text{Me}_2\text{SiCl}_2/\text{Me}_2\text{SiH}_2$ dismutation equilibrium, in fact, suggests much higher Me_2SiClH yields under thermodynamic control ($\text{Me}_2\text{SiCl}_2 + \text{Me}_2\text{SiH}_2 \rightarrow 2 \text{ Me}_2\text{SiClH}$; $\Delta G^\circ = -0.7$ kcal mol⁻¹). In fact, catalytic $\text{R}_3\text{SiH}_2/\text{R}_2\text{SiCl}_2$ dismutation to hydrochlorosilanes has been reported in the literature, and the experimentally derived equilibrium constant for R = Me ($\Delta G^\circ_{\text{exp}} \approx -1.3$ kcal mol⁻¹) is in close agreement with our computational estimate.²⁵

As a strategy to maintain thermodynamic control, weaker bases than NEt₃ ($\text{p}K_{\text{a,MeCN}} = 18.8$)²⁶ were screened. With 2,6-lutidine ($\text{p}K_{\text{a,MeCN}} = 14.1$)²⁷ excess base is required for full conversion (97 %). Furthermore, Me_2SiClH and 2,6-lutidinium triflate eliminate dihydrogen under argon suggesting approximately thermoneutral hydrogenolysis with the conjugate base. High selectivities in Me_2SiClH vs. Me_2SiH_2 (> 10:1) are obtained for hydrogenolysis of a $\text{Me}_2\text{SiCl}_2/\text{Me}_2\text{SiOTf}_2$ (10:1)²⁸ mixture with 2,6-lutidine (10 eq.) as base (Scheme 5). Following the reaction by ¹H NMR (Figure 3) reveals that the reaction is considerably slower than bistriflate hydrogenolysis. Furthermore, the selectivity slightly changes over time in favor of Me_2SiClH . Therefore, high substrate conversion (> 90 %) and Me_2SiClH yields over 50 %²⁴ require about a week under these conditions.

Figure 3. Time-dependent concentration profiles of the reaction depicted in Scheme 5.

In summary, several catalytic hydrogenolysis routes to organohydro- and halohydrosilanes are reported. Mild reaction conditions (1–4 bar H_2 , r.t.) at low catalyst loadings (0.1–1 mol-%) and reaction times could be obtained. Especially bistriflate (semi)hydrogenolysis rapidly affords the organohydrosilane building blocks Me_2SiH_2 and $Me_2SiHOTf$ in excellent yields. Experimental and computational evaluation supports a catalytic cycle via outer-sphere hydride transfer and H_2 heterolysis. Chlorosilane hydrogenolysis is enabled by chloride precipitation with $NaBAR^F_4$, presumably via base stabilized silyl cations as key intermediates. In combination, the hydrogenolysis of chlorosilane/silyl triflate mixtures can be optimized to directly give the hydrochlorosilane Me_2SiClH in moderate yields.

EXPERIMENTAL DETAILS

General Information

All experiments were carried out under argon (Linde, 5.0) atmosphere using Schlenk or glove-box techniques (O_2 , H_2O below 0.1 ppm). NMR tubes were silanized with Me_2SiCl_2 and all glassware was heated in vacuum prior to use. C_6H_6 , Et_2O (stabilized with 2,6-Di-*tert*-butyl-4-methylphenol) and pentane (HPLC grade Roth, VWR or Sigma Aldrich) were degassed and dried by passing through columns packed with activated alumina. Fluorobenzene was degassed and dried over molecular sieves (4 Å). Deuterated solvents were purchased from Deutero GmbH and dried over CaH_2 (CD_2Cl_2) or Na/K (THF- D_8 , C_6D_6) and trap-to-trap transfer in vacuo. NEt_3 was dried over KOH, distilled and stored over Molecular Sieves (4 Å). 2,6-lutidine was dried over $AlCl_3$, distilled and stored over molecular sieves (4 Å). Me_3SiCl , Me_2SiCl_2 , Me_2SiHCl , Me_3SiOTf , $tBuMe_2SiOTf$ and $MeOTf$ were degassed and distilled prior to use. 1,2,4,5-tetramethylbenzene and $KOtBu$ were sublimed prior to use. $NaBPh_4$, $NaBF_4$, $NaSbF_6$, KPF_6 and $NaOTf$ were dried *in vac.* prior to use. HOTf (ABCR) was used without further purification. H_2 (Linde, 6.0) was dried by passing through a spiral cooling system which was immersed in N_2 (l). $NaBAR^F_4$,²⁹ 2,6-lutidinium triflate,³⁰ **1**³¹ and **2**³² were prepared following published procedures.

