Research Article

Unlocking the Catalytic Hydrogenolysis of Chlorosilanes into Hydrosilanes with Superbases

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ABSTRACT: The efficient synthesis of hydrosilanes by catalytic hydrogenolysis of chlorosilanes is described using an iridium (III) pincer catalyst. A careful selection of a nitrogen base (including sterically hindered guanidines and phosphazenes) can unlock the preparation of Me_3SiH, Et_3SiH, and Me_2SiHCl in high yield (up to 98%) directly from their corresponding chlorosilanes.
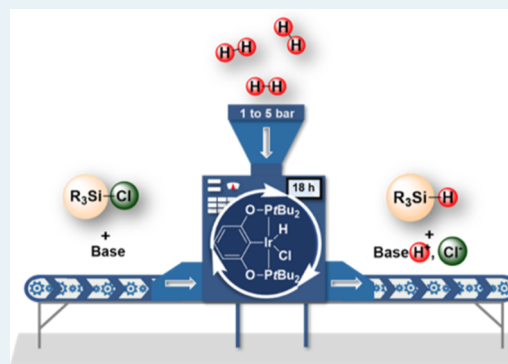
KEYWORDS: hydrosilane synthesis, hydrogenolysis, homogeneous catalysis, superbases, iridium pincer complex

Hydrosilanes are useful molecules in the industry for the production of a variety of organosilicon compounds through hydrosilylation of alkenes or dehydrocoupling reactions.[1,2] In organic synthesis, these mild reducing agents promote reactions with high selectivity and efficiency such as reduction of esters into aldehydes[3] or ethers[4] and amides into amines or enamines.[5,6] Where the use of hydrogen as a reductive source suffers from thermodynamic limitations,[7] hydrosilanes provide convenient alternatives, and recent studies have highlighted new utilizations to recover catalytically the valuable organic content of oxygenated feedstocks (lignin, plastics, and CO_2) through C−O bond reduction or to develop phosphine-catalyzed Wittig reactions.[8] However, hydrosilanes are produced via energy-intensive processes and their utilization also generates quantities of siloxanes.[9] The recycling of these wastes begins with an acidic treatment (HCl) to provide chlorosilanes which are key intermediates in the synthetic route to hydrosilanes.[10] At this time, the most used reagents to reduce [Si−Cl] bonds in chlorosilanes are anionic metal hydrides, such as $LiAlH_4$ (Scheme 1).[11] The catalytic conversion of [Si]−Cl into [Si]−H derivatives using dihydrogen as a reductive source remains highly challenging.

Catalytic hydrogenolysis of halosilanes and triflates was recently introduced by Shimada et al. in 2017 and Schneider et al. in 2018 (Scheme 1). They reported the efficient transformation of R_3SiX (X = OTf, I, Br) into R_3SiH under dihydrogen with the use of noble transition-metal catalysts in the presence of a nitrogen base to drive the thermodynamics of the transformation. This reaction is however particularly difficult with chlorosilanes because Si−Cl is much stronger
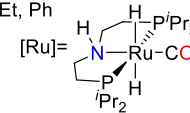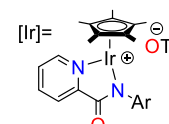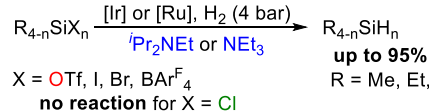
Scheme 1. Different Synthetic Ways from Chlorosilanes to Hydrosilanes
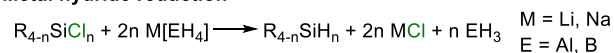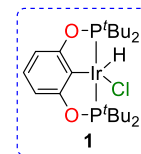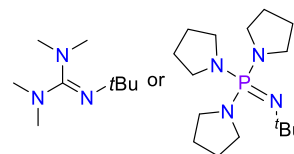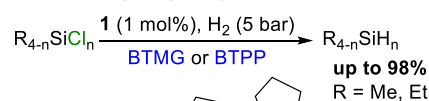
than the Si−Br and Si−I bonds, with bond dissociation energies of 456, 343, and 339 kJ mol^{-1}, respectively.[12] As such, a single example supplied the direct hydrogenolysis of Me$_3$SiCl into Me$_3$SiH but in a near stoichiometric yield (7%).[13] To tackle these limitations, before initiating catalytic hydrogenolysis in presence of a base, a chloride abstractor such as NaI or Na[B(C$_6$H$_3$-3,5-(CF$_3$)$_2$)$_4$] was first added, which greatly improved the yields in hydrosilane (up to 84%).[13,14] We present here an efficient catalytic hydrogenolysis of chlorosilanes into hydrosilanes using an iridium (III) pincer catalyst. This novel route based on the careful choice of the base (guanidine or phosphazene) avoids the use of chloride abstractors and enables the formation of Me$_3$SiH, Me$_2$SiHCl, and Et$_3$SiH in yields up to 98%.

