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Metal-Free Catalytic Hydrogenolysis of Chlorosilanes into Hydrosilanes with “Inverse” Frustrated Lewis Pairs**

Gabriel Durin,^[a] Jean-Claude Berthet,^[a] Pierre Thuéry,^[a] Emmanuel Nicolas,^[a] and Thibault Cantat^{*[a]}

The challenging metal-free catalytic hydrogenolysis of silyl chlorides to hydrosilanes is unlocked by using an inverse frustrated Lewis pair (FLP), combining a mild Lewis acid (C_2BCl) and a strong phosphazene base (BTTP) in mild conditions (10 bar of H_2 , r. t.). In the presence of a stoichiometric amount of the base, the hydrosilanes R_3SiH ($\text{R} = \text{Me, Et, Ph}$) are generated

in moderate to high yields (up to 95%) from their chlorinated counterparts. A selective formation of the valuable difunctional monohydride Me_2SiHCl is also obtained from Me_2SiCl_2 . A mechanism is proposed based on stoichiometric experiments and DFT calculations; it highlights the critical role of borohydride species generated by the heterolytic splitting of H_2 .

Introduction

Hydrosilanes are important compounds for the production of a variety of organosilicon compounds^[1] and attract increasing interest in catalysis for their ability to reduce, in mild conditions, a variety of functional groups such as esters or amides,^[2] with high selectivity and efficiency. In particular, they offer thermodynamic and kinetic advantages over the utilization of dihydrogen^[3] to reduce a variety of oxygenated molecules and materials (lignin, plastics, and CO_2) viewed as an alternative feedstock to replace oil.^[4] Their synthesis however currently involves potent reducing agents such as NaH and LiAlH_4 ,^[5] resulting in energy intensive overall processes. Their formation using H_2 , a mild and cheap reductant, which is also easily formed from renewable energy and water, would be an attractive and more sustainable route to such compounds.^[6]

Catalytic hydrogenolysis of halosilanes (I, Br) and triflate (OTf) derivatives has been introduced very recently by the groups of Shimada, Schneider, and Cantat with the use of molecular complexes of noble metals (Ru and Ir).^[7] In this transformation, a stoichiometric quantity of a base is required to drive the thermodynamics of the reaction by trapping the HX proton generated upon hydrogenolysis. The $\text{Si-X} \rightarrow \text{Si-H}$ reaction is sensitive to the steric hindrance of the silane, and the reactivity is in the order $\text{OTf} > \text{I} > \text{Br} \gg \text{Cl}$. In all cases, chlorosi-

lanes proved almost inert^[8] and could only be activated by the addition of a stoichiometric amount of additive (NaI , $\text{Na}(\text{BAR}^F_4)$ ($\text{Ar}^F = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3$)) that favors halide exchanges. A key milestone was achieved by combining an iridium(III) catalyst with a judicious base to access highly reactive iridium polyhydride intermediates, able to promote the catalytic hydrogenolysis of chlorosilanes without the need for a chloride abstractor (Scheme 1).^[9]

The critical steps in the hydrogenolysis of Si-X bonds rely on the formation, from H_2 and a stoichiometric base, of transient neutral or anionic hydride species, reactive enough to transfer further a hydride group to the silicon atom. To avoid the use of noble metal complexes, we considered the use of boron-based organocatalysts, able to engage in Frustrated Lewis Pairs (FLPs) reactivity to activate H_2 and generate borohydrides (Scheme 2), the latter species being known to react with chlorosilanes.^[10] We have previously reported the first metal-free hydrogenolysis of silyl triflate and halides (I, Br) into hydrosilanes with a variety of di- or triarylfuoroboranes, which behave as classical FLPs with amines, such as 2,2,6,6-tetramethylpiperidine (TMP).^[11] A similar procedure was described for the hydrodehalogenation of benzyl halides.^[12] Yet, this catalytic system could not convert the less reactive chlorosilanes (Scheme 2).