NMR spectra were recorded on Bruker Avance III HD 300, 400 or 500 (w. broadband cryoprobe) spectrometers and calibrated to the residual proton resonance of the solvent (C_6D_6 : $\delta_H = 7.16$ ppm; $\delta_C = 128.06$ ppm, THF- D_8 : $\delta_H = 1.72$ ppm / 3.58 ppm; $\delta_C = 25.31$ ppm / 67.21 ppm, CD_2Cl_2 : $\delta_H = 5.32$ ppm; $\delta_C = 53.84$ ppm). ^{31}P and ^{29}Si NMR chemical shifts are reported relative to phosphoric acid ($\delta_P = 0.0$ ppm) and $SiMe_4$ ($\delta_{Si} = 0.0$ ppm), respectively. Signal multiplicities were abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sept (septet), m (multiplet), br (broad). LIFDI mass spectra were measured under inert conditions. Elemental analyses were obtained with an Elementar Vario EL 3 analyzer. IR spectra were recorded as powder on a Bruker ALPHA FT-IR spectrometer with Platinum ATR module.

Catalytic Protocols

Hydrogenolysis of silyl chlorides: $NaBAR^F_4$, **1** and base were dissolved in PhF in a J Young NMR tube, and the solution was frozen in N_2 (l). Chlorosilane was condensed onto the mixture in static vacuum and the headspace was refilled with H_2 (1.2 bar). The sample was thawed and immediately shaken. For reactions at 4 bar the NMR tube was nearly completely immersed in N_2 (l) for 1 min during addition of H_2 before the tube was closed. Products were identified by 1H and 1H - ^{29}Si HMBC spectroscopy and quantified by relative integration of the Me_xSi signals vs. an internal standard (1,2,4,5-tetramethylbenzene).

Hydrogenolysis of pure silyl triflates: Silyl triflate, **1** and base were dissolved in C_6D_6 in a J Young NMR tube. The mixture was frozen in N_2 (l) and the headspace was evacuated, refilled with H_2 (1.2 bar) and sealed. For reactions at 4 bar the NMR tube was nearly completely immersed in N_2 (l) for 1 min during addition of H_2 before the tube was closed. Products were identified by 1H and 1H - ^{29}Si HMBC spectroscopy and quantified by relative integration of the Me_xSi signals vs. an internal standard (1,2,4,5-tetramethylbenzene).

Hydrogenolysis of Mixtures of silyl triflates and -chlorides: Me_2SiOTf_2 , Me_2SiCl_2 and catalyst were dissolved in C_6D_6 in a J Young NMR tube and shaken for 1.5 h. Base was added and the NMR tube was frozen in N_2 (l). The headspace was evacuated, refilled with H_2 (1.2 bar) and cooled for 1 min. After sealing, the tube was warmed to room temperature giving a pressure of about 4 bar. Products were identified by 1H and 1H - ^{29}Si HMBC spectroscopy and quantified by relative integration of the Me_xSi signals vs. an internal standard (1,2,4,5-tetramethylbenzene).

Synthetic Procedures

Synthesis of Me_2SiOTf_2 : Me_2SiCl_2 (6.0 mL, 0.05 mol, 1.0 eq) is stirred at 0 °C and HOTf (12.5 mL, 0.14 mol, 2.8 eq) added via syringe. The mixture is heated to 60 °C for 2 d with occasional removal of the HCl atmosphere by a stream of Argon. Excess acid was neutralized by careful addition of NEt_3 (8 mL, 0.07 mol, 1.4 eq) at 0 °C. Removal of volatiles *in vac.* and distillation (0.3 mbar, 37 °C) gave Me_2SiOTf_2 as a colorless oil (9 mL, 0.04 mol, 79 %) in 97 % purity according to 1H and ^{19}F NMR. 1H NMR (300.13 MHz, C_6D_6 , 300K): δ (ppm) = -0.01 (s, CH_3). ^{19}F NMR (282.37 MHz, C_6D_6 , 298K): δ (ppm) = -76.66 (s, CF_3). ^{29}Si

NMR (59.63 MHz, C₆D₆, 298K): δ (ppm) = -14.6 (determined by ¹H-²⁹Si HMBBC).