The hydrogenolysis of silyl halides into hydrosilanes is thermodynamically unfavoured and, as shown in Scheme 1, requires a base to form the corresponding ammonium salt as a byproduct and overcome the thermodynamic limitations. Schneider et al. have computed that trialkylamines are not basic enough to perform the hydrogenolysis of chlorosilanes with their Ru(II) complex and a stoichiometric amount of additives was needed with NEt$_3$ or iPr$_2$NEt to induce the reaction (Scheme 1).[14] We chose iridium (III) pincer complexes as potential catalysts because they are competent in a number of hydrogenation[15] and hydrosilylation[16] reactions with the formation of reactive [Ir]−H entities which transfer hydrides readily.

We thus turned to the precursor [Ir(^{tBu}POCOP)HCl][17] (**1**) (^{tBu}POCOP = (C$_6$H$_3$){1,3-OPtBu$_2$}$_2$) as a possible catalyst for the Si−X to Si−H transformation. Beyond its thermodynamic role, the base is kinetically determinant to favor the formation of a metal hydride intermediate from a metal chloride and H$_2$ (Scheme 2). The choice of the base is thus crucial and must be

Scheme 2. Proposed Mechanism for the Catalytic Hydrogenolysis of Silyl Chlorides and Nucleophilic Substitution
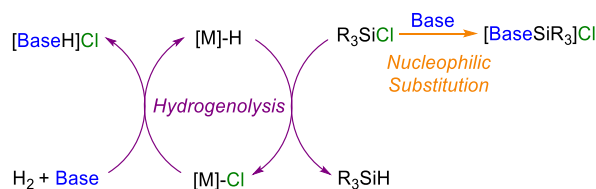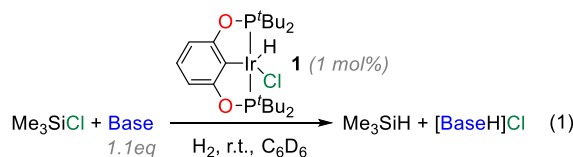

rationalized. Organic superbases such as amidines, guanidines, and phosphazenes are neutral bases, stronger than alkylamines, and are well-known activators in a variety of base-mediated organic transformations as well as in catalysis.[18] Hydroxide or alkoxide bases are not compatible with chlorosilanes, and a series of six neutral bases (NEt$_3$, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TBDH = 1,5,7-triazabicyclo[4.4.0]dec-5-ene, MeTBD = 7-methyl-1,5,7-triaza-bicyclo[4.4.0]dec-5-ene, BTMG = 2-tBu-1,1,3,3-tetramethyl-guanidine, BTPP = (tBu-imino)tri(pyrrolidino)-phosphorane) differing by their Brønsted basicity (pK_a) and steric hindrances have thus been considered in this work.

The role of the base was evaluated in the catalytic hydrogenolysis of Me$_3$SiCl (5 bar of H$_2$, room temperature, in benzene) with **1** (1 mol %) (eq 1). In the presence of NEt$_3$, no reaction occurred even after 48 h (Table 1, entry 1). While Shimada et al. observed by using an Ir(I) complex and DBU the near stoichiometric formation of Me$_3$SiH with a TON of

1.4 after 7 days,[13] **1** provided Me$_3$SiH in a promising 6% yield (TON = 6) after 18 h (eq 1, entry 2). TBDH proved ineffective and reacted immediately with Me$_3$SiCl to give a white precipitate of the silylium adduct [TBDHSiMe$_3$]Cl (Scheme 2, right). The silylium species [TBDHSiMe$_3$]Cl remained inert under hydrogenolysis conditions, even after 48 h at 90 °C in benzene (Table 1, entry 3). This result was further supported by calculations (*vide infra*). Even in CD$_2$Cl$_2$, where [TBDHSiMe$_3$]Cl is soluble and formed as a major product, only traces of Me$_3$SiH were detected (Table 1, entry 4). Interestingly, Me$_3$SiH was obtained in 25% yield after 18 h (Table 1, entry 5) with the use of MeTBD. Using BTMG and BTPP superbases, yields in Me$_3$SiH were considerably improved, up to 54% after 18 h (Table 1, entries 6 and 7). Despite the fact that the catalyst is still active (*vide infra,* as compound **2**), longer reaction times did not lead to increased yields, demonstrating that the reaction is in full equilibrium. These results represent the first efficient generation of a hydrosilane by hydrogenolysis of a chlorosilane derivative, without an activator. As the BTPP base is relatively expensive, its recycling would be appealing. A solution might come from electrodialysis to recover the BTMG or BTPP bases from their corresponding hydrogen chloride salt, a process which has been successfully applied to generate ammonia from ammonium chloride, albeit in water.[19] Such a process must first be transposed to organic media in the case of phosphazene or guanidine bases.

