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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 Me₃SiH, Et₃SiH and Me₂SiHCl 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 aldehydes³ or ethers⁴ 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 CO₂) 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 LiAlH₄ (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 R₃SiX (X = OTf, I, Br) into R₃SiH 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 Me₃SiCl into Me₃SiH 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(C₆H₃-3,5-(CF₃)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 Me₃SiH, Me₂SiHCl and Et₃SiH in yields up to 98%.

Metal hydride reduction

Hydrogenolysis of SiX bonds

Shimada, 2017 and Schneider, 2018:

This work: Hydrogenolysis of SiCl bonds

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 NEt₃ or *i*Pr₂NEt to induce the reaction (Scheme 1).¹⁴ We chose iridium(III) pincer complexes as potential catalysts because they are competent in a number of hydrogenation¹⁵ or hydrosilylation¹⁶ reactions with formation of reactive [Ir]–H entities which transfer hydrides readily.

We thus turned to the precursor [Ir(^{*t*}BuPOCOP)HCl]¹⁷ (**1**) (^{*t*}BuPOCOP = (C₆H₃){1,3-OPtBu₂})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 H₂

(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 days¹³ **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) Δ*G*₁ for hydrogenolysis (in purple) and Δ*G*₂ 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

En-try	H ₂ pressure (bar)	Base	<i>p</i> K _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

^aGeneral 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). ^bConversions, selectivities, and yields were determined by ¹H NMR spectroscopy, through integration of the R₃Si signals versus an internal standard (1,3,5-trimethylbenzene). ^c*p*K_a in MeCN²⁰. ^din CD₂Cl₂.

Scheme 3. Calculated ΔG_{C6H6} by DFT (PBE0-D3/6-311+G(d,p), SMD: benzene) of the hydrogenolysis process $\text{Me}_3\text{SiCl} + \text{H}_2 + \text{Base} \rightarrow \text{Me}_3\text{SiH} + [\text{BaseH}]\text{Cl}$ (ΔG_1) and the reaction $\text{Me}_3\text{SiCl} + \text{Base} \rightarrow [\text{BaseSiMe}_3]\text{Cl}$ (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_3SiCl as reflected in the drop of ΔG_1 from -1.2 to -4.6 kcal.mol $^{-1}$ from DBU to BTTP. 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 $[\text{BaseH}]\text{Cl}$. Interestingly, with DBU, MeTBD, BTMG and BTTP, formation of the silylium $[\text{BaseSiMe}_3]\text{Cl}$ 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 $[\text{TBDH}_2]\text{Cl}$.²¹ However, the absence of Me_3SiH production in the presence of TBDH therefore results either from the lower ΔG_2 balance compared to ΔG_1 or the low solubility of $[\text{TBDHSiMe}_3]\text{Cl}$ which was observed to rapidly precipitate in C_6D_6 .

Experimental and computational results show that BTTP is the most suitable base for the production of Me_3SiH 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 $[\text{BaseSiMe}_3]\text{Cl}$. Since the formation of the hydrogenolysis by-product $[\text{BaseH}]\text{Cl}$ 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_3SiCl (1–5 bar H_2 , r.t., 18 h), catalyzed by **1** (1 mol%) in the presence of BTTP (Eqn 2, Table 2). Replacing benzene with toluene or THF, at 1 bar of H_2 , somewhat decreased the yields in Me_3SiH 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_3SiH 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 $[\text{BTTPSiMe}_3]\text{Cl}$, which is detrimental to the catalysis. Finally, at 1 bar H_2 , the highest conversion (56 %) with excellent yield and selectivity in Me_3SiH (56 % and 99 % respectively) were achieved in dichloromethane (entry 4). Importantly, under 5 bar H_2 , Me_3SiH was obtained in near quantitative yield (98 %) from Me_3SiCl (entry 5).

Capitalizing on these findings, the hydrogenolysis of Et_3SiCl and Me_2SiCl_2 was attempted (Scheme 4; Eqns 3–5). The conversion of Et_3SiCl with BTTP proved more difficult than Me_3SiCl requiring 40 h to afford Et_3SiH 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_2SiCl_2 , which is more electrophilic²² than Me_3SiCl , proved less reactive in our conditions (Scheme 4, Eqn 4) and a mixture of Me_2SiHCl (13 %) and Me_2SiH_2 (3 %) was observed after 40 h. This result matches the hydrogenolysis of $\text{Me}_2\text{Si}(\text{OTf})_2$ by an iridium catalyst reported to be much slower