Synthesis of [RuH(OTf)CO(HPNP^{Pr})] (3): [Ru(H)₂CO(HPNP^{Pr})] (1) (100 mg, 0.23 mmol, 1.0 eq) is dissolved in Et₂O (6 mL) in a J Young flask and HOTf (20 μ L, 0.23 mmol, 1.0 eq) is added. The solution is evaporated to 5 mL *i.vac.* and the precipitated product decanted off. After washing with pentane (3 x 3 mL) and drying *i.vac.*, crude (99.5 % purity) **3** (80 mg, 0.14 mmol, 60 %) is obtained as white solid. After lyophilization, a suspension in Et₂O (0.5 mL) is stirred over night, decanted off and dried *i.vac.* to give **3** as white solid (75 mg, 0.13 mmol, 56 %). Crystals suitable for X-ray crystallography were grown by cooling a saturated Et₂O solution to -40 °C. ¹H{³¹P} NMR (500.25 MHz, C₆D₆, 298K): δ (ppm) = 4.52 (t (br), ³J_{HH} = 11.3 Hz, 1H, NH), 2.68 (hept, ³J_{HH} = 7.3 Hz, 2H, CH^{syn}), 2.44 (m, 2H, NCH₂), 1.88 (m, 2H, PCH₂), 1.78 (hept, ³J_{HH} = 6.9 Hz, 2H, CH), 1.55 (m, 4H, superposition of PCH₂ and NCH₂), 1.52 (d, ³J_{HH} = 7.3 Hz, 6H, CH₃), 1.03 (d, ³J_{HH} = 6.9 Hz, 6H, CH₃^{anti}), 1.00 (d, ³J_{HH} = 7.3 Hz, 6H, CH₃), 0.73 (d, ³J_{HH} = 6.9 Hz, 6H, CH₃), -20.9 (s, 1H, Ru-H (²J_{HP} = 18.0 Hz by ¹H NMR)). ¹³C{¹H} NMR (125.80 MHz, C₆D₆, 298K): δ (ppm) = 205.5 (t, ²J_{CP} = 11.5 Hz, CO), 120.2 (obtained by ¹⁹F-¹³C HSQC), 54.0 (vt, N = |¹J_{CP} + ³J_{CP}| = 8.8 Hz, NCH₂), 29.6 (vt, N = |²J_{CP} + ³J_{CP}| = 18.5 Hz, PCH₂), 28.1 (vt, N = |¹J_{CP} + ³J_{CP}| = 21.6 Hz, CH), 23.9 (vt, N = |¹J_{CP} + ³J_{CP}| = 26.1 Hz, CH^{anti}), 20.7 (vt, N = |²J_{CP} + ⁴J_{CP}| = 6.5 Hz, CH₃), 20.1 (vt, N = |²J_{CP} + ⁴J_{CP}| = 6.5 Hz, CH₃), 18.7 (vt, br, N = |²J_{CP} + ⁴J_{CP}| = 1.9 Hz, CH₃), 16.9 (vt, N = |²J_{CP} + ⁴J_{CP}| = 3.5 Hz, CH₃). Assignments were confirmed by 2D-NMR. ³¹P{¹H} NMR (202.52 MHz, C₆D₆, 298K): δ (ppm) = 73.8 (s). ¹⁹F NMR (470.67 MHz, C₆D₆, 298K): δ (ppm) = -77.6 (s). LIFDI-MS: m/z (%) = 585.0 (100) [M]⁺, 436.1 (80) [M-OTf]⁺. IR: ν (cm⁻¹): 3248 (N-H), 2934, 2871, 2035 (Ru-H), 1920 (C≡O), 1879, 1468, 1278, 1231, 1221, 1214, 1188, 1164, 1025, 829, 636, 622. Anal. calcd for C₈H₃₈F₃NO₄P₂RuS: C, 36.98; H, 6.55; N, 2.40. Found: C, 37.13; H, 6.42; N, 2.34.

Synthesis of [RuH(OTf)CO(MePNP^{Pr})] (2): **2** (35.3 mg, 74.3 μ mol, 1.0 eq) and KO^tBu (10.1 mg, 90 μ mol, 1.2 eq) are suspended in Et₂O (2 mL) and stirred for 3 h at r.t. The mixture is filtered through a fritted funnel and the resulting yellow solution dried *i.vac.* After extraction with pentane (4x4 mL total) MeOTf (8.4 μ L, 77 μ mol, 1.0 eq) is added. The precipitated product is filtered off, washed with pentane (3x1.5 mL) and extracted with benzene (3x0.5 mL). Evaporation of the solvent *i.vac.* gives [RuH(OTf)CO(MePNP^{Pr})] as a white powder (33 mg, 74 %). Crystals suitable for X-ray crystallography were grown from a saturated solution of Et₂O at -40 °C. ¹H{³¹P} NMR (500.25 MHz, C₆D₆, 298K): δ (ppm) = 2.69 (hept, ³J_{HH} = 7.2 Hz, 2H, CH^{syn}), 2.06 (s, 3H, NCH₃), 1.91-1.82 (m, 4H, NCHⁱ superposition), 1.79 (hept, ³J_{HH} = 6.9 Hz, 2H, CH^{anti}), 1.60 (d, ³J_{HH} = 7.2 Hz, 6H, CH₃), 1.59-1.51 (m, 2H, PCH₂^{syn}), 1.43-1.38 (m, 2H, PCH₂), 1.06 (d, ³J_{HH} = 6.9 Hz, 6H, CH₃^{anti}), 0.97 (d, ³J_{HH} = 7.2 Hz, 6H, CH₃), 0.73 (d, ³J_{HH} = 6.9 Hz, 6H, CH₃^{anti}), -20.56 (s, 1H, Ru-H (²J_{HP} = 19.0 (i) (a) Park, S.; Chang, S. Catalytic Dearomatization of N-Heteroarenes with Silicon and Boron Compounds. *Angew. Chem. Int. Ed.* **2017**, *56*, 7720; (b) Lipke, M. C.; Liberman-Martin, A. L.; Tilley, T. D. Electrophilic Activation of Silicon-Hydrogen Bonds in Catalytic Hydrosilations. *Angew. Chem. Int. Ed.* **2017**, *56*, 2260;

