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Abstract

Hydrosilylation reactions are commonly used for the reduction of carbonyl bonds in fine chemistry, catalyzed by transition metal complexes. The current challenge is to expand the scope of metal-free alternative catalysts, including in particular organocatalysts. This work describes the organocatalyzed hydrosilylation of benzaldehyde with a phosphine, introduced at 10 mol %, and phenylsilane at room temperature. The activation of phenylsilane was highly dependent on the physical properties of the solvent such as the polarity, and the highest conversions were obtained in acetonitrile and propylene carbonate with yields of 46 % and 97 %, respectively. The best results of the screening over 13 phosphines and phosphites were displayed by linear trialkylphoshines (PMe_3, P^nBu_3, $POct_3$), indicating the importance of their nucleophilicity, with yields of 88 %, 46 % and 56 %, respectively. With the help of heteronuclear ^1H–^{29}Si NMR spectroscopy, the products of the hydrosilylation ($PhSiH_{3-n}(OBn)_n$) were identified, allowing a monitoring of the concentration in the different species, and thereby of their reactivity. The reaction displayed an induction period of *ca.* 60 min, followed by the sequential hydrosilylations presenting various reaction rates. In agreement with the formation of partial charges in the intermediate state, we propose a mechanism based on a hypervalent silicon center *via* the Lewis base activation of the silicon Lewis acid.

Introduction

As a synthetic strategy, hydrosilylation reactions are widely used in industry for the transformation of alkenes to organosilanes,[1] and more generally explored in academia for the hydrogenation of carbonyl compounds to primary alcohols,[2] and that of CO_2 to formic acid or methanol.[3] Along with hydroboranes, hydrosilane reagents, R_nSiH_{4-n} (R = alkyl, aryl, alkoxy, halo), attracted interest as most of them are chemically stable, readily available and easy to handle: they serve as hydride source *via* the polarized $Si^{(\delta+)}$–$H^{(\delta-)}$ bond.[4] In the context of carbonyl reduction, the addition of Si–H to the C=O bond leads to the formation of a silyl ether in a single step under mild conditions, which can be further hydrolyzed to form an alcohol. Applications in industrial settings generally favor the use of cheap PMHS (polymethylhydrosiloxane, $(\text{-SiMeHO-})_n$), or TMDS (tetramethyldisiloxane, $HMe_2SiOSiMe_2H$), but academic works often report reactions with Et_3SiH, $(EtO)_3SiH$, Ph_2SiH_2, $PhMe_2SiH$ or $PhSiH_3$, more reactive for "proof of concept" studies and less prone to form siloxane gels.[5] Among possible paths, the activation of the silane can rely on transition metal complexes or nanoparticles *via* an oxidative addition resulting in two moieties, R_3Si^- and H^-, coordinated to the metal center, such as platinum-based Speier's and Karstedt's catalysts that are the industrial standards.[4,6] A large library of transition metal complexes has been explored for the hydrosilylation of carbonyls, including noble metals but also first-row transition metals such as manganese, iron, cobalt and nickel.[7] The high activity of some of them is evidenced by the mild conditions used, as well as the low catalytic loadings, down to 0.02 mol %. Using transition metals obviously comes with advantages in terms of chemo- and stereoselectivities *via* the fine tuning of the catalyst structure, but is also limited by the cost of the metals, the synthesis of the ligands or the removal of the metal traces for the following steps.[8]

Alternative organocatalytic pathways were therefore developed, recently reviewed by Nikonov *et al.*,[8] and Hreczycho *et al.*[2] The catalysis mechanism may consist in the electrophilic activation of the aldehyde with Brønsted or Lewis acids, *via* the weakening of the C=O bond, in the electrophilic activation of the silane with Lewis acids, *via* the weakening of the Si–H bond, or in the nucleophilic activation of the silane with Lewis bases, *via* the formation of a hypervalent silicate $[R_3(base)SiH]^{(-)}$ complex.[9] Works with Lewis bases were mostly performed with anions such as fluorides,[10–12] alkoxides,[9,13,14] hydroxides,[14] or carbonates[15,16] (**Figure 1**), but more rarely with neutral molecules, yet more adapted to organic solvents. Nicholls *et al.* still reported the use of guanidine derivatives for the reductive amination of CO_2 and Courtemanche *et al.* that of phosphazenes for the formation of silyl formates from CO_2.[17,18] Another possible Lewis base substitute consists in phosphines, which have attracted interest these past decades as standalone organocatalysts.[19] While these suffer from limitations regarding their practical use, such as air-sensitivity, the possibility to explore their reactivity as a family of molecules rather than as stand-alone catalysts, *e.g.* by gradually varying critical parameters like steric hindrance and nucleophilicity, seems appealing for mechanistic understanding of phosphine reactivity in general.

