Unlocking the catalytic hydrogenolysis of chlorosilanes into hydrosilanes with superbases

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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 (incl. 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.

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 that 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 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 the Si–Cl is much stronger 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_3SiCl into Me_3SiH 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 $Na[B(C_6H_3-3,5-(CF_3)_2)_4]$ 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 additional additives and enables the formation of Me_3SiH, Me_2SiHCl and Et_3SiH in yields up to 98%.
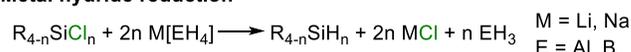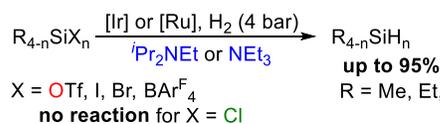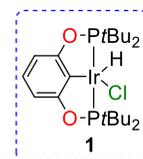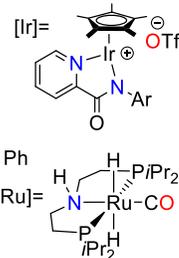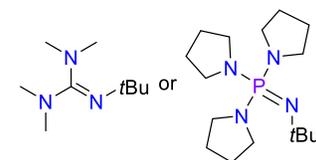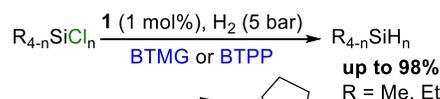

Scheme 1. Different synthetic ways from chlorosilanes to hydrosilanes.

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_2NEt 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] or hydrosilylation[16] reactions with formation of reactive [Ir]–H entities which transfer hydrides readily.

We thus turned to the precursor $[Ir(^{tBu}POCOP)HCl]^{17}$ (**1**) (^{tBu}-POCOP = $(C_6H_3)\{1,3-OPtBu_2\}_2$) as a possible catalyst for the Si−X to Si−H transformation. Beyond its thermodynamic role, the base is kinetically determinant to favour 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 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 (NEt₃, 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-*t*Bu-1,1,3,3-tetramethyl-guanidine, BTPP = (*t*Bu-imino)tri(pyrrolidino)phosphorane) differing by their Brønsted basicity (*p*K$_a$) and steric hindrances have thus been considered in this work.

The role of the base was evaluated in the catalytic hydrogenolysis of Me₃SiCl (5 bar of H₂, room temperature, in benzene) with **1** (1 mol%) (Eqn 1). In the presence of NEt₃, 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 Me₃SiH with a TON of 1.4 with DBU after 7 days[13] **1** provided Me₃SiH in a promising 6 % yield (TON=6) after 18 h (Eqn 1, entry 2). TBDH proved ineffective and reacted immediately with Me₃SiCl to give a white precipitate of the silylium adduct [TBDHSiMe₃]Cl (Scheme 2, right). In contrast to what previously reported,[13] here, the formation of this silylium [BaseSiMe₃]Cl did not increase the reactivity of the chlorosilane as it remained inert even after 48 h at 90°C in benzene (Table 1, entry 3). This result was further supported by calculations (*vide infra*). Even in CD₂Cl₂ where [TBDHSiMe₃]Cl is soluble and formed as major product, only traces of Me₃SiH were detected (Table 1, entry 4). Interestingly, Me₃SiH was obtained in 25 % yield after 18 h (Table 1, entry 5) with the use of MeTBD. Using BTMG and BTPP superbases, yields in Me₃SiCl were considerably improved, up to 54 % after 18 h (Table 1, entries 6 and 7). 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.[19]

In contrast to TBDH, the silylium adducts [BaseSiMe₃]Cl were not formed in benzene with the bases MeTBD, BTMG, and BTPP, while the hydrogenolysis by-product [BaseH]Cl deposited gradually, except for [BTPPH]Cl which is soluble in benzene. Decreasing the H₂ pressure to 1 bar somewhat decreased the conversion of Me₃SiCl (23%) and the yield in Me₃SiH (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 favour hydrogenolysis. The ability of the above bases to favour either the hydrogenolysis process or a nucleophilic substitution on Me₃SiCl was correlated with thermodynamic DFT calculations (Scheme 3). Gibbs free energies (in kcal.mol⁻¹) ΔG₁ for hydrogenolysis (in purple) and ΔG₂ for nucleophilic substitution (in orange) were computed at the PBE0-D3/6-311+G(d,p) level of theory, using the SMD model solvation model in benzene (see SI page S21 for details).
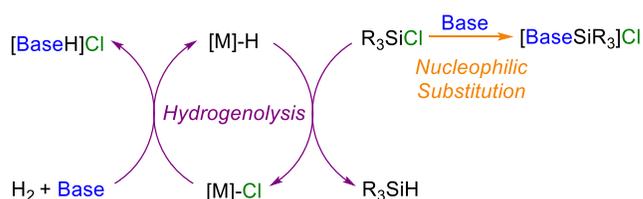
Scheme 2. Proposed mechanism for the catalytic hydrogenolysis of silyl chlorides and nucleophilic substitution.