We report here an efficient catalytic route to convert chlorosilanes into hydrosilanes (with yields up to 95%) under a low pressure of dihydrogen by using C_2BX ($\text{X} = \text{H, Cl}$) boranes as catalysts. The mild Lewis acids can react as an *inverse* FLP when the phosphazene BTTP is used as a superbases (BTTP = *tert*-Butylimino-tri(pyrrolidino)phosphorane).

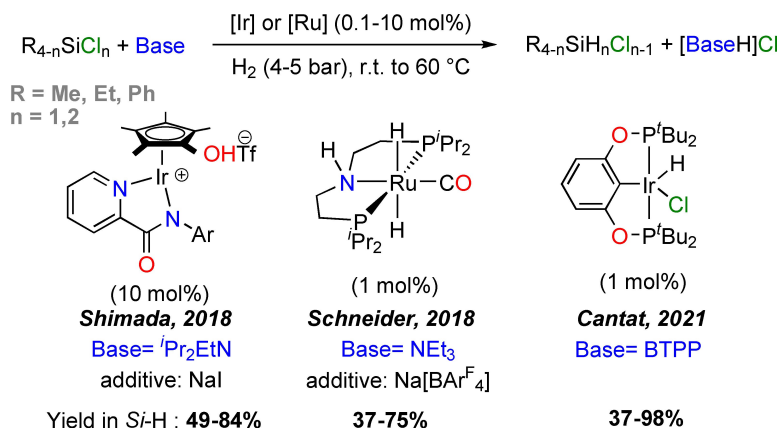
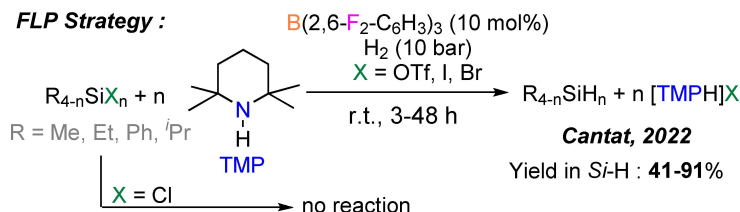
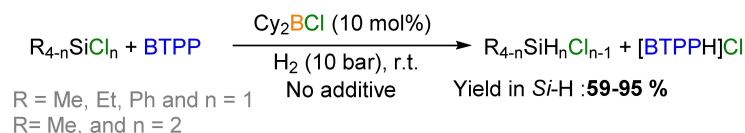
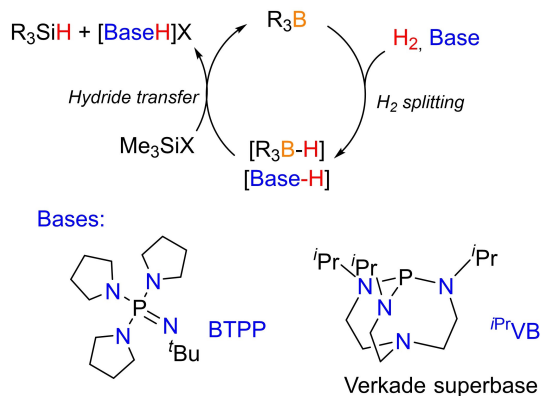
To tackle the metal-free hydrogenolysis of chlorosilanes, we felt it might be successful to increase the hydridic character of the $[\text{B}]\text{-H}^-$ species obtained by H_2 splitting with an FLP. However, a decrease in the Lewis acidity of the borane must be counterbalanced by an increase in the basicity of the amine in order to activate H_2 .^[13] This was demonstrated by Krempner et al. in their pioneering work on the *inverse* frustrated Lewis pairs that relied on the combination of a weak or moderate Lewis acid and a strong Lewis base to cleave H_2 heterolytically

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Metal-based strategy :**FLP Strategy :****This work : Inverse FLP****Scheme 1.** Hydrogenolysis routes for the conversion of chlorosilanes to hydrosilanes ($Ar^F = 3,5-(CF_3)_2C_6H_3$).**Scheme 2.** Hydrogenolysis of Me_3SiX by Frustrated Lewis pairs and H_2 activation by inverse FLPs.

