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Hydrosilylation

Hydrosilylation of Ketones, Imines and Nitriles Catalysed by Electrophilic Phosphonium Cations: Functional Group Selectivity and Mechanistic Considerations

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Abstract: The electrophilic phosphonium salt, $[(C_6F_5)_3PF][B(C_6F_5)_4]$, catalyses the efficient hydrosilylation of ketones, imines and nitriles at room temperature. In the presence of this catalyst, adding one equivalent of hydrosilane to a nitrile yields a silylimine product, whereas adding a second equivalent produces the corresponding disilylamine. $[(C_6F_5)_3PCl][B(C_6F_5)_4]$ and $[(C_6F_5)_3PBr][B(C_6F_5)_4]$ are also synthesised and tested as catalysts. Competition experiments demonstrate that the reaction exhibits selectivity for the following functional groups in order of preference: ketone > nitrile > imine > olefin. Computational studies reveal the reaction mechanism to involve initial activation of the Si–H bond by its interaction with the phosphonium centre. The activated complex then acts cooperatively on the unsaturated substrate.

Introduction

Hydrosilylation reactions account for some of the most important catalytic processes employed industrially,[1] due to the diverse applications of silicon-containing materials. For example, silicones are used extensively within sealants, adhesives, lubricants, medicines, cookware, and insulation.[2] A plethora of transition metal catalysts have been exploited for the hydrosilylations of ketones,[3] imines[4] and nitriles.[5] Furthermore, metal-free methods have also been developed using acids,[6] bases[7] or alkali fluorides[8] to effect these transformations, although such methods have mostly required harsh reaction conditions. Tin[9] and aluminium[10] species have also been used as catalysts. Piers and co-workers demonstrated that $B(C_6F_5)_3$ acts as a highly effective catalyst for hydrosilylation,[11] and the reaction mechanism was further illuminated by Oestreich and co-workers.[12] More recently, Piers and co-workers[13] isolated a borole–silane adduct, a model intermediate. Furthermore, Beller and co-workers showed that $[Bu_4N]F$ functions as a catalyst;[5g] however this method requires the use of a highly reactive silane.

While the field of organocatalysis has emerged from efforts to develop metal-free catalysts,[14] our efforts to these ends have focused on developing a variety of metal-free Lewis acids for frustrated Lewis pair (FLP) chemistry.[15] Whereas the bulk of the early work exploited boron-based Lewis acids, more recently we have turned our attention to Lewis acidic phosphonium cations. Previous work showed that P^V cations can catalyse additions to polar unsaturated compounds[14c] and Diels-Alder reactions.[16] Gabbaï and co-workers recently demonstrated the utility of such phosphonium species as acceptors for fluoride ion sensing applications.[17] Radosevich and co-workers also recently exploited the redox chemistry of P^{III} and P^V systems within transfer hydrogenation catalysis.[18] In our initial investigation, we used a Lewis acidic P^V centre to capture CO_2.[19] Targeting amplified Lewis acidity, we then prepared $[(C_6F_5)_3PF][B(C_6F_5)_4]$. The electrophilic phosphonium cation (EPC), $[(C_6F_5)_3PF]^+$, was shown to catalyse the hydrodefluorination of fluoroalkanes in the presence of hydrosilane.[20] Subsequently, we demonstrated that $[(C_6F_5)_3PF][B(C_6F_5)_4]$ catalysed olefin isomerisations, hydrosilylations of olefins and alkynes,[21] and dehydrocouplings of hydrosilanes with amines, thiols, phenols or carboxylic acids.[22] Furthermore, the H_2 generated by the dehydrocoupling reaction could be transferred to an olefin in situ. This reactivity clearly demonstrates that the presence of the electron-withdrawing fluoro and perfluoroaryl substituents at P provides a potent Lewis acid. Herein we extend our earlier work dealing with the hydrosilylation of olefins and alkynes by demonstrating that the salts, $[(C_6F_5)_3PX][B(C_6F_5)_4]$ (X = F, Cl, Br),