In contrast to TBDH, the silylium adducts [BaseSiMe$_3$]Cl were not formed in benzene with the bases MeTBD, BTMG, and BTPP, while the hydrogenolysis byproduct [BaseH]Cl deposited gradually, except for [BTPPH]Cl, which is soluble in benzene. Decreasing the H$_2$ pressure to 1 bar somewhat decreased the conversion of Me$_3$SiCl (23%) and the yield in Me$_3$SiH (18% after 18 h) (Table 1, entry 8).[13,14] These experiments underline the crucial role of the base which must be as strong as DBU to favor hydrogenolysis. The ability of the above bases to favor either the hydrogenolysis process or a nucleophilic substitution on Me$_3$SiCl was correlated with thermodynamic DFT calculations (Scheme 3). Gibbs free energies (in kcal mol^{-1}) ΔG_1 for hydrogenolysis (in purple) and ΔG_2 for nucleophilic substitution (in orange) were computed at the PBE0-D3/6-311+G(d,p) level of theory using the SMD solvation model in benzene (see Supporting Information page S24 for details).

The highest positive ΔG values are found for the amine NEt$_3$ in agreement with the absence of reactivity noted experimentally. Increasing the Brønsted basicity of the base favors the hydrogenolysis of Me$_3$SiCl as reflected in the drop of ΔG_1 values from +2.6 to −3.9 kcal mol^{-1} from DBU to BTPP. While the hydrogenolysis of chlorosilanes (ΔG_1) with DBU, MeTBD, and BTMG is slightly endergonic (+2.6, +1.6, and +0.9 kcal mol^{-1}, respectively), the reaction proceeds in benzene as it is driven by the precipitation of the byproduct salt [BaseH]Cl. Interestingly, with DBU, MeTBD, BTMG, and BTPP, the formation of the silylium salts [BaseSiMe$_3$]Cl is disfavored with ΔG_2 values ranging from +3.6 to +16.7 kcal mol^{-1}. The high values obtained for BTMG and BTPP (+14.9 and +16.7 kcal mol^{-1}, respectively) are presumably due to unfavorable steric interactions. The transition states for the S$_N$2 pathway range from +10.5 to +22.8 from DBU to BTPP (see the Supporting Information, Section 4.4). The [Base-SiMe$_3$]Cl compounds are therefore kinetically accessible. A distinct behavior is observed for TBDH, where both reactions

Table 1. Screening of Bases for the Hydrogenolysis of Me$_3$SiCl in C$_6$D$_6$ with 1[a]

$$\text{Me}_3\text{SiCl} + \text{Base} \xrightarrow[\text{H}_2, \text{ r.t., C}_6\text{D}_6]{\text{1 (1 mol%)}} \text{Me}_3\text{SiH} + [\text{BaseH}]\text{Cl} \quad (1)$$

1.1 eq

entry	H$_2$ pressure (bar)	base	pK$_a$[c]	conversion[b] (%)	yield (selectivity)[b] (%)	reaction time (h)
1	5	NEt$_3$	18.8	0	0 (0)	48
2	5	DBU	24.3	10	6 (60)	18
3	5	TBDH	26.0	0	0 (0)	48
4[d]	5	TBDH	26.0	1	<1	18
5	5	MeTBD	25.5	30	25 (83)	18
6	5	BTMG	26.5	55	42 (76)	18
7	5	BTPP	28.4	59	54 (92)	18
8	1	BTPP	28.4	23	18 (78)	18