(Scheme 2).^[14] We thus investigated the hydrogenolysis of Me_3SiCl in the presence of the *inverse* FLPs Ph_3B or Mes_2BH (10 mol%) ($Mes = 1,3,5$ -trimethylphenyl), with $BTPP$ (1 eq), under 10 bar of H_2 in CD_2Cl_2 (Table 1). After 24 h at room temperature, Me_3SiH was obtained in 20% and 11%, respectively (Table 1, entries 1 and 2), and the yields did not significantly improve after prolonged reaction times (less than 5% increase after 7 days for the two reactions). The selectivity in Me_3SiH was good to excellent (69%–90%), clearly demon-

strating the potential of inverse FLPs to unlock the conversion of chlorosilanes. Replacing the arylborane (Ph_3B , Mes_2BH) with an alkylborane, e.g., 9-BBN (9-borabicyclo[3.3.1]nonane) or Cy_2BH , significantly increased the yields in Me_3SiH . They reached 44% and 84%, respectively, after 24 h, and the selectivity was excellent (Table 1, entries 3 and 4). However, no reaction took place with catecholborane ($CatBH$) (Table 1, entry 6). Chlorodicyclohexylborane (10 mol%) proved to be the best catalyst affording selectively Me_3SiH in 92% yield after 24 h (95% after 38 h) in dichloromethane (Table 1, entry 7). Halving the catalyst loading (5 mol%) led to a slight decrease of the yield in Me_3SiH (92% to 89%, Table 1, entry 8), while a decrease of the H_2 pressure (from 10 to 5 bar) had a more significant influence on the yield, down to 64% (Table 1, entry 9). When the reaction is performed without H_2 , only 4% of Me_3SiH is formed when Cy_2BH is used as a Lewis acid, confirming that H_2 is the hydride source (Table 1, entry 5, and Scheme 4). This is corroborated by a labeling experiment under D_2 (10 bar), where the signal of the Me_3Si moiety (a doublet for Me_3SiH) becomes a singlet as expected for the formation of Me_3SiD (see Supporting Information Section 2.1.2).

With the catalyst Cy_2BCl in hand, the role of the superbases was evaluated in the catalytic hydrogenolysis of Me_3SiCl , exchanging the phosphazene $BTPP$ for the guanidine $BTMG$ (2-*tert*-butyl-1,1,3,3-tetramethylguanidine) and the phosphazene

P_1^tBu (*tert*-Butylimino-tris(dimethylamino)phosphorane). Although these two nitrogen bases have similar steric hindrances, they differ by their pKa (26.5 for BTMG and 27.0 for P_1^tBu in MeCN, compared to 28.4 for BTTP).^[15] While no traces of Me_3SiH could be detected with BTMG, the yield in hydrosilane reached 14% with P_1^tBu (Table 1, entries 10 and 11), far from the >95% yield obtained with BTTP (Table 1, entry 7). An increase in the basicity thus leads to higher yields in the formation of the hydrosilane.

The scope of the hydrogenolysis was then extended to other mono and dichlorosilanes, namely Et_3SiCl , Ph_3SiCl , and Me_2SiCl_2 , using the optimized conditions (Table 2). Increased

steric hindrance in the chlorosilane did not significantly alter the yields in hydrosilane: Et_3SiH and Ph_3SiH are obtained in slightly lower yields albeit much more slowly (84% and 86% respectively in 48 h) than Me_3SiH (Table 2, entries 1 and 2). This broader applicability contrasts with previous reports using metal catalysts that are much more sensitive to substrate steric hindrance (Ru, Ir).^[7a-c,9] For example, with an iridium(I) carbene catalyst, the group of Shimada reported that while Me_3SiH is obtained from Me_3SiOTf in 93% yield after 8 h, the hydrogenolysis of Et_3SiOTf to Et_3SiH (84%) requires 4 days of reaction.^[7a] A drop of 20% in yield was also reported when Me_3SiCl was switched for Et_3SiCl in the NaI-promoted, Ir(I)-