Table 1. Screening of bases for the hydrogenolysis of Me₃SiCl in C₆D₆ with 1.[a]

Me₃SiCl + Base   →   Me₃SiH + [BaseH]Cl   (1)
1.1eq   H₂, r.t., C₆D₆
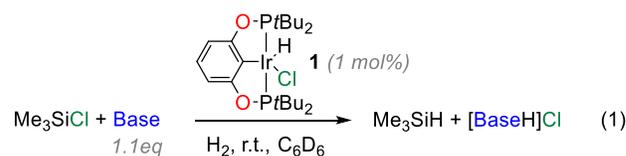
Entry	H₂ pressure (bar)	Base	*p*K$_a$[c]	Conversion[b] (%)	Yield (Selectivity)[b] (%)	Reaction Time (h)
1	5	NEt₃	18.8	0	0 (0)	48
2	5	DBU	24.3	10	6 (60)	18
3	5	TBDH	26.0	0	0 (0)	48
4[d]	5	TBDH	26.0	1	<1	18
5	5	MeTBD	25.5	30	25 (83)	18
6	5	BTMG	26.5	55	42 (76)	18
7	5	BTPP	28.4	59	54 (92)	18
8	1	BTPP	28.4	23	18 (78)	18

[a]General conditions: 0.1 mmol of Me₃SiCl, 0.11 mmol of base, 1 μmol of catalyst, 0.6 mL of solvent, at room temperature under 5 bar H₂ except entry 7 (1 bar). [b]Conversions, selectivities, and yields were determined by ¹H NMR spectroscopy, through integration of the R₃Si signals versus an internal standard (1,3,5-trimethylbenzene). [c]pKa in MeCN[20]. [d]in CD₂Cl₂.
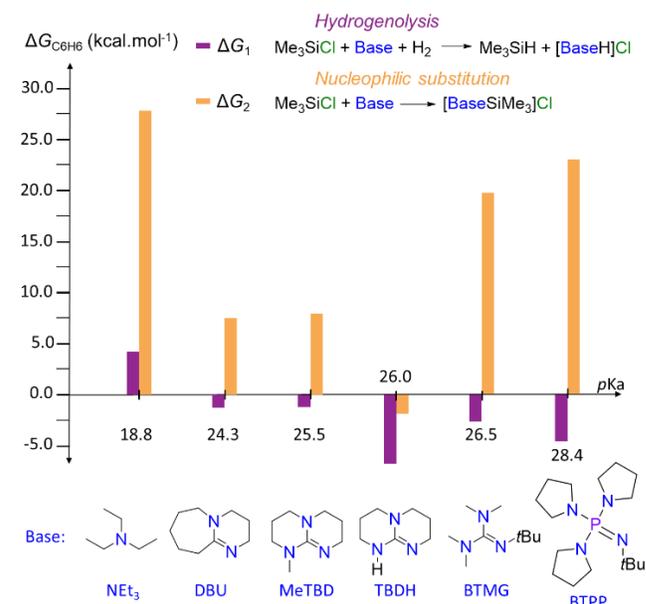
Scheme 3. Calculated ΔG_{C6H6} by DFT (PBE0-D3/6-311+G(d,p), SMD: benzene) of the hydrogenolysis process $Me_3SiCl + H_2 + Base \rightarrow Me_3SiH + [BaseH]Cl$ (ΔG_1) and the reaction $Me_3SiCl + Base \rightarrow [BaseSiMe_3]Cl$ (ΔG_2) plotted against the pK_a of the base in MeCN.