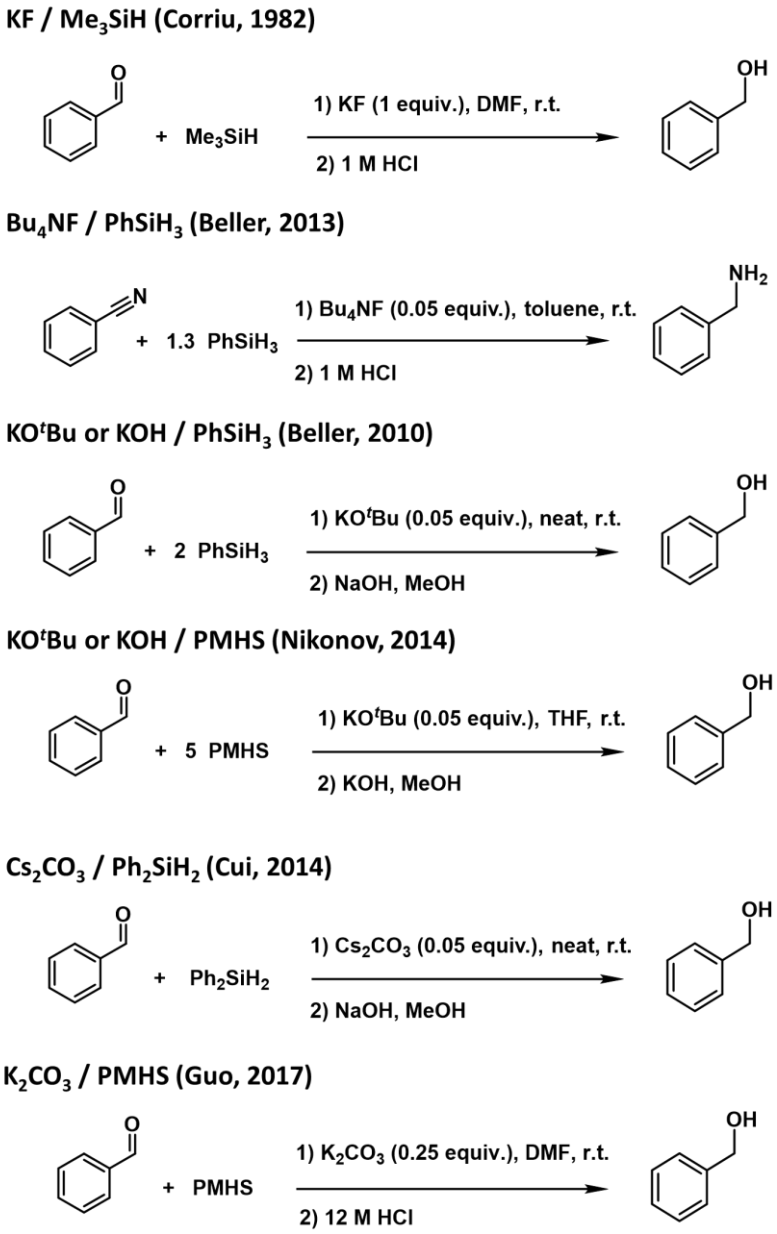

Figure 1. Selection of reported Lewis base-catalyzed hydrosilylations of unsaturated bonds (aldehydes and nitriles) from references [11], [12], [14], [9], [16] and [15] (from top to bottom).

In this work, we report the metal-free hydrosilylation of benzaldehyde with $PhSiH_3$ using tertiary phosphines as Lewis bases. The optimization of the reaction conditions is first presented, in particular as to the solvent and the nature of phosphine. The products were partially identified by means of ^{1}H–^{29}Si NMR experiments, and their formation was followed using ^{1}H NMR, giving insight into the reaction mechanism and the relative reactivity of the reagents. While trialkylphosphines are not expected to substitute classical catalysts such as

K_2CO_3 or TBAF (tetra-*n*-butylammonium fluoride), this works offers a new entry point to the design of alternative organocatalysts in a variety of solvents and provides tools to rationalize the mechanisms at stake in hydrosilane Lewis-base activation. Besides, such a catalytic activity displayed by a phosphine alone may shed a new light on similar works reporting the use of transition metal complexes coordinated by phosphine ligands.

Results and discussion

Hydrosilylation reaction. Blank reactions were first performed. The catalyst-free (no phosphine) hydrosilylation of benzaldehyde (PhCHO, 2.5 equiv.) with phenylsilane ($PhSiH_3$, 1 equiv.) was performed in dry acetonitrile (ACN) and did not lead to conversion of either the silane or the aldehyde. Besides, benzaldehyde and trimethylphosphine (PMe_3) did not react together in ACN (**Figure S3**). However, a solution of $PhSiH_3$ and PMe_3 turned slightly yellow in a few minutes and bubbling was observed, indicating that a reaction was taking place, leading to production of H_2 as indicated by ^{1}H NMR (singlet signal at 4.57 ppm) (**Figure S4**).[20] Dihydrogen is thought to originate from the phosphine-catalyzed decomposition of $PhSiH_3$ with traces of protic molecules (*e.g.* water).[21]

The catalytic hydrosilylation was then studied with P^nBu_3 as the catalyst. In dry ACN, the reaction of PhCHO (0.2 mol/L) with $PhSiH_3$ (0.08 mol/L), introduced in slight excess (0.4 equiv. *versus* PhCHO), proceeded smoothly in the presence of P^nBu_3 (10 mol % *versus* the silane), to afford silylethers overnight at room temperature (**Figure 2A**). The progression of the reaction was characterized by ^{1}H NMR with the decrease of the aldehydic peak of PhCHO and the growth of "benzyloxy" (Ph-C**H**$_2$-O) singlets in the 4.65–4.25 ppm region (**Figure S5A**). Approximately half of the benzaldehyde was converted in 16 h, with an error bar estimated to be *ca.* 10 % (conversions ranging from 35 % and 52 % for four repetitions of the experiment) (**Table 1**, entry 1). The identification of the multiple products detected after

reaction will be discussed later, taking into account that the reaction intermediates are expected to exhibit different reaction rates. Overall, this first set of experiments confirmed that P^nBu_3 was a suitable catalyst.

Solvent screening. Varying the solvent is an interesting manner to obtain insights into the reaction mechanism. In particular, the charges developed by transition states or reaction intermediates were expected to be better stabilized in polar solvents, leading to higher conversions. A screening over solvents of various polarities and protic characters was performed (**Table 1**). No benzaldehyde conversion was recorded for reactions run in the less polar solvents: *n*-hexane, toluene, dimethylcarbonate (DMC), and tetrahydrofuran (THF) (**Table 1**, entries 2-5). Although isopropanol (iPrOH) was reported to react with $PhSiH_3$ in the presence of a suitable catalyst to form H_2 and $Ph(iPrO)SiH_2$,[22] no gas evolution nor modification of the NMR spectrum were observed in the present case, ruling out this possibility. The benzaldehyde hydrosilylation did not proceed in this solvent neither (**Table 1**, entry 6). Benzonitrile was used as a second nitrile solvent and led to a limited conversion of 7 % (**Table 1**, entry 7). Anhydrous propylene carbonate (PC), a highly polar and aprotic solvent (ε_r = 65), led to a quasi-quantitative conversion (**Table 1**, entry 8). Mixtures of ACN and toluene were finally investigated: the higher the volume fraction of ACN, the higher the conversion (**Table 1**, entries 9-10).

As similar products were obtained for ACN and propylene carbonate, we concluded that the chemical reactivity of the C≡N bond was not involved. Rather, the impact of the solvent was limited to its physical properties (*e.g.* dielectric constant, polarity). Although propylene carbonate appeared to be an efficient solvent, ACN was used in the following to facilitate the interpretation of the ^{1}H NMR data. Interestingly, the relative polarity according to Miller's chart was not a suitable parameter to rationalize the evolution of the conversion (**Table 1** and **Figure S1**): conversions from 0 % to 97 % were found for close relative

polarities, from 0.40 to 0.55. Interestingly, the conversion was found to increase with the relative dielectric constant ε_r (**Table 1** and **Figure 2B**). This was consistent with charged intermediates and/or transition states being formed during the reaction, which will be discussed later.