[a]General conditions: 0.1 mmol of Me$_3$SiCl, 0.11 mmol of the base, 1 μmol of the catalyst, 0.5 mL of the solvent, at room temperature under 5 bar H$_2$ except entry 8 (1 bar). [b]Conversions, selectivities, and yields were determined by ^{1}H NMR spectroscopy through integration of the R$_3$Si signals versus an internal standard (1,3,5-trimethylbenzene). [c]pK$_a$ in MeCN.[20] [d]In CD$_2$Cl$_2$.
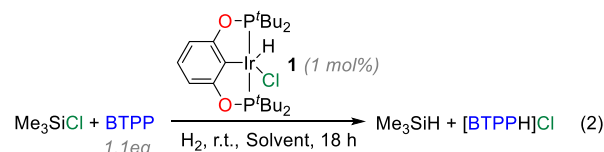
Scheme 3. Calculated ΔG$_{C_6H_6}$ by DFT (M06-2X-D3/6-311+G(d,p), SMD: Benzene) of the Hydrogenolysis Process Me$_3$SiCl + H$_2$ + Base → Me$_3$SiH + [BaseH]Cl (ΔG$_1$) and the Reaction Me$_3$SiCl + Base → [BaseSiMe$_3$]Cl (ΔG$_2$) Plotted against the pK$_a$ of the Base in MeCN[20]
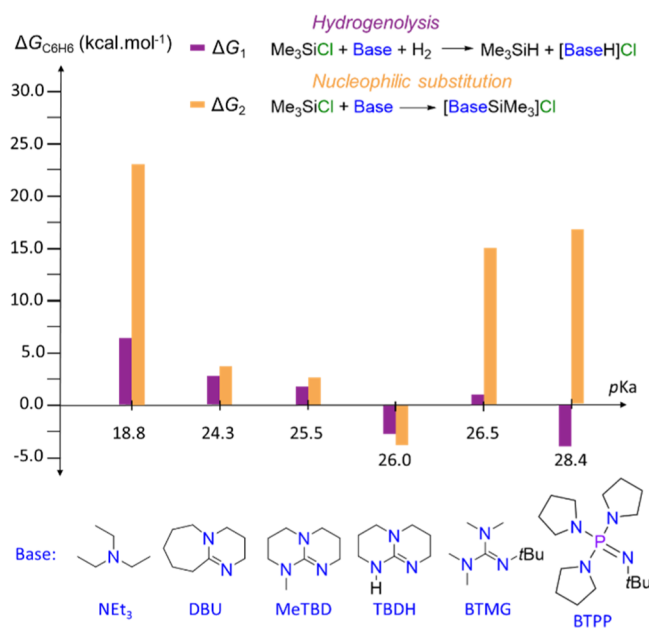
are thermodynamically favorable. The negative value of ΔG$_1$ compared to other bases may be related to the high stability of [TBDH$_2$]Cl,[21] and the absence of Me$_3$SiH production may result from either the higher exergonicity for the formation of silylium compared to the hydrogenolysis (ΔG$_1$ − ΔG$_2$ = +1.0 kcal mol^{-1}) or its low solubility and precipitation in C$_6$D$_6$.

Experimental and computational results show that from a thermodynamic standpoint, BTPP is the most suitable base for the production of Me$_3$SiH because it presents a large ΔG$_1$ − ΔG$_2$ difference with a negative ΔG$_1$ value of −3.9 kcal mol^{-1}, and it is able to favor the thermodynamics of the hydrogenolysis while preventing the formation of the silylium side product [BaseSiMe$_3$]Cl. Since the formation of the hydrogenolysis byproduct [BaseH]Cl can drive the catalysis and

because its solubility is strongly related to the nature of the solvent, we investigated the influence of some polar and nonpolar solvents in the hydrogenolysis of Me$_3$SiCl (1–5 bar H$_2$, r.t., 18 h), catalyzed by 1 (1 mol %) in the presence of BTPP (eq 2, Table 2). Replacing benzene with toluene or

Table 2. Influence of the Solvent on the Hydrogenolysis of Me$_3$SiCl[a]

$$\text{Me}_3\text{SiCl} + \text{BTPP} \xrightarrow[\text{H}_2, \text{ r.t., Solvent, 18 h}]{\text{1 (1 mol%)}} \text{Me}_3\text{SiH} + [\text{BTPPH}]\text{Cl} \quad (2)$$