Hz by ¹H NMR)). ¹³C{¹H} NMR (125.80 MHz, C₆D₆, 298K): δ (ppm) = 205.8 (t, ²J_{CP} = 12.1 Hz, CO), 121.0 (q, ¹J_{CF} = 320.1 Hz, CF₃), 65.1 (vt, N = |²J_{CP} + ³J_{CP}| = 9.0 Hz, NCH₂), 45.6 (s, NCH₃), 29.9 (vt, N = |¹J_{CP} + ³J_{CP}| = 20.5 Hz, CH^{syn}), 28.1 (vt, N = |¹J_{CP} + ³J_{CP}| = 18.0 Hz, PCH₂), 24.3 (vt, N = |¹J_{CP} + ³J_{CP}| = 26.6 Hz, C), 20.9 (superposition of two vt), N = |²J_{CP} + ⁴J_{CP}| = 6.0 Hz, CH₃), 19.2 (s, CH₃), 17.1 (vt, N = |²J_{CP} + ⁴J_{CP}| = 3.5 Hz, CH₃). Assignments were confirmed by 2D-NMR. ³¹P{¹H} NMR (202.52 MHz, C₆D₆, 298K): δ (ppm) = 68.8 (s). ¹⁹F NMR (470.67 MHz, C₆D₆, 298K): δ (ppm) = -77.5 (s). LIFDI-MS: m/z (%) = 599.1 (4) [M]⁺, 450.2 (100) [M-OTf]⁺. IR: ν (cm⁻¹): 2960, 2932, 2873, 2056 (Ru-H), 1917 (C≡O), 1460, 1295, 1235, 1220, 1155, 1032, 882, 821, 695, 633, 518. Anal. calcd for C₉H₄₀F₃NO₄P₂RuS: C, 38.12; H, 6.74; N, 2.34. Found: C, 38.05; H, 6.72; N, 2.33.

ASSOCIATED CONTENT

Detailed experimental procedures, characterization of products and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

AG performed all synthetic and spectroscopic work, supervised by SSch. JIS, USK and MD carried out the quantum chemical studies, supervised by MCH. Crystallographic characterization was done by CW. The manuscript was written by AG, JIS, MCH and SSch. All authors commented on the manuscript and approved the final version.

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ABBREVIATIONS

Rxn, reaction; OTf, triflate, trifluoromethanesulfonate (O₃SCF₃⁻); eq, equivalents; NMR, nuclear magnetic resonance; IR, infrared; LIFDI-MS, liquid injection field desorption ionization mass spectrometry; conv, conversion; K_{eq}, equilibrium constant; c, concentration; ΔG° , standard Gibbs free energy; pK_{a,MeCN}, negative decadic logarithm of the acidity constant of the conjugate acid (measured in acetonitrile); t, time; h, hour(s); L, liter.

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- (23) The ¹⁹F NMR signals for Me₂SiClOTf and Me₂SiOTf₂ collapse to a single resonance upon addition of base evidencing rapid triflate exchange. ¹H NMR and ¹H-²⁹Si HMBC spectroscopy allow for unequivocal assignment of all equilibrium species.
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Synopsis: Catalytic hydrogenolysis of chlorosilanes and silyl triflates is reported at mild conditions using a bifunctional ruthenium catalyst. With NEt_3 as base, chlorosilane hydrogenolysis requires additional driving force, e.g. by chloride abstraction with $\text{NaBAR}^{\text{F}}_4$. In contrast, silyl triflate hydrogenolysis is facile without additive, giving Me_3SiH , Me_2SiH_2 and Me_2SiHOTf in high yields and selectivity. Hydrogenolysis of chlorosilane/silyl triflate mixtures gives access to valuable Me_2SiClH in yields over 50%.