Table 1. Screening of Lewis acid and base for the hydrogenolysis of Me_3SiCl .^[a]

$Me_3SiCl + Base \xrightarrow[CD_2Cl_2, r.t.]{LA (10 mol\%), H_2 (10 bar), 1.1 eq} Me_3SiH + [BaseH]Cl$							
Entry	$p(H_2)$ [bar]	Lewis Acid (LA)	Hydricity [kcal mol ⁻¹] ^[16]	Base	Conv. [%] ^[b]	%yield [Select.] ^[b]	Reaction time [h]
1	10	Ph_3B	36	BTTP	22	20 (91)	24
2	10	Mes_2BH	34	BTTP	16	11 (69)	24
3	10	9-BBN	33	BTTP	50	44 (88)	24
4	10	Cy_2BH	30	BTTP	85	84 (99)	24
5 ^[c]	0	Cy_2BH	30	BTTP	6	4 (67)	24
6	10	CatBH	26	BTTP	0	–	48
7	10	Cy_2BCl	35	BTTP	95	92 (97)	24
					99	95 (96)	38
8 ^[d]	10	Cy_2BCl	35	BTTP	91	89 (98)	24
9	5	Cy_2BCl	35	BTTP	65	64 (99)	24
10	10	Cy_2BCl	35	P_1^tBu	20	14 (70)	48
11	10	Cy_2BCl	35	BTMG	0	–	48

[a] General conditions: 0.1 mmol of Me_3SiCl , 0.11 mmol of the base, 10 μ mol of LA (10 mol%), 0.5 mL of solvent, room temperature. [b] Conversions, selectivities, and yields were determined by ¹H NMR integration of the R_3Si signals versus an internal standard (1,3,5-trimethylbenzene). [c] Under argon atmosphere. [d] 5 mol% of LA.

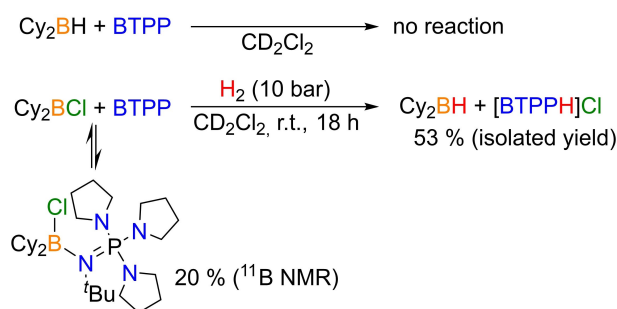
Table 2. Scope of the hydrogenolysis of chlorosilanes with BTTP and Cy_2BCl .^[a]

$R_{4-n}SiCl_n + BTTP \xrightarrow[CD_2Cl_2, r.t.]{Cy_2BCl (10 mol\%), H_2 (10 bar), 1.1 eq} R_{4-n}SiH_nCl_{n-1} + [BTTPH]Cl$					
Entry	Chlorosilane	Product	Conv. [%] ^[b]	Yield (Select.) [%] ^[b]	Time [h]
1	Et_3SiCl	Et_3SiH	85	84 (99)	48
2	Ph_3SiCl	Ph_3SiH	89	86 (97)	48
3	Me_2SiCl_2	Me_2SiHCl	76	59 (78)	300
		Me_2SiH_2		6 (9)	
4 ^[c]	Me_2SiCl_2	Me_2SiHCl	98	48 (48)	72
		Me_2SiH_2		10 (10)	

[a] General conditions: 0.1 mmol of Me_3SiCl , 0.11 mmol of BTTP, 10 μ mol of LA, 0.5 mL of solvent at room temperature. [b] Conversions, selectivity, and yields were determined by ¹H NMR integration of the R_3Si signals versus an internal standard (1,3,5-trimethylbenzene). [c] 2 equiv. of BTTP was used. A complex mixture of silylated side products was also obtained.