Entry	Solvent	Relative polarity (Miller's chart)[a]	Relative dielectric constant (ε_r)	Benzaldehyde conversion[b]
1	ACN	0.46	37	46 %
2	*n*-hexane	0.01	1.9	0 %
3	Toluene	0.10	2.4	0 %
4	DMC	0.23	3.1	0 %
5	THF	0.20	7.6	0 %
6	iPrOH	0.55	20	0 %
7	Benzonitrile	0.33	26	7 %
8[c]	Propylene carbonate	0.47	65	97 %
9[d]	ACN/Toluene (5:5)	0.28	25	2 %
10[d]	ACN/Toluene (9:1)	0.42	33	25 %

Table 1. Solvent screening for benzaldehyde hydrosilylation. Reaction conditions: $PhSiH_3$ (50 µL, 0.4 mmol, 1 equiv.), PhCHO (100 µL, 1 mmol, 2.5 equiv.), mesitylene (internal standard) (55 µL, 0.4 mmol, 1 equiv.), P^nBu_3 (10 µL, 0.04 mmol, 0.1 equiv.), solvent (5 mL), r.t., 24 h. *[a]* Relative polarity from reference.[23] *[b]* The benzaldehyde conversion was set as the ratio of half of the "benzyloxy" protons *versus* the benzaldehyde leftover + half of the "benzyloxy" protons, determined by ^{1}H NMR. *[c]* The "benzyloxy protons" in ^{1}H NMR are masked by the signal of the solvent, the benzaldehyde conversion was determined *via* a ^{1}H NMR measurement before and after P^nBu_3 addition. *[d]* Polarities were estimated as linear combinations of those of toluene and ACN, and dielectric constants extracted from reference.[24]

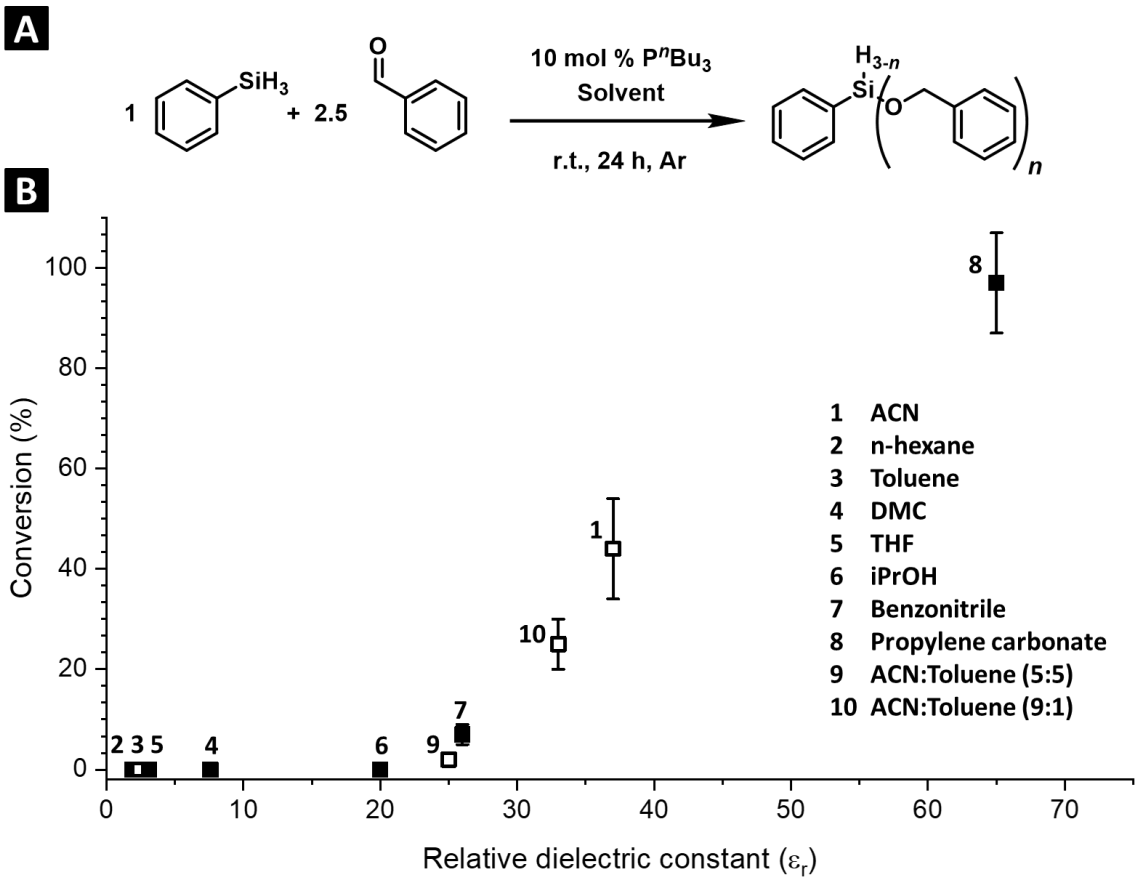

Figure 2. (A) Hydrosilylation of benzaldehyde catalyzed by P^{n}Bu$_3$ (reaction conditions as outlined in **Table 1**). (B) Dependance over the polarity of the solvent (relative dielectric constant ε_r). Open squares correspond to toluene, ACN and mixtures thereof (volume ratio indicated). THF: tetrahydrofuran, DMC: dimethylcarbonate, ACN: acetonitrile.

Phosphine screening. The impact of the chemical nature of the phosphine was then evaluated with a range of alkyl- and arylphosphines, as well as with a phosphine oxide and a phosphite (**Table 2** and **Figure 3A**). All the reactions were performed in ACN with a catalyst loading of 10 mol %. A moderate to high conversion of benzaldehyde was obtained with three linear trialkylphosphines, PMe_3 (88 %), P^{n}Bu$_3$ (46 %) and P^{n}Oct$_3$ (56 %), and one alkylarylphosphine, PMe_2Ph (12 %) (**Table 2**, entries 1, 2, 5 and 8). Low conversions were recorded with three other trialkylphosphines (P^{i}Bu$_3$, P^{t}Bu$_3$ and PCy_3) and two secondary phosphines, PH^{t}Bu$_2$ and $PHPh_2$ (**Table 2**, entries 6, 7 and 9-11), while no conversion was obtained with di- and triarylphoshines ($PMePh_2$, PPh_3, 1,4-bis(diphenylphosphino)butane

(dppb)), triphenylphosphite ($P(OPh)_3$) and diphenyl phosphine oxide ($PHPh_2O$) (**Table 2**, entries 3, 4 and 12-14).

Entry	Catalyst (10 mol %)	Benzaldehyde conversion[a]
1[b]	PMe_3	88 %
2[b]	PMe_2Ph	12 %
3	$PMePh_2$	0 %
4	PPh_3	0 %
5[c]	P^nBu_3	46 %
6[b]	P^iBu_3	6 %
7	P^tBu_3	1 %
8[b]	$POct_3$	56 %
9[b]	PCy_3	5 %
10	$PHPh_2$	2 %
11	PH^tBu_2	6 %
12	dppb	0 %
13	$P(OPh)_3$	0 %
14	$PHPh_2O$	0 %

Table 2. Catalyst screening for benzaldehyde hydrosilylation. Reaction conditions: $PhSiH_3$ (50 µL, 0.4 mmol, 1 equiv.), PhCHO (100 µL, 1 mmol, 2.5 equiv.), mesitylene (internal standard) (55 µL, 0.4 mmol, 1 equiv.), catalyst (0.04 mmol, 0.1 equiv.), acetonitrile (5 mL), r.t., 24 h. [a] The benzaldehyde conversion was set as the ratio of half of the "benzyloxy" protons *versus* the benzaldehyde leftover + half of the "benzyloxy" protons, determined by ^1H NMR. [b] Average result on two runs. [c] Average result on four runs.