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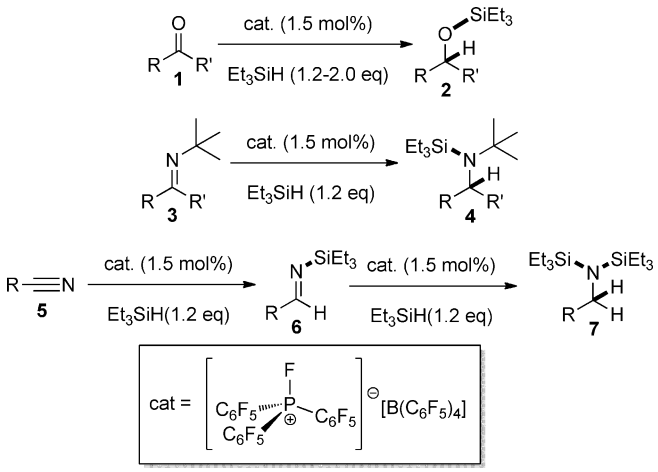
also catalyse the hydrosilylation of ketones, imines, and nitriles. The reaction's selectivity for these functional groups is probed experimentally, and a computational study supports a mechanism for metal-free hydrosilylation catalysis.

Results and Discussion

Hydrosilylation catalysis

Aliphatic ketones were found to undergo efficient hydrosilylation using $[(C_6F_5)_3PF][B(C_6F_5)_4]$ as the catalyst (Scheme 1).



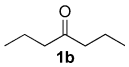
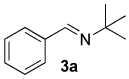
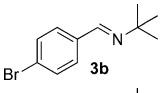
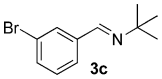
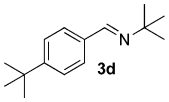
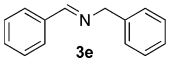
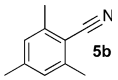
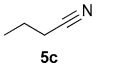
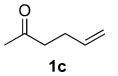
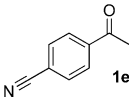
Scheme 1. $[(C_6F_5)_3PF][B(C_6F_5)_4]$-catalysed hydrosilylation of ketones (**1**), imines (**3**), and nitriles (**5**) to silyl enol ethers (**2**), *N*-silylamines (**4**), and *N*-silylimines (**6**) or *N*,*N*-disilylamines (**7**), respectively.

The reaction of 1-cyclohexylethanone **1a** with an excess of Et_3SiH in the presence of $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (1.5 mol%) afforded the hydrosilylated product, $CyCH(Me)OSiEt_3$ **2a** in an isolated yield of 83% (Table 1, entry 1). In a similar manner, treatment of heptan-4-one **1b** with Et_3SiH in the presence of $[(C_6F_5)_3PF][B(C_6F_5)_4]$ yielded the hydrosilylated product, $nPr_2CH(OSiEt_3)$ **2b** (Table 1, entry 2). Extending this reactivity to a series of aldimines also proved possible. The hydrosilylation of *N*-benzylidene-*tert*-butylamine **3a** with Et_3SiH by $[(C_6F_5)_3PF][B(C_6F_5)_4]$ gave the corresponding *N*-silylated amine **4a** in 97% yield after 12 h (Table 1, entry 3). Similarly 4- and 3-bromobenzylidene, and 4-*tert*-butylbenzylidene derivatives (**3b**, **c** and **d**, respectively) were catalytically reduced in quantitative yields (Table 1, entries 4–6, respectively). It is noteworthy that using less sterically encumbering substituents at N did not result in imine hydrosilylation, presumably because the relatively unprotected N atom is able to interact with the Lewis acidic phosphonium centre (Table 1, entry 7).