catalyzed hydrogenolysis reaction, as reported by the Shimada group.^[7b] Of interest, Me_2SiCl_2 was successfully converted to Me_2SiHCl in 59% yield after 300 h. A good selectivity of 78% was obtained, Me_2SiH_2 being formed as a side-product (Table 2, entry 3). This is the best selectivity reported so far for the formation of Me_2SiHCl , by hydrogenation. Such hydrido-chloro compounds involving two reactive sites (H and Cl) are interesting in the industry since they can promote further functionalization in silicon polymer chemistry.^[17] Adding a second equivalent of BTTP to the previous reaction increased the conversion to 98% but did not result in the selective formation of Me_2SiH_2 , which is formed in 10% yield, while Me_2SiHCl (48%) remained the major product. The decrease in selectivity mainly reflects secondary redistribution reactions, similar to those described by Holthausen and Auner.^[18]

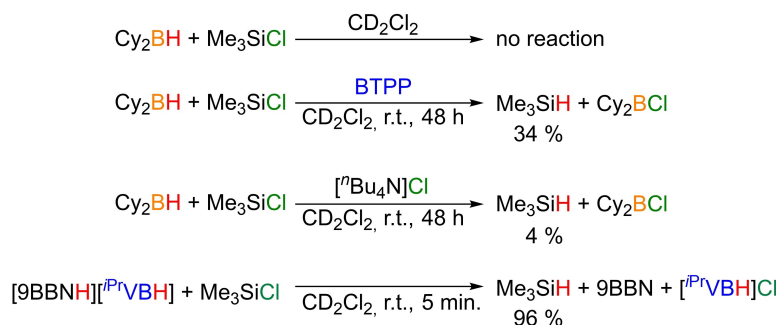
We were then interested in the mechanism of the reaction and, more precisely, in the nature of the active hydride species able to reduce the Si–Cl bond. First, the behavior of the superbases with the reagents (boranes and chlorosilanes) was investigated, starting with the stoichiometric addition of the base to a solution of Cy_2BX in CD_2Cl_2 ($\text{X}=\text{H}, \text{Cl}$). When combined in a 1:1 ratio, Cy_2BH and BTTP gave a colorless solution in CD_2Cl_2 . No interaction could be detected from the ^1H spectrum, the signals being those of the free compounds (Scheme 3 and see Supporting Information Section 2.2.2). However, in contrast, a CD_2Cl_2 solution of Cy_2BCl turned immediately yellow in the presence of BTTP: a new species with broadened ^1H NMR signals was observed, indicating significant interaction between the chloroborane and the base. The ^{11}B NMR spectrum of the mixture evidenced two singlets, one for the free Cy_2BCl ($\delta=66.9$ ppm)



Scheme 3. Stoichiometric reactions between Cy_2BX ($\text{X}=\text{H}, \text{Cl}$), BTTP, and H_2 .

and another shifted upfield at 6.98 ppm, characteristic of tetrahedral boron, which we assigned to the $\text{Cy}_2\text{BCl}\leftarrow\text{BTTP}$ adduct, obtained in ca. 20% yield (Scheme 3 and see Supporting Information Section 2.2.1). Of interest, no reaction was observed by ^1H NMR between Me_3SiCl and BTTP in dichloromethane.^[11] Moreover, we already showed in a previous report that Me_3SiCl is more reactive than $[\text{Me}_3\text{SiBTTP}]\text{Cl}$ for hydride transfers.^[9] Despite the presence of a $\text{Cy}_2\text{BCl}\leftarrow\text{BTTP}$ adduct, its formation is reversible, and the H_2 splitting still occurs.^[19] Indeed, exposing a solution of Cy_2BCl and BTTP under 10 bar of H_2 led to the formation of dicyclohexylborane after 18 h, which was isolated (53% yield) (Scheme 3).