The nature of the substituents has a dramatic impact on the basicity (Lewis and Brønsted) of the phosphorus atom because of a combination of steric hindrance and of electronic effect. Classifying the phosphines as to their catalytic activity is generally difficult when using a sole descriptor such as the Tolman cone angle (characteristic of the steric

hindrance), the Tolman Electronic Parameter (TEP) (characteristic of the electron donation from the phosphorus atom), the energy level of the HOMO or the pKa of the Brønsted acid/base couple. Accordingly, the benzaldehyde conversion plotted as a function of the Tolman cone angles, as historically reported (**Figure S2A**),[25] or recomputed by Jover *et al.* (**Figure S2B**),[26] or as a function of the TEP (**Figure S2C**),[25] does not follow any clear trend. As the recomputation of the Tolman cone angles by Jover *et al.* in 2019 sensibly updated the values for a few phosphines such as P^nBu_3 (from 132° to 160°, **Table S1**), the He8_steric parameter was finally chosen to classify the steric hindrance around the phosphorus atom. The values correspond to the destabilization energy (in kcal/mol) of the interaction of the ligand with a ring of eight helium atoms and give rise to a steric hindrance scale in arbitrary units.[26–28] The corresponding plot is on **Figure S2D** and here also, no clear trend was observed.

At this stage, it was concluded that a simple trend with electronic or steric effects was not able to capture the complexity of the situation. To discuss crossed impact of steric and electronic effects, Tolman proposed to plot the studied parameter (in our case, the conversion) on stereo–electronic maps, *i.e.*, with the Tolman cone angle and the TEP as variables.[25] In the present work, the He8_steric parameter was used to describe the steric hindrance, instead of the Tolman cone angle (**Figure 3B)**. The highest conversions were obtained for phosphines presenting both low steric hindrance and low TEP, *i.e.*, with a pronounced electron-donor character from the phosphorus center (bottom left region of **Figure 3B**), which would coincide with a strong nucleophilic character.

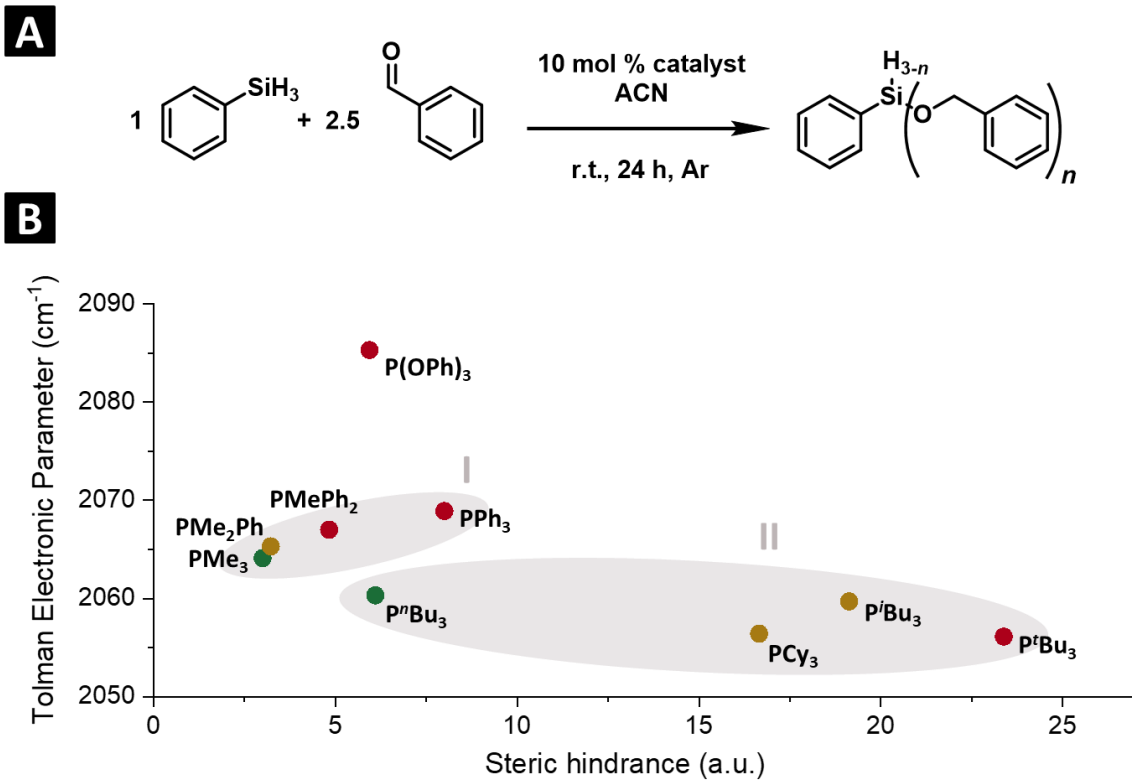

Figure 3. (A) Phosphine screening for the hydrosilylation of benzaldehyde catalyzed in ACN (reaction conditions as outlined in **Table 2**) and corresponding (B) stereo–electronic map. The color code indicates the benzaldehyde conversion for several phosphines (green: > 40 %, orange: < 15 %, red: 0 %). Two zones (labeled I and II) are plotted as grey ellipses as a guide for the eye.

The series {PMe_3, PMe_2Ph, $PMePh_2$, PPh_3} with the gradual substitution of the methyl groups by phenyl ones, leading to a total loss of catalytic activity for $PMePh_2$ and PPh_3, clearly illustrates that alkylphosphines are better catalysts than arylphosphines for this reaction (zone I in **Figure 3B**). The C sp^3 orbital at the origin of the P–C bond in the alkylphosphines has indeed a higher energy than the equivalent C sp^2 orbital in the arylphosphines. Upon interaction with the orbitals of phosphorus, the resulting filled orbital of the P–C bond is therefore more centered on the phosphorus atom in alkylphosphines, making them better electron donors than arylphosphines. Accordingly, the Brønsted basicity of the phosphine decreases in the order {PMe_3, PMe_2Ph, $PMePh_2$, PPh_3} with pKa of respectively 8.6, 6.5, *n.d.* and 2.7,[29,30] as well as their nucleophilicity, ranked by Buckler *et al.*, from 2.24

(a.u.) for PMe_3 to 0.04 for PPh_3.[31] In this series, the trends for both the steric hindrance and the electron donation from the phosphorus atom go along: a strongly donating and poorly hindered phosphine is favorable.