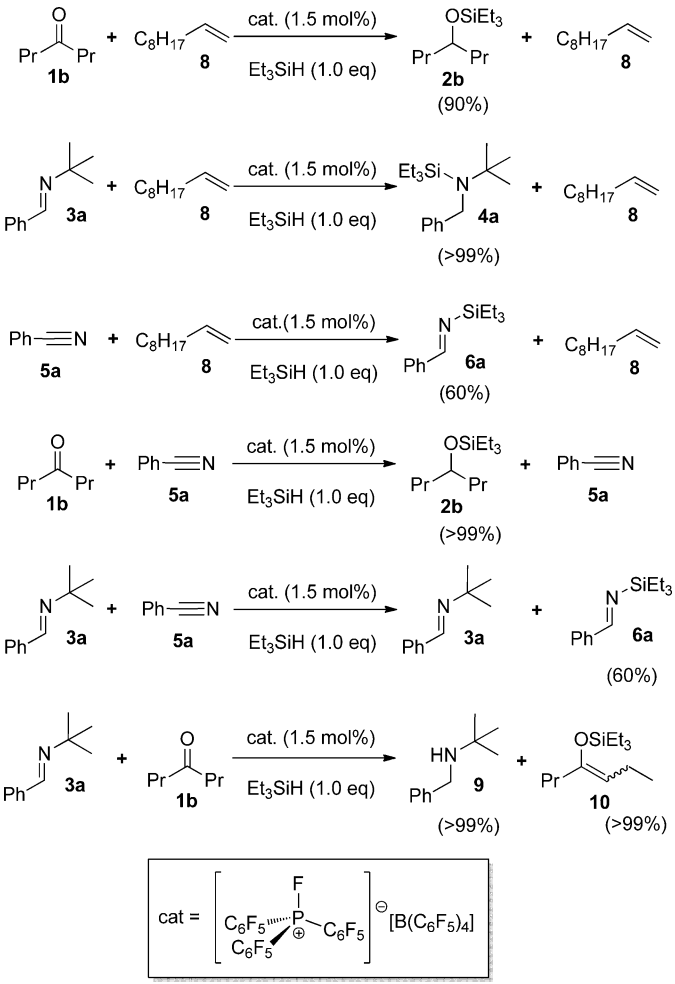
The catalyst was also found to effect the hydrosilylation of benzonitrile (**5a**). In the presence of 1.2 equivalents of Et_3SiH at room temperature, the corresponding *N*-silylimine, $PhC(H)=NSiEt_3$ (**6a**) was obtained after 1 d at 25 °C (Table 1, entry 8). However, in the presence of 2.4 equivalents of Et_3SiH at 100 °C, benzonitrile was completely reduced to the *N*,*N*-disilylamine, $PhCH_2N(SiEt_3)_2$ (**7a**; Table 1, entry 9). Interestingly, sterically encumbered mesityl nitrile **5b** did not undergo hydrosilylation at room temperature. At 100 °C, however, selective formation of *N*-silylimine **6b** was observed to occur independently of the amount of silane employed (Table 1, entry 10). Conversely, propionitrile underwent hydrosilylation in the presence of excess Et_3SiH at 100 °C to afford *N*,*N*-disilylamine **7c** (Table 1, entry 11) after 2 d.

Competition studies were undertaken to determine the selectivity of $[(C_6F_5)_3PF][B(C_6F_5)_4]$-catalysed hydrosilylations with respect to the various functional groups. Initially, reaction mixtures containing a ketone, imine, or nitrile in the presence of 1-decene, were subjected to $HSiEt_3$ in the presence of $[(C_6F_5)_3PF][B(C_6F_5)_4]$. In each case, the olefin was unaltered and

Table 1. Hydrosilylation of substrates **1**, **3**, and **5**.

Entry	Substrate	$HSiEt_3$ [equiv]	T [°C]	t [h]	Yield [%][a]
1	 **1a**	2.0	25	1	99 (83)
2	 **1b**	2.0	25	1	99 (86)
3	 **3a**	1.2	25	12	99 (97)
4	 **3b**	1.2	25	72	99
5	 **3c**	1.2	25	24	99
6	 **3d**	1.2	25	24	99
7	 **3e**	1.2	25–100	24	0
8	 **5a**	1.2	25	24	99 (88)[b]
9	 **5a**	2.4	100	24	99 (98)[c]
10	 **5b**	2.4	100	24	96[b]
11	 **5c**	2.4	100	48	99[c]
12	 **1c**	2.0	25	6	95
13	 **1d**	2.0	25	12	96
14	 **1e**	2.0	25	12	99

[a] Conditions: To a solution of the catalyst $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (6 mg, 1.5 mol%) in CH_2Cl_2 or C_6H_5Br (2.5 mL) was added Et_3SiH (1.0–2.4 equiv) and then substrate (1.0 equiv) at 25 °C. Values in parentheses refer to yields of isolated product; [b] yield of *N*-silylimine product (**6**); [c] yield of *N*,*N*-disilylamine product (**7**).