Next, we investigated the hydride transfer step. The stoichiometric reaction between dicyclohexylborane (Cy_2BH) and Me_3SiCl showed no trace of Me_3SiH . However, when BTTP (1 eq) was added to a dichloromethane solution of Cy_2BH and Me_3SiCl , we observed the slow formation of Me_3SiH (4% in 24 h and 34% after 48 h) (see Table 1, entry 5 and Scheme 4). This led us to consider the transient formation of an anionic $[\text{Cy}_2\text{BHCl}]^-$ species as the reactive hydride donor. Indeed, BTTP and Me_3SiCl can react to form the silylium salt $[(\text{BTTP})\text{SiMe}_3]\text{Cl}$,^[9] which can further transfer its chloride to Cy_2BH to form $[\text{Cy}_2\text{BHCl}][\text{BTTP}(\text{SiMe}_3)]$. To support this hypothesis, we reacted $[\text{t}^{\text{Bu}}\text{N}]\text{Cl}$ and Cy_2BH in $\text{THF}-d_8$ and observed the formation of $[\text{Cy}_2\text{BHCl}][\text{t}^{\text{Bu}}\text{N}]$ ($\delta=8.20$ ppm in the ^{11}B NMR spectrum; see Supporting Information Section 2.2.4). This chloroborohydride did react, albeit very slowly, in CD_2Cl_2 and under argon, with Me_3SiCl to give the hydrosilane, and only 4% of Me_3SiH were obtained after 48 h (see Supporting Information Section 2.2.5), compared to a catalytic reaction proceeding to full conversion within 24 h (Table 1, entry 7). While $[\text{Cy}_2\text{BHCl}]^-$ cannot be ruled out as one of the active species, other hydride donors may be involved. We thus considered the formation of dihydride $[\text{Cy}_2\text{BH}_2]^-$ that might arise from the reaction between Cy_2BH , H_2 , and BTTP. This species is a stronger hydride donor than $[\text{Cy}_2\text{BCH}]^-$ as highlighted by a lower hydricity value (30 vs. 35).^[16] Despite our efforts, we could not generate $[\text{Cy}_2\text{BH}_2]^-$. However, similar dihydride species have already been obtained from H_2 splitting and structurally characterized.^[14a,20] To confirm this hypothesis, we have synthesized the stable $[\text{9-BBNH}][\text{t}^{\text{Pr}}\text{VBH}]$ compound ($\text{t}^{\text{Pr}}\text{VB}=\text{2,8,9-Triisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo [3.3.3]undecane}$, the Verkade base) previously reported



Scheme 4. Stoichiometric reactions between hydroboranes and Me_3SiCl .

by Krempner.^[14a] Addition of a solution of Me_3SiCl in CD_2Cl_2 on ca. 5 equiv. of this borohydride readily gave Me_3SiH almost quantitatively (see Supporting Information Section 2.2.7). Such a reaction occurs within minutes at r.t. and suggests that the most active hydride transfer species would be the transient anionic boron dihydride $[\text{Cy}_2\text{BH}_2]^-$.