Additionally, the series {P^nBu_3, P^iBu_3, P^tBu_3} with tributylphosphines of diverse branching demonstrates a negative impact of bulky groups on the benzaldehyde conversion (zone II in **Figure 3B**). The nature of the alkyl group has little impact on the Brønsted basicity of the trialkylphosphines, which is of the same order of magnitude for P^nBu_3, P^iBu_3, P^tBu_3 and PMe_3,[29,30,32] whereas the nucleophilicity by Buckler *et al.* decreased from 1.62 (a.u.) for P^nBu_3 to 0.14 for P^iBu_3.[31] This trend matches with our experimental observations: the apparent critical factor for the catalytic activity is the nucleophilicity, well anticipated from the Lewis basicity. Besides, P^tBu_3 seems to be too sterically hindered for the reaction to proceed.

The order of reactivity unveiled in the present work ($P(OPh)_3$, $PPh_3 << PCy_3 < P^nBu_3$) is coherent with Mayr's attempt at ranking the nucleophilicity of phosphines *via* the use of four parameters: the σ-donor capacity (χ_d), the cone angle (θ), the secondary electronic effect (E_{ar}) and the π-electron acceptor capacity (π_p). Interestingly, the comparison with other types of nucleophiles suggests that butylamine and piperidine would be stronger Lewis bases than P^nBu_3 and thereby could be used for the activation of $PhSiH_3$.[33]

Overall, the phosphine screening revealed that a low steric hindrance and a high nucleophilicity are required for the reaction to proceed with phenylsilane and benzaldehyde.

Product identification. Phenylsilane may provide up to three hydrides and thereby hydrogenate three benzaldehyde molecules. This sequential reactivity of $PhSiH_3$ results in three products $PhSiH_{3-n}(OBn)_n$ (n = 1, 2, 3) whose identification would give insight into the mechanisms *via* the time monitoring of the different species. The corresponding ^1H and ^{29}Si

chemical shifts were determined *via* a combination of ^{1}H and ^{1}H–^{29}Si sequences (**Figure 4** and **Table 3,** see Supplementary Information for details). To the best of our knowledge, the ^{29}Si chemical shifts were not referenced for the synthesized benzyloxysilanes, but that of $PhSi(OBn)_3$ (-56.7 ppm) is coherent with the shift reported for a similar compound, $PhSi(OEt)_3$ (-55.6 ppm).[34] The evolution of the ^{29}Si chemical shift in the series is delicate to rationalize as it corresponds to the substitution of a hydride "ligand" H^- by an alkoxy one BnO^-, both transferring electron density toward the silicon atom. Accordingly, the values measured for the two intermediate compounds, $PhSiH_2(OBn)$ (-66.6 ppm) and $PhSiH(OBn)_2$ (-28.2 ppm) are outside the range defined by $PhSiH_3$ and $PhSi(OBn)_3$ (respectively -59.8 ppm and -56.7 ppm). The possibility of an aliasing in the ^{1}H–^{29}Si experiments that would lead to an incorrect ^{29}Si position was ruled out with an experiment with a larger spectral width (SW) in the indirect dimension.

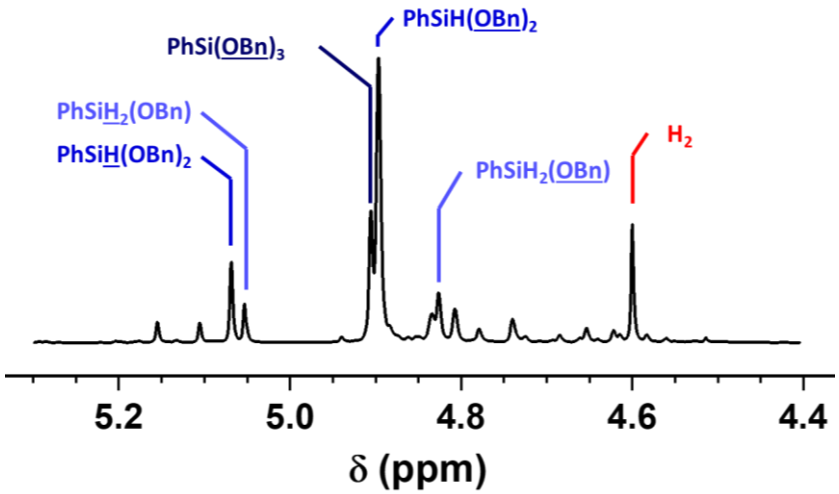

Figure 4. Details of the ^{1}H NMR spectrum of a solution of PhCHO, $PhSiH_3$ and PMe_3 in acetonitrile after 2 h, with assignment of the species $PhSiH_{3-n}(OBn)_n$ (n = 1, 2, 3).

Species	^{29}Si (ppm)	Si – ^{1}H (ppm)	– C^{1}H$_2$– (ppm)
PhSiH$_3$	-59.8	4.18	*n.a.*
PhSiH$_2$(OBn)	-66.6	5.05	4.82
PhSiH(OBn)$_2$	-28.2	5.07	4.89
PhSi(OBn)$_3$	-56.7	*n.a.*	4.90

Table 3. ^{1}H and ^{29}Si chemical shifts of phenylsilane and of the three formed benzyloxysilanes PhSiH$_{3-n}$(OBn)$_n$. The CH_3CN peak was calibrated at 1.96 ppm.

Depending on the reaction conditions, unidentified species (US) were detected in limited amounts with characteristic ^{1}H signals *ca.* 6 ppm coupling with carbons at *ca.* 98 ppm (**Figure S5-6** and **Table S2**). Among the three major ones, US1 and US2 present at least one Si–H bond, to the contrary of the third one, US3 (**Figure S9**). Besides, it appeared that US1 and US2 further reacted as the intensity of their peaks decreased after a few hours, while that of US3 only increased (**Figure S10-11**). We therefore suggest that these species also follow a reaction pattern ruled by successive hydrosilylations of benzaldehyde molecules. Neither the nature of these molecules nor the conditions of their production could be formally identified. We nonetheless suggest they may be linked to a ligand rearrangement around the silicon atom, as reported for alkoxy-, alkyl- and arylsilanes in the presence of nucleophiles,[9,35] or to a partial hydrolysis due to water traces.