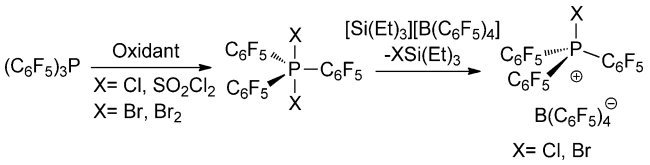


Scheme 2. Functional group competition experiments. Percentage values in parentheses are yields determined by ^{1}H NMR spectroscopy.

the polar unsaturated compound underwent hydrosilylation (Scheme 2). In a similar fashion, the polar unsaturated compounds themselves were systematically compared to each other to determine their relative propensity to undergo $[(C_6F_5)_3PF][B(C_6F_5)_4]$-catalysed hydrosilylation. For instance, heptan-4-one **1b** was selectively reduced in the presence of benzonitrile **5a**, whereas **5a** was selectively reduced in the presence of *N*-benzylidene-*tert*-butylamine **3a** (Scheme 2). Interestingly, the competition experiment involving heptan-4-one **1b** and *N*-benzylidene-*tert*-butylamine **3a** resulted in no reaction at 25 °C, even on standing for 2 d. However, heating the reaction mixture to 100 °C for 12 h resulted in the complete reduction of the imine **3a** to amine **9** with concomitant formation of silyl enol ether **10**. In this case, stabilisation of an intermediate is thought to result from the imine's Brønsted basicity, which, at elevated temperatures, triggers deprotonation of the activated ketone with simultaneous delivery of hydride to the iminium carbon.

Generally, these competition experiments indicate that hydrosilylation occurs in the following order of decreasing preference: ketone > nitrile > imine > olefin. This notion was further confirmed by some examples of intramolecular competitions. For example, hex-6-en-2-one **1c** was treated with Et_3SiH in the presence of $[(C_6F_5)_3PF][B(C_6F_5)_4]$, resulting in the exclusive formation of the silyl ether containing the unchanged olefinic fragment (Table 1, entry 12). Similar treatment of 2-methylcyclohex-2-enone **1d** gave the silyl enol ether via a formal 1,4-addition (Table 1, entry 13). Lastly the hydrosilylation of 4-acetylbenzonitrile **1e** resulted in the selective reduction of the carbonyl group with the nitrile being unaffected (Table 1, entry 14).

As a comparative study, we prepared analogous phosphonium salts by exchanging the halide from fluoride to chloride or bromide to give $[(C_6F_5)_3PCl][B(C_6F_5)_4]$ and $[(C_6F_5)_3PBr][B(C_6F_5)_4]$, respectively (Scheme 3). The syntheses of these compounds



Scheme 3. Preparation of $[(C_6F_5)_3PCl][B(C_6F_5)_4]$ and $[(C_6F_5)_3PBr][B(C_6F_5)_4]$.

are similar to that of $[(C_6F_5)_3PF][B(C_6F_5)_4]$, albeit with alternate oxidants; initial oxidation of the phosphine, $(C_6F_5)_3P$, was done with either SO_2Cl_2 or Br_2, resulting in the corresponding dihalophosphoranes. Subsequent halide abstraction was performed with $[Et_3Si][B(C_6F_5)_4]$. The bromophosphonium salt $[(C_6F_5)_3PBr][B(C_6F_5)_4]$ was characterised crystallographically (Figure 1) and incorporates a P—Br bond length of 2.1314(9) Å, which is considerably longer than the P—F bond length in the related cation $[(C_6F_5)_2PhPF]^+$ (1.533(2) Å).[20]