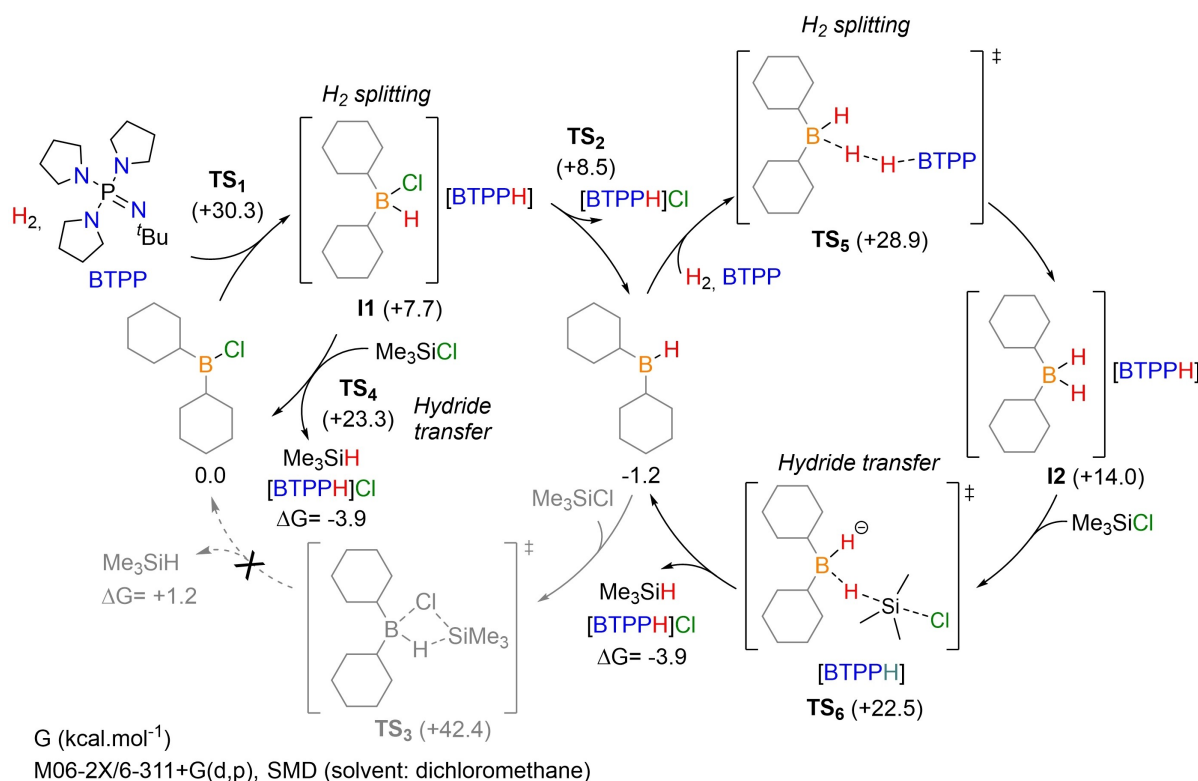
To support the experimental data and to get further mechanistic insights, DFT calculations have been performed at the M06-2X/6-311+G(d) level, using the SMD model to account for the solvation in CH_2Cl_2 (Scheme 5; see Supporting Information Section 3 for details). Starting from Cy_2BCl , heterolytic splitting of H_2 by the $\text{Cy}_2\text{BCl}:\text{BTTPP}$ *inverse* FLP gives the chloroborohydride species $[\text{Cy}_2\text{BHCl}][\text{BTTPPH}]$ ($\Delta G = +7.7 \text{ kcal mol}^{-1}$) through a high energy transition state at $+30.3 \text{ kcal mol}^{-1}$. The latter borohydride can then transfer its hydride to Me_3SiCl to form Me_3SiH and the byproduct $[\text{BTTPPH}]\text{Cl}$ ($\Delta G = -3.9 \text{ kcal mol}^{-1}$; $\Delta G^\ddagger = +23.3 \text{ kcal mol}^{-1}$). The borohydride $[\text{Cy}_2\text{BHCl}][\text{BTTPPH}]$ can also easily release its chloride anion to give the borane Cy_2BH ($\Delta\Delta G = -8.9 \text{ kcal mol}^{-1}$; $\Delta\Delta G^\ddagger = +0.8 \text{ kcal mol}^{-1}$). The latter borane cannot transfer its hydride directly to Me_3SiCl due to an inaccessible transition state ($\Delta\Delta G^\ddagger = +43.6 \text{ kcal mol}^{-1}$), in line with the experimental observations (see above).

Splitting of H_2 by the *inverse* FLP $\text{Cy}_2\text{BH}:\text{BTTPP}$ to give $[\text{Cy}_2\text{BH}_2][\text{BTTPPH}]$ is endergonic ($\Delta\Delta G = +15.2 \text{ kcal mol}^{-1}$) with an energy barrier of $28.9 \text{ kcal mol}^{-1}$. This dialkylboron dihydride can readily transfer a hydride to Me_3SiCl in an exergonic process ($\Delta\Delta G = -17.9 \text{ kcal mol}^{-1}$) via a TS at $+22.5 \text{ kcal mol}^{-1}$. Cy_2BH is

then regenerated concomitantly to the formation of the hydrosilane and the byproduct $[\text{BTTPPH}]\text{Cl}$, thereby closing a catalytic cycle with an overall exergonicity of $3.9 \text{ kcal mol}^{-1}$. The total energetic span of the catalytic cycle, $30.1 \text{ kcal mol}^{-1}$, is only slightly higher than expected within the reaction conditions (24 h at r.t. under 10 bar of H_2) and defined by the formation of the borohydride $[\text{Cy}_2\text{BH}_2][\text{BTTPPH}]$ from the splitting of H_2 with Cy_2BH and BTTP (TS₅).