Time evolution of the reaction products. The hydrosilylation reaction was monitored by ^{1}H NMR in deuterated acetonitrile at different catalyst loadings (10 mol %, 17 mol % and 80 mol % of PMe_3) for mechanistic purposes. The evolution of the three compounds of general formula PhSiH$_{3-n}$(OBn)$_n$ (n = 1, 2, 3) was similar in the three experiments and will only be commented in the case of 10 mol % (**Figure 5**) (see **Figure S14-19** for 17 mol % and 80 mol %). First, an induction period of 2 h (shorter for catalyst loadings of 17 mol % and 80 mol %) was observed during which the concentrations in $PhSiH_3$ and

PhCHO decreased by respectively *ca.* 15 mmol/L and *ca.* 20 mmol/L, Meanwhile, the concentration of H_2 increased by *ca.* 40 mmol/L, while merely no other compound was detected by ^{1}H NMR (**Figure S12**, red for H_2 and blue for $PhSiH_{3-n}(OBn)_n$ (n = 1, 2, 3)). The phosphine possibly activated the silane molecules to react with adventitious water to form H_2 and phenylsilanetriol $PhSi(OH)_3$, which further condensed as polymers, hence the absence of signal in ^{1}H NMR.[36] The amount of produced H_2 indeed corresponds to slightly less than three times that of consumed $PhSiH_3$. The decrease of the benzaldehyde concentration, while no production of benzyl alcohol was recorded, suggests either a further reaction with the so-formed polymer, or a partial hydrosilylation of $PhSiH_3$ in $PhSiH_2(OBn)$, directly followed by the hydrolysis of the remaining hydrides and condensation of the formed silanol. The identification of these hypothetic polymeric structures is nonetheless out of the scope of the present work. The end of the production of H_2 marked the appearance of $PhSiH_2(OBn)$ and a faster consumption of $PhSiH_3$ and PhCHO, we therefore hypothesize that the activated silanes by the phosphine were available to react with benzaldehyde only once all the labile protons had reacted.

For an initial concentration in $PhSiH_3$ of 80 mmol/L, the concentration in $PhSiH_2(OBn)$ increased rapidly up to 11 mmol/L after 4 h of reaction and then decreased down to 2 mmol/L in the following hours (**Figure 5A**). The production of $PhSiH(OBn)_2$ started immediately with that of $PhSiH_2(OBn)$ and its concentration reached 43 mmol/L after 18 h, before slowly decreasing to the benefit of $PhSi(OBn)_3$. It is noteworthy that the sum of the estimated concentrations of the four species $PhSiH_{3-n}(OBn)_n$ (dotted line on **Figure 5A**) was roughly constant after a drop by 10 % during the induction time.

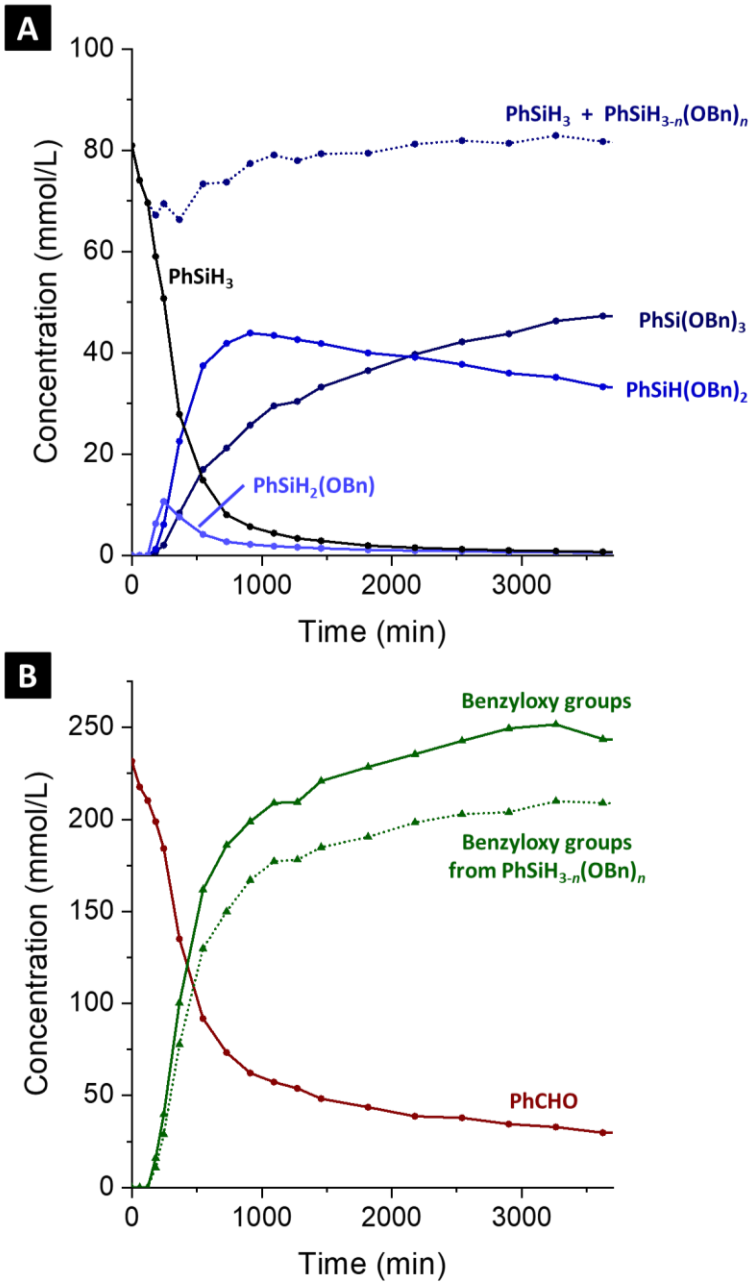

Figure 5. Time monitoring of benzaldehyde hydrosilylation catalyzed by PMe_3 (10 mol %). (A) Concentrations of the phenylsilane and of the three hydrosilylation products, and sum of the four species (dotted line). (B) Concentrations in benzaldehyde, integration of the benzyloxy region and sum of the benzyloxy groups from $PhSiH_{3-n}(OBn)_n$ for n = 1, 2, 3 (dotted line).