1.1 eq

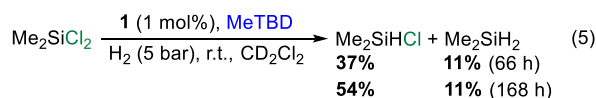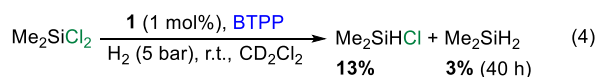| entry	p(H$_2$) (bar)	solvent	conv.[b] (%)	yield (select.)[b] (%)	ε[c]
1	1	C$_6$D$_6$	23	18 (78)	2.3
2	1	Tol-d_8	15	13 (89)	2.4
3	1	THF-d_8	17	17 (99)	7.6
4	1	CD$_2$Cl$_2$	56	56 (99)	8.9
5	5	CD$_2$Cl$_2$	99	98 (99)	8.9
6	1	CD$_3$CN	12	4 (30)	36.6
7	1	DMF-d_7	18	0 (0)	38.3
8	1	DMSO-d_6	9	0 (0)	46.7

[a]General conditions: 0.1 mmol of Me$_3$SiCl, 0.11 mmol of BTPP, 1 μmol of 1 (1 mol %), 0.5 mL of the solvent, room temperature (r.t.). [b]Conversions, selectivities, and yields were determined by ^{1}H NMR integration of the Me$_3$Si signals versus an internal standard (1,3,5-trimethylbenzene). [c]Dielectric constant of the solvents.

THF, at 1 bar of H$_2$, somewhat decreased the yields in Me$_3$SiH to 13 and 17%, respectively (Table 2, entries 2 and 3). In the more polar solvents DMF, DMSO, and MeCN, the conversion rates at 1 bar H$_2$ are low, and Me$_3$SiH is observed only in MeCN and in low quantity (4%) (Table 2, entries 6–8). NMR analyses actually revealed in the later solvents the formation of large quantities of the soluble silylium salt [BTPPSiMe$_3$]Cl, which is detrimental to the catalysis. Finally, at 1 bar H$_2$, the highest conversion (56%) with excellent yield and selectivity in Me$_3$SiH (56 and 99%, respectively) was achieved in dichloromethane (entry 4). Importantly, under 5 bar H$_2$, Me$_3$SiH was obtained in near quantitative yield (98%) from Me$_3$SiCl (entry 5). In the case of 1 bar of H$_2$, longer reaction times did not

lead to increased yields similar to the previous observations in C$_6$D$_6$. The normalized profiles in Me$_3$SiH production in CD$_2$Cl$_2$ at 1 and 5 bar of H$_2$ have been drawn (see the Supporting Information, 2.1.5). The two curves almost overlap, which suggests that the pressure mostly influences the thermodynamics rather than the kinetics of the reaction.

Capitalizing on these findings, the hydrogenolysis of Et$_3$SiCl and Me$_2$SiCl$_2$ was attempted (Scheme 4; eqs 3−5). The

**Scheme 4. Catalytic Hydrogenolysis by 1 (1 mol %) of Et$_3$SiCl and Me$_2$SiCl$_2$ with BTMG or MeTBD in CD$_2$Cl$_2$[a]**

$$Et_3SiCl \xrightarrow[\text{H}_2 \text{ (5 bar), r.t., CD}_2\text{Cl}_2]{\textbf{1} \text{ (1 mol\%), BTPP}} Et_3SiH \quad (3)$$
$$\textbf{59\%} \text{ (40 h)}$$

$$Me_2SiCl_2 \xrightarrow[\text{H}_2 \text{ (5 bar), r.t., CD}_2\text{Cl}_2]{\textbf{1} \text{ (1 mol\%), BTPP}} Me_2SiHCl + Me_2SiH_2 \quad (4)$$
$$\textbf{13\%} \qquad \textbf{3\%} \text{ (40 h)}$$

$$Me_2SiCl_2 \xrightarrow[\text{H}_2 \text{ (5 bar), r.t., CD}_2\text{Cl}_2]{\textbf{1} \text{ (1 mol\%), MeTBD}} Me_2SiHCl + Me_2SiH_2 \quad (5)$$
$$\textbf{37\%} \qquad \textbf{11\%} \text{ (66 h)}$$
$$\textbf{54\%} \qquad \textbf{11\%} \text{ (168 h)}$$
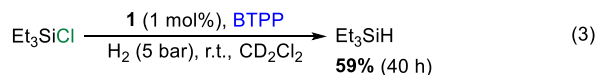
[a]Yields were determined by ^{1}H NMR integration of the R$_n$Si ($n = 2$ and 3) signals versus an internal standard (1,3,5-trimethylbenzene).