Conclusions

The catalytic hydrogenolysis of chlorosilanes is highly challenging due to the strength of the Si–Cl bond, and all the rare reports use noble metal catalysts (Ru, Ir). We have developed a new transition metal-free catalytic pathway that combines mild Lewis acid catalysts (boranes) with a nitrogen superbases in an *inverse* FLP strategy. The *inverse* FLP combining Cy_2BH , particularly the cost-efficient Cy_2BCl , with BTTPP, proved the most efficient to afford hydrosilanes in high yields and under mild conditions (r.t., 10 bar H_2). Experimental evidence and theoretical calculations support a mechanism where reactive borohydride species (Cy_2BH_2^-) issued from the heterolytic splitting of H_2 are the key hydride transfer agents.



Scheme 5. Computed mechanism for the hydrogenolysis of Me_3SiCl with $\text{Cy}_2\text{BX}:\text{BTTPP}$ ($X = \text{H}, \text{Cl}$) FLP systems (at the M06-2X/6-311+G(d,p) level of theory, using the SMD model to account for the solvent effects: dichloromethane).

Experimental Section

General procedure for the catalytic hydrogenolysis of silyl chlorides: In the glovebox, a New Era NMR tube was charged with the borane catalyst (10 μmol , 10 mol%), the base (0.11 mmol, 1.1 equiv.), mesitylene Mes (7 μL , 0.05 mmol, 0.5 equiv.) and silyl chloride (0.10 mmol) in 0.5 mL of solvent. The solution was frozen in liquid nitrogen ($\text{N}_2(\text{l})$) and degassed twice before the headspace on the solution is filled with H_2 (10 bar). The tube is immediately shaken and maintained at r.t. for the reaction. The products were identified by ^1H NMR spectroscopy and quantified by relative integration of the ^1H NMR $\text{R}_\text{x}\text{Si}$ signals versus those of Mes (internal standard).

Deposition Number(s) 2249952 (for $[\text{P}^t\text{BuH}][\text{Ph}_3\text{BCl}]\cdot\text{C}_6\text{H}_6$), and 2249953 (for $[\text{P}^t\text{BuH}]\text{Cl}$) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Supporting Information

The authors have cited additional references within the Supporting Information.^[21]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: boron · frustrated Lewis pairs · hydrogenolysis · hydrosilanes · phosphazenes

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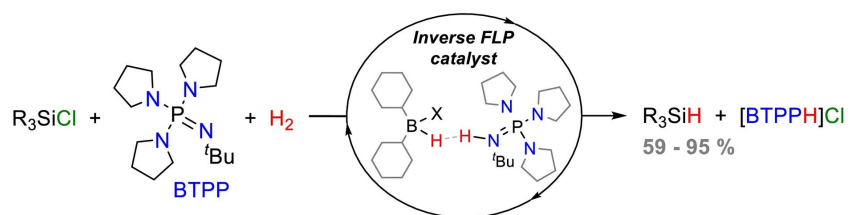
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RESEARCH ARTICLE



Hydrosilanes can be synthesized from chlorosilanes and H_2 , thanks to a combination of a superbases and a borane catalyst, forming an inverse FLP. A

mechanistic study demonstrates that the key intermediate species is a highly reactive borohydride, arising from H_2 heterolytic splitting.

Dr. G. Durin, Dr. J.-C. Berthet, Dr. P. Thuéry, Dr. E. Nicolas, Dr. T. Cantat*

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Metal-Free Catalytic Hydrogenolysis of Chlorosilanes into Hydrosilanes with “Inverse” Frustrated Lewis Pairs