At the maximal concentration recorded for $PhSiH_2(OBn)$ after 4 h, the production of $PhSiH_2(OBn)$ from $PhSiH_3$ roughly compensated its consumption for a further hydrosilylation to form $PhSiH(OBn)_2$, hence a plateau in concentration was observed. If we hypothesize the hydrosilylation mechanism is similar for the three successive reactions, the expression of the

reaction rate displays the same orders of reaction respectively to the silane, the benzaldehyde and the phosphine (**Figure S20**). At all times, the part of the reaction rate linked to the concentration in benzaldehyde and in phosphine is identical for the first and the second steps. Therefore, the maximum concentration of $PhSiH_2(OBn)$ only depended on the concentrations of the silanes $PhSiH_3$ and $PhSiH_2(OBn)$ and of the corresponding reaction rate constants k_0 and k_1, respectively. As this maximum was reached at a lower concentration in $PhSiH_2(OBn)$ (11 mmol/L) than in $PhSiH_3$ (51 mmol/L), we can conclude that $PhSiH_2(OBn)$ is more reactive than $PhSiH_3$ and that k_0 is lower than k_1. A ratio of 0.22 was obtained for the relative reaction rates values k_0/k_1. A similar analysis on the plateau of $PhSiH(OBn)_2$ after 18 h ($[PhSiH_2(OBn)]$ = 2 mmol/L, $[PhSiH(OBn)_2]$ = 43 mmol/L), led us to the conclusion that k_1 is higher than k_2, with a k_1/k_2 ratio of 22. Results of similar orders of magnitude were observed for the reactions run with 17 mol % of PMe_3 and 80 mol % of PMe_3 with ratios k_0/k_1 of 0.31 and 0.10, respectively, and ratios k_1/k_2 of 4.6 and 16, respectively (**Table S3**). As expected, the reaction times at which these plateaus were observed were smaller when the PMe_3 concentration was larger, indicating a non-null partial order with respect to the phosphine. The superior reactivity of $PhSiH_2(OBn)$ compared with $PhSiH_3$ and $PhSiH(OBn)_2$ is in line with literature work using a cobalt complex for the three successive hydrosilylation reactions, though no justification was proposed.[37]

The benzaldehyde and benzyloxy groups concentrations were estimated on the basis of the integration in ^1H NMR of respectively the aldehydic peak at 10 ppm (**Figure S5A**) and the benzyloxy region, *i.e.*, 5–4.5 ppm in CD_3CN (**Figure 4**). The decrease in PhCHO concentration was clearly correlated with the increase of that of the benzyloxy groups (red *vs.* solid green in **Figure 5B**). Roughly 80 % of the benzyloxy peaks may be accounted to the different products of the hydrosilylation $PhSi_{3-n}(OBn)_n$ (dotted green in **Figure 5B**), indicating the presence of secondary or degradation products. This percentage was however

dependent on the reaction and was of 60 % and 85 % for respectively the 17 mol % and 80 mol % phosphine loadings (**Figures S14B** and **S17B**). The workup of these secondary products bearing benzyloxo groups is nonetheless expected to eventually lead to the desired alcohol as well.

Mechanistic considerations. The strong dependence of the benzaldehyde conversion over the dielectric constant of the solvent suggests that charges are developed on the activated complex of the rate-limiting step of the reaction. Besides, a screening over different phosphines established that the best catalysts are Lewis bases that present a limited steric hindrance and a high nucleophilicity at the phosphorus center. It should be noted that if a phosphine catalyzes the reaction, the corresponding phosphine oxide does not. Indeed, when PMe_3 was oxidized by exposure to air, no further conversion was detected.

All these observations are coherent with a mechanism, showed in **Figure 6**, during which the phosphine PR_3 interacts with the silane ***1*** with the lone pair of the phosphorus, in order to form a *penta*-valent silicate ***2***, with partial charges δ+ and δ- developed on respectively the phosphorus and the silicon atom. A reorganization of the electronic density occurs in *penta*-valent silicon species leading to a lengthening of the bonds between Si and the peripheral ligands (H^- here) and an enhancement of the nucleophile character of these last ones.[4,38] The first step is therefore followed by an attack of the activated hydride H^- on the aldehydic carbon of benzaldehyde to form the ion pair ***3*** which further reacts to form ***4***. A concerted mechanism of the attack of the hydride and of the formed alkoxide on the silicon center to yield the compound ***4*** directly from ***2*** cannot be ruled out, especially considering the high reactivity of the hypothetically formed silylium cation. The intermolecular hydride transfer is expected to be the limiting step, in agreement with the crucial role of the polarity of the solvent. The dissociation of PMe_3 finally leads to the benzyloxysilane ***5***. The higher reactivity observed for $PhSiH_2(OBn)$ compared to $PhSiH_3$ and $PhSiH(OBn)_2$ may be due to a

competition of two antagonist effects: $PhSiH_2(OBn)$ is more Lewis acidic than $PhSiH_3$ but less sterically hindered than $PhSiH(OBn)_2$. This interplay of sterics and electronic allows for more efficient phosphine coordination to $PhSiH_2(OBn)$.

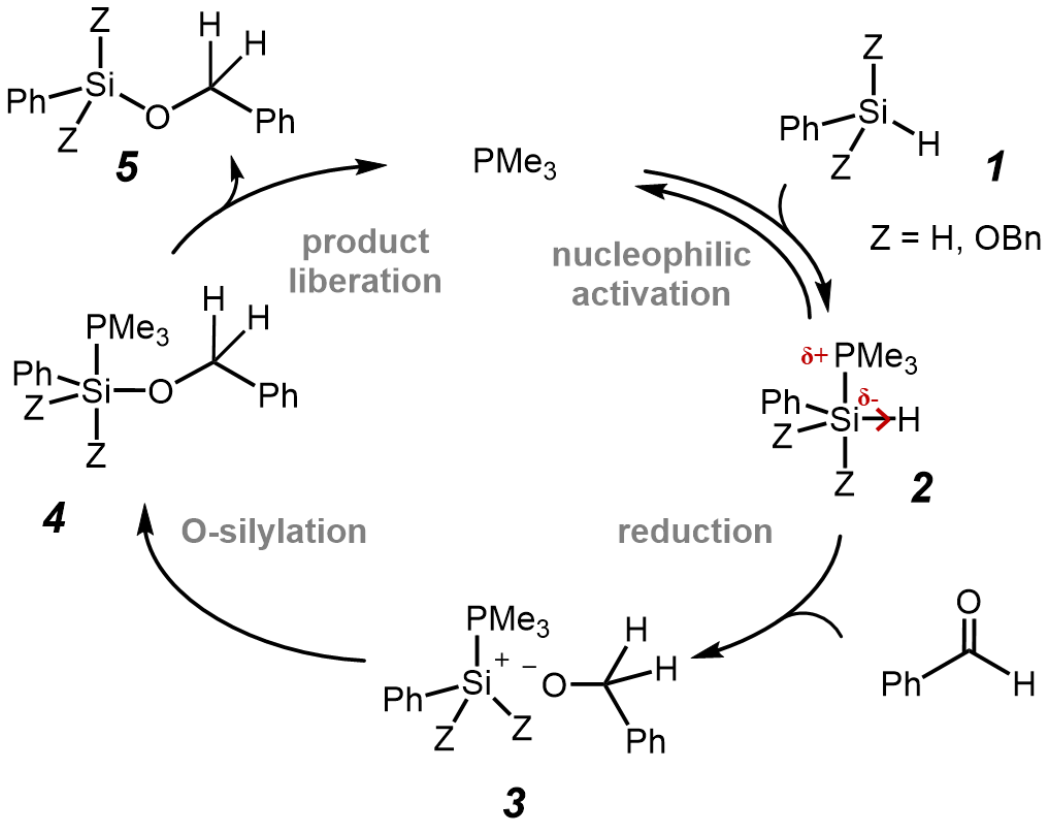

Figure 6. Proposed mechanism for the hydrosilylation of benzaldehyde catalyzed by trimethylphosphine (PMe_3).