conversion of Et$_3$SiCl with BTPP proved more difficult than Me$_3$SiCl, requiring 40 h to afford Et$_3$SiH selectively in 59% yield. This is in agreement with the observation of the Shimada and Schneider groups that an increase in the steric hindrance of the silyl iodides or triflates led to longer reaction times.[13,14] Interestingly, Me$_2$SiCl$_2$, which is more electrophilic[22] than Me$_3$SiCl, proved less reactive under our conditions (Scheme 4, eq 4), and a mixture of Me$_2$SiHCl (13%) and Me$_2$SiH$_2$ (3%) was observed after 40 h. This result matches the hydrogenolysis of Me$_2$Si(OTf)$_2$ by an iridium catalyst reported to be much slower (7 days vs 8 h for Me$_3$SiOTf).[13] These poor yields in hydrosilanes demonstrated that the hydrogenolysis of dialkylchlorosilanes must be optimized. Replacing BTPP with MeTBD (Scheme 4, eq 5) favored a higher conversion rate in Me$_2$SiCl$_2$ (48%) and the formation of Me$_2$SiHCl as the major product (37% yield). Increased reaction times led to higher yields in Me$_2$SiHCl (54% after 7 days). No trace of the silylium [MeTBDSiClMe$_2$]Cl could be detected by ^{1}H NMR in dichloromethane. The latter results evidence the formation of R$_2$SiHCl species from R$_2$SiCl$_2$ under smooth conditions, while Me$_2$SiH$_2$ is the major product with strong reducing agents (such as LiAlH$_4$).[23]

To gain insights into the mechanism of the catalysis under the optimized conditions (5 bar H$_2$ in CH$_2$Cl$_2$) (Scheme 5), we focused on the iridium complexes that might form from 1 either by stoichiometric addition of the reagents (eqs 6, 7, and 8) or under catalytic conditions. The ^{1}H NMR spectrum of 1 is not modified by addition of 1 equiv. of Me$_3$SiCl or BTPP or when pressurized under H$_2$. 1 is however converted in 1 h into [Ir(^{tBu}POCOP)H$_2$(H$_2$)][24] (2) (81%), when treated with BTPP under 5 bar H$_2$. 2 is the only complex detected by ^{1}H NMR during the catalysis and at its end. Hydrogenolysis of Me$_3$SiCl with [Ir(^{tBu}POCOP)H$_2$] (3) (1 mol %) also led to 2 as the only observable iridium species (see Supporting Information Figure S7).[24] However, 2 and 3 do not react with stoichiometric quantities of Me$_3$SiCl to give Me$_3$SiH. Our hypothesis for the active species is based on the formation of the anionic hydride species [Ir(^{tBu}POCOP)H$_3$]$^-$ for which the

Scheme 5. Stoichiometric Reactions[a]
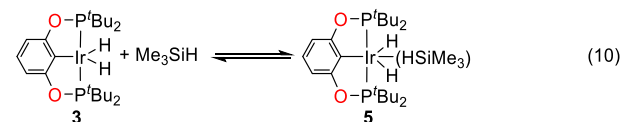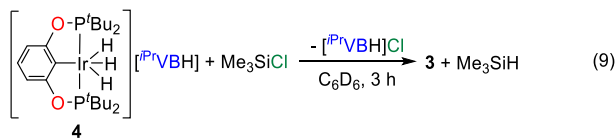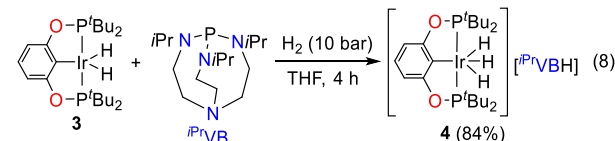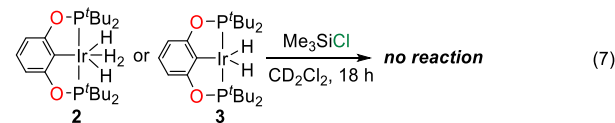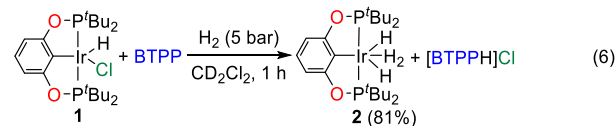
[a]Reaction (7) with 2 has been conducted under 1 bar of H$_2$.