(7 days vs 8 h for Me_3SiOTf).¹³ These poor yields in hydrosilanes demonstrated that the hydrogenolysis of dialkylchlorosilanes must be optimized. Replacing BTTP with MeTBD (Scheme 4, Eqn 5) favoured higher conversion rate in Me_2SiCl_2 (48 %) and formation of Me_2SiHCl as the major product (37 % yield). Increased reaction times led to higher yields in Me_2SiHCl (54% after 7 days). No trace of the silylium $[\text{MeTBDSiClMe}_2]\text{Cl}$ could be detected by ^1H NMR in dichloromethane. The latter results evidence the formation of R_2SiHCl species from R_2SiCl_2 in smooth conditions while Me_2SiH_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_3SiCl .^a

1 (1 mol%)

$$\text{Me}_3\text{SiCl} + \text{BTTP} \xrightarrow[\text{H}_2, \text{r.t., Solvent, 18 h}]{1.1 \text{ eq}} \text{Me}_3\text{SiH} + [\text{BTTPH}]\text{Cl} \quad (2)$$

Entry	p(H_2) (bar)	Solvent	Conv. ^b (%)	Yield (Select.) ^b (%)	ϵ^c
1	1	C_6D_6	23	18 (78)	2.3
2	1	Tol- <i>d</i> ₈	15	13 (89)	2.4
3	1	THF- <i>d</i> ₈	17	17 (99)	7.6
4	1	CD_2Cl_2	56	56 (99)	8.9
5	5	CD_2Cl_2	99	98 (99)	8.9
6	1	CD_3CN	12	4 (30)	36.6
7	1	DMF- <i>d</i> ₇	18	0 (0)	38.3
8	1	DMSO- <i>d</i> ₆	9	0 (0)	46.7

^a General conditions: 0.1 mmol of Me_3SiCl , 0.11 mmol of BTTP, 1 μmol of **1** (1 mol%), 0.6 mL of solvent, room temperature (r.t.).

^bConversions, selectivity and yields were determined by ^1H NMR integration of the Me_3Si signals versus an internal standard (1,3,5-trimethylbenzene). ^cDielectric constant of the solvents.

Scheme 4. Catalytic hydrogenolysis by **1 (1 mol%) of Et_3SiCl and Me_2SiCl_2 with BTMG or MeTBD in CD_2Cl_2 . Yields were determined by ^1H NMR integration of the R_nSi ($n = 2$ 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_2Cl_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 ^1H NMR spectrum of **1** is not modified by addition of 1 equiv. of Me_3SiCl or BTTP 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 1H during the catalysis and at its end. Hydrogenolysis of Me_3SiCl with $[Ir^{(tBu)POCOP}H_2]$ (**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_3SiCl to give Me_3SiH . Our hypothesis for the active species is based on the formation of the anionic hydride species $[Ir^{(tBu)POCOP}H_3]^-$ 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, $[Ir^{(tBu)POCOP}H_3]Na^{24}$ 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 $iPrVB$ ($iPrVB = 2,8,9$ -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 $[Ir^{(tBu)POCOP}H_3][iPrVBH]$ (**4**), featuring both the expected anionic hydride and the phosphonium salt. Complex **4** shows 1H NMR signals similar to those reported in $[Ir^{(tBu)POCOP}H_3]Na^{24}$. It is not stable in CD_2Cl_2 ,²⁵ but reacted in C_6D_6 with 1 equiv. Me_3SiCl to give Me_3SiH quantitatively after 4 h (Eqn 9). The resulting complexes **3** and $[Ir^{(tBu)POCOP}H_2(HSiMe_3)]$ (**5**) were identified by NMR (Eqn 10 and SI Fig. S17/S18). Complex **5** is analogous to the previously reported $[Ir^{(tBu)POCOP}H_2(HSiEt_3)]^{26}$ and displays an Ir–H hydride signal at -8.56 ppm by 1H 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).

Scheme 5. Stoichiometric reactions. Reaction (7) with **2** has been conducted under 1 bar of H_2 .

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_3SiCl with BTPP and **1** or **3**. Energies are reported compared to **3**, H_2 , BTPP and Me_3SiCl .