An alternative mechanism may consist in the coordination of the benzaldehyde to the silicon center of ***2*** *via* the oxygen atom to form a *hexa*-valent silicon species, followed by an intramolecular attack of a hydride. While the attack of the Lewis basic phosphine on the silicon center seems natural, the Lewis acidity of the negatively charged silicon center in ***2*** is unclear. Such a behavior would be described as the Lewis base activation of silicon Lewis acids, and was suggested in particular by Oestreich and Denmark for the activation of silanes with fluoride and carbonate ions.[4,38]

Conclusion

In summary, we reported herein the activation of phenylsilane catalyzed by simple neutral organic bases such as PMe_3 and P^nBu_3. The reaction consists in the hydrosilylation of benzaldehyde with $PhSiH_3$, performed at room temperature. The polarity of the solvent is beneficial to the reaction and the highest yields were obtained in acetonitrile ($\varepsilon_r = 37$) and propylene carbonate ($\varepsilon_r = 65$), with conversions of 46 % and 97 %, respectively. A screening over 13 phosphines indicated that the nucleophilicity of the phosphine allows the silane activation, with an optimum in the case of PMe_3. The successive stages of the hydrosilylation of benzaldehyde with phenylsilane, $PhSiH_{3-n}(OBn)_n$ (n = 1, 2, 3), were identified through a combination of ^1H–^{29}Si experiments and this attribution allowed a time monitoring of the concentration of the species. The most notable point is the higher reactivity of $PhSiH_2(OBn)$ compared to $PhSiH_3$ and $PhSiH(OBn)_2$. The dependance over the solvent and the phosphine is consistent with a mechanism of Lewis base activation of the silicon Lewis acid. The conditions presented herein, *i.e.*, the use of $PhSiH_3$ and of air-sensitive trialkylphosphines, are not designed for large scale applications but they open a way to the use of neutral organic bases, which may bring interest to the catalysis community for further development of alternative catalysts (*e.g.* amines) and for mechanistic considerations.

Experimental section

Catalytic tests. In a glovebox under argon (< 0.5 O_2 ppm, < 0.5 H_2O ppm), a 10 mL vial was loaded with dry acetonitrile (5 mL), phenylsilane (50 µL, 0.4 mmol, 1 equiv.), benzaldehyde (102 µL, 1 mmol, 2.5 equiv.), mesitylene (internal standard) (55 µL, 0.4 mmol, 1 equiv.) and PR_3 (0.04 mmol, 0.1 equiv.). The reagents were taken with a glass micro syringe, with an error of ± 10 %. The reaction was stirred at room temperature for 24 h. Gas formation was observed for the more concentrated reactions and in propylene carbonate. An aliquot of the liquid phase was collected for analysis by ^{1}H NMR in $CDCl_3$. All NMR kinetic experiments were performed under argon atmosphere using J. Young NMR tubes equipped with Teflon valves directly on the reaction crude with the use of CD_3CN instead of CH_3CN.

Multinuclear NMR spectroscopy. All NMR experiments were performed on a Bruker Avance-III 300 spectrometer (300.13, 75.47 and 59.63 MHz for ^{1}H, ^{13}C and ^{29}Si, respectively) equipped with a BBFO 5mm grad z probe. $^{29}Si–\{^{1}H\}$ NMR experiments were carried out with an inverse gated decoupling to avoid NOE effect that can lead to a loss of signal because of the negative gyromagnetic ratio of ^{29}Si. Gradient enhanced HSQC ($^{1}H–^{13}C$ and $^{1}H–^{29}Si$) and HMBC ($^{1}H–^{29}Si$) experiments were performed with sequences directly taken from the Bruker's library (hsqcetgp and hmbcetgpnd). For $^{1}H–^{13}C$ HSQC, a J coupling value of 145 Hz was chosen. For $^{1}H–^{29}Si$ HSQC and $^{1}H–^{29}Si$ HMBC, J coupling values of 200 Hz and 6 Hz were chosen, respectively.

List of contributions

R. F. A., A. P. and C. P. performed the catalytic experiments and the interpretation of the data. R. F. A and F. R. ran and interpretated the heteronuclear NMR experiments. A. P. conceived the project, S. C. spearheaded it. R. F. A. and S. C. co-wrote the manuscript, all authors approved its final version.

Conflict of interest

The authors declare no conflict of interest.

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Keywords

Hydrosilylation, hypervalent silicon, Lewis base, organocatalysis, phosphine

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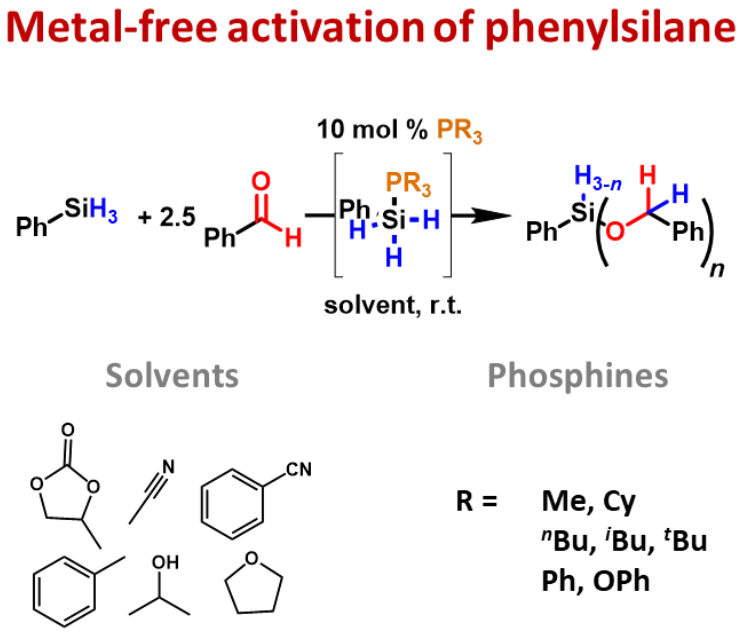
Table of Content

Trialkylphosphines were used as organocatalysts for the hydrosilylation of benzaldehyde to arylbenzyloxyhydrosilanes at room temperature. The products were obtained in yields up to 97 %. The nucleophilicity of the catalyst was demonstrated to be critical *via* a stereo-electronic map and a Lewis base activation mechanism with a hypervalent silicon intermediate species was proposed.



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