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 favours the hydrogenolysis of Me$_3$SiCl as reflected in the drop of ΔG_1 from –1.2 to –4.6 k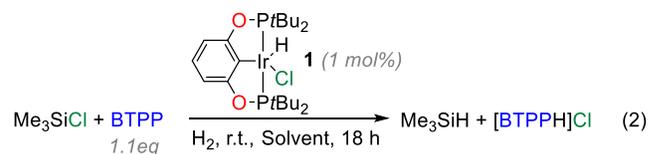cal.mol^{-1} from DBU to BTPP. While the hydrogenolysis of chlorosilanes (ΔG_1) with DBU and MeTBD is only slightly exergonic (–1.2 and –1.1 kcal.mol^{-1} respectively), the reaction proceeds in benzene as it is driven by the precipitation of the by-product salt [BaseH]Cl. Interestingly, with DBU, MeTBD, BTMG and BTPP, formation of the silylium [BaseSiMe$_3$]Cl is disfavoured with ΔG_2 values ranging from +7.6 to +23.4 kcal.mol^{-1}, presumably due to unfavourable steric interactions. TBDH exhibits a very different behaviour: the two reactions being thermodynamically favourable, the more negative value of ΔG_1 may be related to the high stability of [TBDH$_2$]Cl.[21] However, the absence of Me$_3$SiH production in the presence of TBDH therefore results either from the lower ΔG_2 balance compared to ΔG_1 or the low solubility of [TBDHSiMe$_3$]Cl which was observed to rapidly precipitate in C$_6$D$_6$.

Experimental and computational results show that 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 –4.6 kcal.mol^{-1}, and it is able to favour the thermodynamics of the hydrogenolysis while preventing the formation of the silylium side-product [BaseSiMe$_3$]Cl. Since the formation of the hydrogenolysis by-product [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 non-polar 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 (Eqn 2, Table 2). Replacing benzene with toluene or 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) were 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).

Capitalizing on these findings, the hydrogenolysis of Et$_3$SiCl and Me$_2$SiCl$_2$ was attempted (Scheme 4; Eqns 3-5). The 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 in our conditions (Scheme 4, Eqn 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, Eqn 5) favoured higher conversion rate in Me$_2$SiCl$_2$ (48 %) and 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$_2$ in smooth conditions while Me$_2$SiH$_2$ is the major product with strong reducing agents (such as LiAlH$_4$).[23]
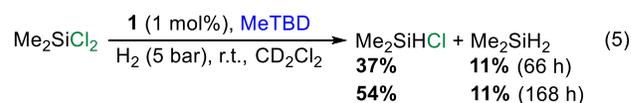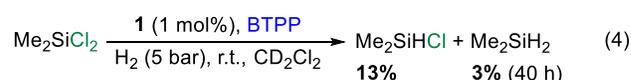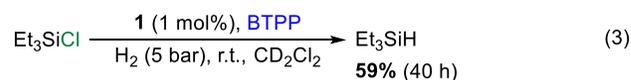
Table 2. Influence of the solvent on the hydrogenolysis of Me$_3$SiCl.[a]

$$Me_3SiCl + \underset{1.1eq}{BTPP} \xrightarrow[H_2, \text{ r.t., Solvent, 18 h}]{\mathbf{1} \, (1 \text{ mol\%})} Me_3SiH + [BTPPH]Cl \quad (2)$$

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%), 0.6 mL of solvent, room temperature (r.t.). [b] Conversions, selectivity 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.

$$Et_3SiCl \xrightarrow[H_2 \,(5 \text{ bar}), \text{ r.t., CD}_2\text{Cl}_2]{\mathbf{1} \,(1 \text{ mol\%}), \, BTPP} \underset{\mathbf{59\%} \,(40 \text{ h})}{Et_3SiH} \quad (3)$$

$$Me_2SiCl_2 \xrightarrow[H_2 \,(5 \text{ bar}), \text{ r.t., CD}_2\text{Cl}_2]{\mathbf{1} \,(1 \text{ mol\%}), \, BTPP} \underset{\mathbf{13\%}}{Me_2SiHCl} + \underset{\mathbf{3\%} \,(40 \text{ h})}{Me_2SiH_2} \quad (4)$$

$$Me_2SiCl_2 \xrightarrow[H_2 \,(5 \text{ bar}), \text{ r.t., CD}_2\text{Cl}_2]{\mathbf{1} \,(1 \text{ mol\%}), \, MeTBD} \underset{\substack{\mathbf{37\%} \\ \mathbf{54\%}}}{Me_2SiHCl} + \underset{\substack{\mathbf{11\%} \,(66 \text{ h}) \\ \mathbf{11\%} \,(168 \text{ h})}}{Me_2SiH_2} \quad (5)$$

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$_2$. 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).