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_3SiCl 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, $\Delta G = -5.0$ 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 : $\Delta G^\ddagger = +27.2$ 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_3SiCl provides **5**, which features the product Me_3SiH 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_N2 mechanism at the silicon atom (TS_3 : $\Delta G^\ddagger = +22.2$ 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 : $\Delta G^\ddagger = +13.5$ 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_3SiCl 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_3SiH , Et_3SiH and Me_2SiHCl) 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 $[Ir^{(tBu)POCOP}H_3]^-$, 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

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

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Marciniak, B. Functionalisation and Cross-Linking of Organosilicon Polymers. In *Hydrosilylation, Advances in Silicon Science*, Springer, **2009**, pp 159–189.
- (2) Rösch, L.; John, P.; Reitmeier, R. Silicon Compounds, Organic. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, **2012**, pp 664–669.
- (3) Aizpurua, M.; Palomo, C. Reagents and Synthetic Methods; 43. A New Practical Preparation of Trimethylsilyl Trifluoromethanesulfonate. *Synthesis*, **1985**, 2, 206–207.
- (4) Cheng, C.; Hartwig, J. F. Catalytic Silylation of Unactivated C–H Bonds. *Chem. Rev.* **2015**, 115, 8946–8975.
- (5) Li, H.; Misal Castro, L. C.; Zheng, J.; Roisnel, T.; Dorcet, V.; Sortais, J.-B.; Darcel, C. Selective Reduction of Esters to Aldehydes under the Catalysis of Well-Defined NHC-Iron Complexes. *Angew. Chem. Int. Ed.* **2013**, 52 (31), 8045–8049.
- (6) (a) Hosokawa, S.; Toya, M.; Noda, A.; Morita, M.; Ogawa, T.; Motoyama, Y. Catalytic Silane-Reduction of Carboxylic Esters and Lactones: Selective Synthetic Methods to Aldehydes, Lactols, and Ethers via Silyl Acetal Intermediates. *ChemistrySelect* **2018**, 3 (11), 2958–2961.; (b) Das, S.; Addis, D.; Junge, K.; Beller, M. Zinc-Catalyzed Chemoselective Reduction of Tertiary and Secondary Amides to Amines. *Chem. Eur. J.* **2011**, 17 (43), 12186–12192.; (c) Pesti, J.; Larson, G. L. Tetramethyldisiloxane: A Practical Organosilane Reducing Agent. *Org. Process Res. Dev.* **2016**, 20 (7), 1164–1181.
- (7) Chauvier, C.; Cantat, T. A Viewpoint on Chemical Reductions of Carbon–Oxygen Bonds in Renewable Feedstocks Including CO₂ and Biomass. *ACS Catal.* **2017**, 7, 2107–2115.
- (8) (a) Monsigny, L.; Feghali, E.; Berthet, J.-C.; Cantat, T. Efficient Reductive Depolymerization of Hardwood and Softwood Lignins with Brookhart's Iridium(III) Catalyst and Hydrosilanes. *Green*

Chem. **2018**, 20 (9), 1981–1986.; (b) Monsigny, L.; Berthet, J.-C.; Cantat, T. Depolymerization of Waste Plastics to Monomers and Chemicals Using a Hydrosilylation Strategy Facilitated by Brookhart's Iridium(III) Catalyst. *ACS Sustain. Chem. Eng.* **2018**, 6 (8), 10481–10488.; (c) Riduan, S. N.; Zhang, Y.; Ying, J. Y. Conversion of carbon dioxide into methanol with silanes over N-heterocyclic carbene catalysts. *Angew. Chem. Int. Ed.*, **2009**, 48, 3322.; For reviews see : (d) Schutyster, W.; Renders, T.; Van den Bosch, S.; Koelewijn, S. F.; Beckham, G. T.; Sels, B. F. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. *Chem. Soc. Rev.*, **2018**, 47, 852.; (e) Payne, J.; McKeown, P.; Jones, M. D. A Circular Economy Approach to Plastic Waste. *Polymer Degradation and Stability*, **2019**, 165, 170–181.; (f) O'Brien, C. J.; Tellez, J. L.; Nixon, Z. S.; Kang, L. J.; Carter, A. L.; Kunkel, S. R.; Przeworski, K. C.; Chass, G. A. Recycling the Waste: The Development of a Catalytic Wittig Reaction. *Angew. Chem. Int. Ed.* **2009**, 48, 6836–6839.

(9) (a) Kalchauer, W.; Pachaly, B. Müller–Rochow Synthesis: The Direct Process to Methylchlorosilanes. In *Handbook of Heterogeneous Catalysis*, Wiley, **2008**, 12, 2635–2647.; (b) Simmler, W. Silicon Compounds, Inorganic. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, **2007**, pp 616–617.