hydride transfer is expected to be much more efficient than that from the neutral derivatives 2 or 3 (eq 7). Such species are known, and [Ir(^{tBu}POCOP)H$_3$]Na[24] was previously reported by Brookhart and co-workers from the treatment of 1 with NaH. Although never detected in our catalytic experiments, anionic species may be an intermediate formed by deprotonation of 2 with a strong base. Attempts to generate such species from 3 using only BTPP and H$_2$ have not been successful. However, the use of a stronger base such as Verkade superbase ^{iPr}VB (^{iPr}VB = 2,8,9-triisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane) in the presence of 3 under 10 bar H$_2$ (eq 8) in THF immediately afforded a white deposit. This solid has been characterized by NMR in acetonitrile as the ion pair [Ir(^{tBu}POCOP)H$_3$][^{iPr}VBH] (4), featuring both the expected anionic hydride and the phosphonium salt. Complex 4 shows ^{1}H NMR signals similar to those reported in [Ir(^{tBu}POCOP)H$_3$]Na.[24] It is not stable in CD$_2$Cl$_2$[25] but reacted in C$_6$D$_6$ with 1 equiv. Me$_3$SiCl to give Me$_3$SiH quantitatively after 4 h (eq 9). The resulting complexes 3 and [Ir(^{tBu}POCOP)H$_2$(HSiMe$_3$)] (5) were identified by NMR (eq 10 and Supporting Information Figure S18/S19). Complex 5 is analogous to the previously reported [Ir(^{tBu}POCOP)-H$_2$(HSiEt$_3$)][26] and displays an Ir−H hydride signal at −8.56 ppm by ^{1}H NMR. This result supports the involvement of the anionic hydride complex [Ir(^{tBu}POCOP)H$_3$][BTPPH] (6) as a key hydride donor in the formation of the hydrosilane. Generated catalytically and prone to reduce Si−Cl bonds, complex 6 would be the first anionic trihydride iridium complex involved in catalytic hydrogenation reactions and would be responsible for the excellent performances of this system (Scheme 5).

Density functional theory calculations (see Supporting Information page S24 for details) were performed to get a deeper insight into the mechanism and to confirm the possible hydride transfer to Me$_3$SiCl from the anionic trihydride species 6. The most favored pathway is depicted in Scheme 6: complex

Scheme 6. Computed Mechanism (PBE0-D3/Def2-TZVP (Ir), 6-311+G(d,p) (Mobile H, Si), 6-31G(d) (Other Atoms))// wB97M-V/Def2-TZVPP, SMD (Solvent: Dichloromethane), for the Hydrogenolysis of Me$_3$SiCl with BTPP and 1 or 3^a
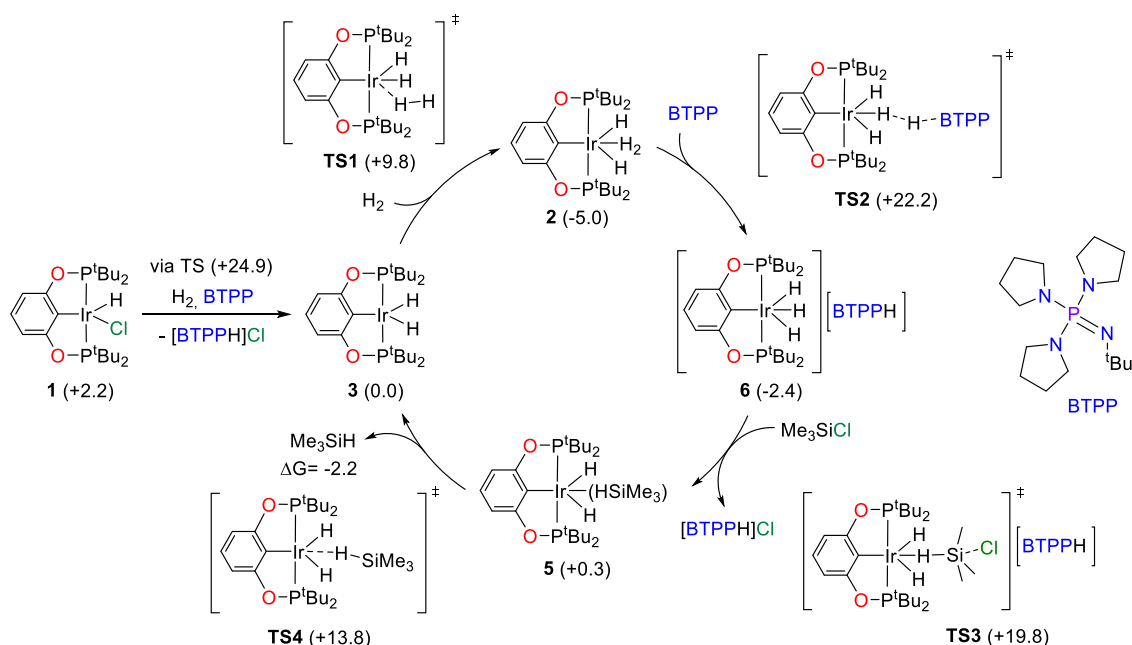
^{a}Gibbs free energies are reported in kcal mol^{-1} compared to 3, H$_2$, BTPP, and Me$_3$SiCl.