To gain insights into the mechanism of the catalysis in 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 (Eqn 6, 7 and 8) or in 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($^{t\text{Bu}}$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 during the catalysis and at its end. Hydrogenolysis of Me$_3$SiCl with [Ir($^{t\text{Bu}}$POCOP)H_2] (**3**) (1 mol%)[24] also led to **2** as the only observable iridium species (see SI Fig. S7). 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($^{t\text{Bu}}$POCOP)H_3]$^-$ for which the hydride transfer is expected to be much more efficient than from the neutral derivatives **2** or **3** (Eqn 7). Such species are known, [Ir($^{t\text{Bu}}$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 $^{i\text{Pr}}$VB ($^{i\text{Pr}}$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 (Eqn 8) in THF immediately afforded a white deposit. This solid has been characterized by NMR in acetonitrile as the ion pair [Ir($^{t\text{Bu}}$POCOP)H_3][$^{i\text{Pr}}$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($^{t\text{Bu}}$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 (Eqn 9). The resulting complexes **3** and [Ir($^{t\text{Bu}}$POCOP)H_2(HSiMe$_3$)] (**5**) were identified by NMR (Eqn 10 and SI Fig. S17/S18). Complex **5** is analogous to the previously reported [Ir($^{t\text{Bu}}$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($^{t\text{Bu}}$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).
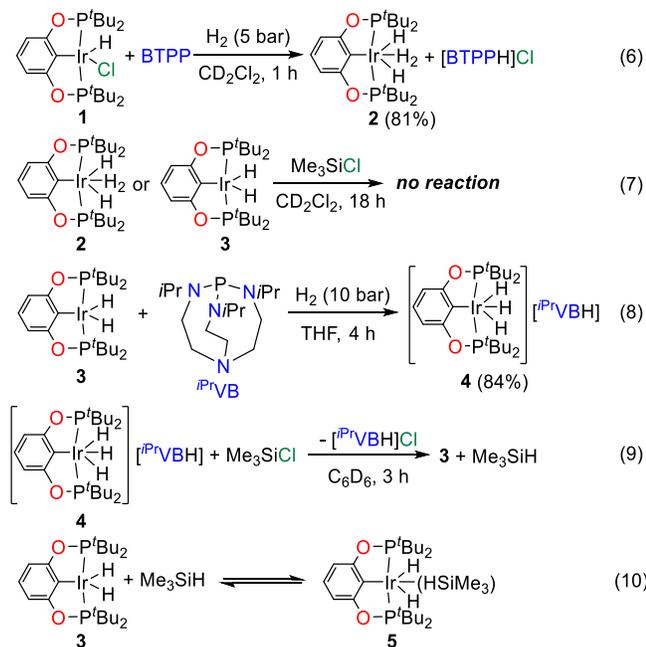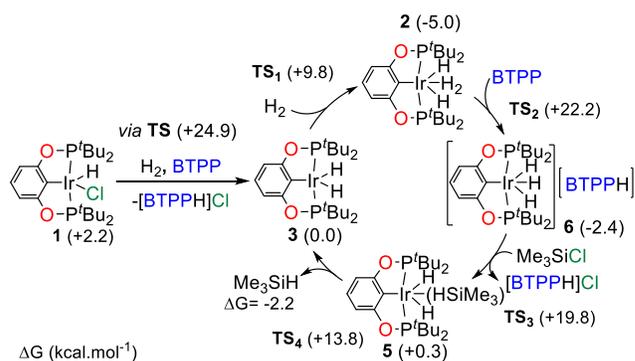
Scheme 6. Computed mechanism (PBE0-D3/Def2-TZVP (Ir), 6-311+G(d,p) (mobile H, Si), 6-31G(d) (other atoms),)//wB97M-V/Def2-TZVPP SMD (Solvent: dichloromethane) for the hydrogenolysis of Me$_3$SiCl with BTPP and 1 or 3. Energies are reported compared to 3, H$_2$, BTPP and Me$_3$SiCl.

Density functional theory calculations(see SI page S21 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 favoured pathway is depicted in Scheme 6: complex **1** is a precatalyst and its deprotonation 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 at 24.9 kcal.mol^{-1} (see SI Fig. S23 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. This step is 20.8 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}. Notably, in agreement with the experiments, the hydride transfer from **3** into Me$_3$SiCl has been discarded computationally (see SI Fig. S21). The total energetic span of the catalytic cycle, 27.2 kcal.mol^{-1}, is only lightly higher than expected compared to the reaction conditions (18 h at r.t. under 5 bar of H_2) and defined by **2** and the base-assisted activation of coordinated H_2 (TS$_2$), which is the rate-determining transition state of the reaction.

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, BTPP) afforded hydrosilanes with moderate to excellent yields and selectivity (up to 98 %). The reaction proceeds in mild conditions (r.t., 1 to 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($^{t\text{Bu}}$POCOP)$H_3$$^-$], formed by the deprotonation of the H_2 complex [Ir($^{t\text{Bu}}$POCOP)$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

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

pre-activation 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

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.
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 File)

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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.

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