(10) (a) Di Giorgio, P. A.; Strong, W. A.; Sommer, L. H.; Whitmore, F. C. Preparation of Triethylchlorosilane from Ethyl Orthosilicate. *J. Am. Chem. Soc.*, **1946**, 68, 1380.; (b) Bailey, D. L.; Sommer, L. H.; Whitmore, F. C. Some Reactions of Trialkylaminosilanes. *J. Am. Chem. Soc.*, **1948**, 70, 435–436.; (c) Masaoka, S.; Bannoa, T.; Ishikawa, M. The synthesis of chlorosilanes from alkoxysilanes, silanols, and hydrosilanes with bulky substituents. *J. Organomet. Chem.*, **2006**, 691, 174–181.; (d) Roberts, J. M.; Eldred, D. V.; Katsoulis, D. E. Synthesis of SiCl₄ from Gaseous HCl and Si(OMe)₄. Reaction Development and Kinetic Studies. *Ind. Eng. Chem. Res.*, **2016**, 55, 1813–1818.

(11) (a) Finholt, A. E.; Bond, A. C.; Wilzbach, K. E.; Schlesinger, H. I. The Preparation and Some Properties of Hydrides of Elements of the Fourth Group of the Periodic System and of their Organic Derivatives. *J. Am. Chem. Soc.*, **1947**, 69, 2692–2696.; (b) Ito, M.; Itazaki, M.; Abe, T.; Nakazawa, H. Hydrogenation of Chlorosilanes by NaBH₄. *Chem. Lett.*, **2016**, 45, 1434–1436.

(12) Cottrell, T. L. In *The Strengths of Chemical Bonds*, 2d ed., Butterworth, London, **1958**.

(13) (a) Tsushima, D.; Igarashi, M.; Sato, K.; Shimada, S. Ir-catalyzed Hydrogenolysis Reaction of Silyl Triflates and Halides with H₂. *Chem. Lett.* **2017**, 46, 1532–1534.; (b) Beppu, T.; Sakamoto, K.; Nakajima, Y.; Matsumoto, K.; Sato, K.; Shimada, S. Hydrosilane synthesis via catalytic hydrogenolysis of halosilanes using a metal-ligand bifunctional iridium catalyst. *J. Org. Chem.*, **2018**, 869, 75–80.

(14) Glüer, A.; Schweizer, J. I.; Karaca, U. S.; Würtele, C.; Diefenbach, M.; Holthausen, M. C.; Schneider, S. Hydrosilane Synthesis by Catalytic Hydrogenolysis of Chlorosilanes and Silyl Triflates. *Inorg. Chem.*, **2018**, 57, 13822–13828.

(15) (a) Clarke, Z. E.; Maragh, P. T.; Dasgupta, T. P.; Gusev, D. G.; Lough, A. J.; Abdur-Rashid, K. A Family of Active Iridium Catalysts for Transfer Hydrogenation of Ketones. *Organometallics*, **2006**, 25, 4113–4117.; (b) Tanaka, R.; Yamashita, M.; Nozaki, K. Catalytic Hydrogenation of Carbon Dioxide Using Ir(III)–Pincer Complexes. *J. Am. Chem. Soc.*, **2009**, 131, 14168–14169.

(16) Park, S.; Brookhart, M. Hydrosilylation of Carbonyl-Containing Substrates Catalyzed by an Electrophilic η¹-Silane Iridium(III) Complex. *Organometallics*, **2010**, 29, 6057–6064.

(17) Göttker-Schnetmann, I.; White, P.; Brookhart, M. Iridium Bis(phosphinite) p-XPCP Pincer Complexes: Highly Active Catalysts for the Transfer Dehydrogenation of Alkanes. *J. Am. Chem. Soc.*, **2004**, 126, 1804–1811. [Ir(^tBuPOCOP)H₂] (**3**) was screened for the catalytic hydrogenolysis of a 1:1 mixture of Me₂SiOTf₂ and Me₂SiCl₂ in the SI of ref. 14.

(18) (a) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Waymouth, R. M.; Hedrick, J. L. Triazabicyclodecene: a simple bifunctional organocatalyst for acyl transfer and ring-opening polymerization of cyclic esters. *J. Am. Chem. Soc.* **2006**, 128, 4556–4557.; (b) Kieseewetter, M. K.; Scholten, M. D.; Kirn, N.; Weber, R. L.; Hedrick, J. L.; Waymouth, R. M. Cyclic Guanidine Organic Catalysts: What Is Magic About Triazabicyclodecene? *J. Org. Chem.* **2009**, 74, 9490–

9496.; (c) Mutlu, H.; Ruiz, J.; Solledera, S. C.; Meier, M. A. R. TBD catalysis with dimethyl carbonate: a fruitful and sustainable alliance. *Green Chem.*, **2012**, *14*, 1728-1735.; (d) von Wolff, N.; Lefèvre, G.; Berthet, J. C.; Thuéry, P.; Cantat, T. Implications of CO₂ Activation by Frustrated Lewis Pairs in the Catalytic Hydroboration of CO₂: A View Using N/Si⁺ Frustrated Lewis Pairs. *ACS Catal.* **2016**, *6*, 4526-4535.; (e) Kondoh, A.; Aoki, T.; Terada, M. Organocatalytic Arylation of α -Ketoesters Based on Umpolung Strategy: Phosphazene-Catalyzed S_NAr Reaction Utilizing [1,2]-Phospha-Brook Rearrangement. *Chem. Eur. J.* **2018**, *24*, 13110–13113.