1 is a precatalyst and its hydrogenolysis with BTPP under H$_2$ is slightly exergonic (-2.2 kcal mol^{-1}) and leads to the dihydride species **3** with a high activation barrier of 22.7 kcal mol^{-1} (see Supporting Information Figure S26 for the full computed pathway). **3** is rapidly transformed into **2** under H$_2$ (TS$_1$: $\Delta G^\ddagger$ = +9.8 kcal mol^{-1}, ΔG = -5.0 kcal mol^{-1}). Deprotonation of **2** with BTPP can then occur, requiring an activation energy of +22.2 kcal mol^{-1} from **3** (TS$_2$: $\Delta\Delta G^\ddagger$ = +27.2 kcal mol^{-1}, $\Delta\Delta G$ = +2.6 kcal mol^{-1}). This step is rate-determining and is key in generating the high-energy, anionic trihydride species **6**. Hydride transfer from **6** to Me$_3$SiCl provides **5**, which features the product Me$_3$SiH coordinated to dihydride **3**,[27] concomitantly with the release of [BTPPH]Cl as a salt. The associated transition state is 19.8 kcal mol^{-1} higher in energy than **3** and follows an S$_N$2 mechanism at the silicon atom (TS$_3$: $\Delta\Delta G^\ddagger$ = +22.2 kcal mol^{-1}, $\Delta\Delta G$ = +2.7 kcal mol^{-1}). By releasing the coordinated silane, **3** is regenerated, thereby closing the catalytic cycle (TS$_4$: $\Delta\Delta G^\ddagger$ = +13.5 kcal mol^{-1}, $\Delta\Delta G$ = -1.9 kcal mol^{-1}), with an overall exergonicity of 1.2 kcal mol^{-1}. The energetic span of the catalytic cycle is defined by **2** and the base-assisted activation of coordinated H$_2$ (**TS$_2$**), which is the rate-determining transition state of the reaction, reaching 27.2 kcal mol^{-1}, which is only slightly higher than expected when considering the reaction conditions (18 h at r.t. under 5 bar of H$_2$). In agreement with the stoichiometric experiments, the direct hydride transfer from **3** to Me$_3$SiCl is also kinetically and theoretically disfavored (see the Supporting Information, Figure S24). Moreover, hydrogenolysis reactions were performed with D$_2$ and H$_2$ under similar conditions and evidenced a kinetic isotope effect (KIE) of 1.26 (±0.14) (see the Supporting Information, Section 3), close to the computed value of 1.30 (see the Supporting Information, Section 4.5). This value confirms that a hydrogen transfer is involved in the rate-determining step (from **2** to **6**).

In summary, hydrogenolysis of some chlorosilanes (Me$_3$SiH, Et$_3$SiH, and Me$_2$SiHCl) catalyzed by an Ir^{III} catalyst in the presence of a sterically hindered guanidine or phosphazene base (MeTBD, BTMG, and BTPP) afforded hydrosilanes with moderate to excellent yields and selectivity (up to 98%). The reaction proceeds under mild conditions (r.t., 1–5 bar H$_2$), with a low catalyst loading (1 mol %), without other additional additives, and requires moderate reaction times (18 h). The active species in the hydride transfer would involve the anionic iridium trihydride complex [Ir(^{tBu}POCOP)H$_3^-$], formed by the deprotonation of the H$_2$ complex [Ir(^{tBu}POCOP)H$_2$(H$_2$)] with a strong base. This complex exhibits an outstanding hydridic character, able to reduce a chlorosilane to a hydrosilane, without the need for a preactivation of the Si–Cl bond. Future works will concern the development of earth-abundant metal or transition-metal-free catalysts to replace the noble metal complex.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c01515.

> Detailed descriptions of experimental methods; procedures for the catalytic reduction of the chlorosilanes; stoichiometric reactions with complexes **1–4**; and computational details (PDF)

> Coordinates for all computed structures (XYZ)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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