(19) Lv, Y.; Yan, H.; Yang, B.; Wu, C.; Zhang, X.; Wang, X. Bipolar membrane electrodialysis for the recycling of ammonium chloride wastewater: Membrane selection and process optimization. *J. Chem. Eng. Res. Design*, **2018**, *138*, 105–115.

(20) See for *pK_a* value: (a) Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. Extension of the Self-Consistent Spectrophotometric Basicity Scale in Acetonitrile to a Full Span of 28 *pK_a* Units: Unification of Different Basicity Scales. *J. Org. Chem.*, **2005**, *70*, 1019-1028.; (b) Zall, C. M.; Linehan, J. C.; Appel, A. M. A Molecular Copper Catalyst for Hydrogenation of CO₂ to Formate. *ACS Catal.*, **2015**, *5*, 5301-5305.

See for *N* parameter (Mayr scale): (c) Ammer, J.; Baidya, M.; Kobayashi, S.; Mayr, H. Nucleophilic reactivities of tertiary alkylamines. *J. Phys. Org. Chem.*, **2010**, *23*, 1029-1035.; (d) Baidya, M.; Mayr, H. Nucleophilicities and carbon basicities of DBU and DBN. *Chem. Commun.*, **2008**, *15*, 1792-1794.; (e) Maji, B.; Stephenson, D.S.; Mayr, H. Guanidines: Highly Nucleophilic Organocatalysts. *ChemCatChem*, **2012**, *4*, 993-999.

(21) Lee, R.; Lim, X.; Chen, T.; Tan, G. K.; Tan, C.-H.; Huang, K.-W. Selective formation of bicyclic guanidinium chloride complexes: implication of the bifunctionality of guanidines. *Tetrahedron Lett.* **2009**, *50*, 1560-1562.

(22) Herzog, U.; Roewer, G. Base catalysed hydrogenation of methylbromooligosilanes with trialkylstannanes, identification of the first methylbromohydrogenoligosilanes. *J. Organomet. Chem.*, **1997**, *527*, 117-124.

(23) (a) Makhmutov, F. A.; Mishkin, R. N.; Shebarshinova, M. G. Process for preparation of methylsilanes by reduction of silyl chlorides with lithium aluminum hydride in alkylaromatic solvent, RU2266293, **2005**.; (b) Selective synthesis of Me₂SiHCl from Me₂SiCl₂ involves the combination of MgH₂ and AlCl₃: Dröse, J.; Knott, W.; Wolfgram, D. Verfahren zur Herstellung von Dimethylmonochlorsilan, EP0878476A1, **1998**.

(24) Göttker-Schnetmann, I.; White, P. S.; Brookhart, M. Synthesis and Properties of Iridium Bis(phosphinite) Pincer Complexes (*p*-XPCP)IrH₂, (*p*-XPCP)Ir(CO), (*p*-XPCP)Ir(H)(aryl), and {(*p*-XPCP)Ir}₂{ μ -N₂} and Their Relevance in Alkane Transfer Dehydrogenation. *Organometallics*, **2004**, *23*, 1766-1776.

(25) Although [(^tBuPOCOP)IrH₃][ⁱPrVBH] is not stable in dichloromethane and slowly transforms into [(^tBuPOCOP)IrHCl], the stoichiometric reaction between [(^tBuPOCOP)IrH₃][ⁱPrVBH] and Me₃SiCl yields Me₃SiH (see SI, Fig. S19/S20).

(26) Metsänen, T. T.; Hrobarik, P.; Klare, H. F. T.; Kaupp, M.; Oestreich, M. Insight into the Mechanism of Carbonyl Hydrosilylation Catalyzed by Brookhart's Cationic Iridium(III) Pincer Complex. *J. Am. Chem. Soc.*, **2014**, *136*, 6912-6915.

(27) For a detailed structural analysis of the nature of [Ir(^tBuPOCOP)H₂(HSiEt₃)] similar to **5**, see ref 25.