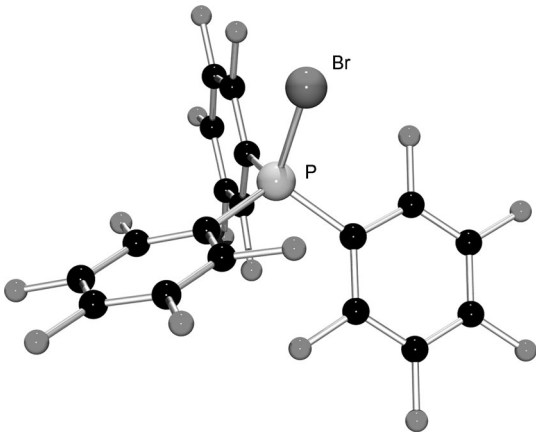
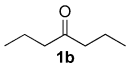
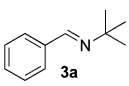


Figure 1. POV-Ray depiction of the cation of $[(C_6F_5)_3PBr][B(C_6F_5)_4]$. The anion is not shown.

To explore the reactivity of the new phosphonium cations, 1-decene was treated with Et_3SiH in the presence of 1.5 mol% of $[(C_6F_5)_3PCl][B(C_6F_5)_4]$ or $[(C_6F_5)_3PBr][B(C_6F_5)_4]$. In both cases, the reaction required longer times than the corresponding $[(C_6F_5)_3PF][B(C_6F_5)_4]$-catalysed reaction. Both reactions went to completion, although that catalysed by $[(C_6F_5)_3PCl][B(C_6F_5)_4]$

Table 2. Hydrosilylation of substrates **1**, **3**, **5** and **8**.

Entry	Substrate	Cat.	$HSiEt_3$ [equiv]	T [°C]	t [h]	Conv. [%]
1	 **8a**	$[(C_6F_5)_3PF]^+$	1.1	25	< 0.5	99
2		$[(C_6F_5)_3PCl]^+$	1.1	25	3	99
3		$[(C_6F_5)_3PBr]^+$	1.1	25	1	99
4	 **1b**	$[(C_6F_5)_3PCl]^+$	2.0	25	1	99
5		$[(C_6F_5)_3PBr]^+$	2.0	25	< 1	99
6	 **3a**	$[(C_6F_5)_3PCl]^+$	1.2	25	24	0
7		$[(C_6F_5)_3PCl]^+$	1.2	100	6	99
8		$[(C_6F_5)_3PBr]^+$	1.2	25	24	0
9		$[(C_6F_5)_3PBr]^+$	1.2	100	6	99
10	 **5a**	$[(C_6F_5)_3PCl]^+$	2.4	25	24	0
11		$[(C_6F_5)_3PCl]^+$	2.4	100	24	90 (**6a**) 10 (**7a**)
12		$[(C_6F_5)_3PBr]^+$	2.4	25	24	0
13		$[(C_6F_5)_3PBr]^+$	2.4	100	24	44 (**6a**) 56 (**7a**)

[a] Conditions: To a solution of the catalyst (6 mg, 1.5 mol%) in CH_2Cl_2 or C_6H_5Br (2.5 mL) was added Et_3SiH (1.0–2.4 equiv) followed by substrate (1.0 equiv) at 25 °C or 100 °C.

proceeded at the slowest rate (Table 2, entries 2 and 3). Using heptan-4-one as the substrate, the reaction proceeded to completion in 1 h or less regardless of the catalyst used (Table 2, entries 4 and 5). In contrast, hydrosilylation of the imine, *N*-benzylidene-2-methylpropan-2-amine, was not catalysed by $[(C_6F_5)_3PCl][B(C_6F_5)_4]$ or $[(C_6F_5)_3PBr][B(C_6F_5)_4]$ after 24 h at 25 °C, whereas $[(C_6F_5)_3PF][B(C_6F_5)_4]$ was effective under these conditions (Table 1, entry 3). Nevertheless, after 6 h at 100 °C, both $[(C_6F_5)_3PCl][B(C_6F_5)_4]$ and $[(C_6F_5)_3PBr][B(C_6F_5)_4]$ could effect complete conversion (Table 2, entries 6–9). Lastly, the hydrosilylation of benzonitrile with Et_3SiH showed that $[(C_6F_5)_3PF][B(C_6F_5)_4]$ was the superior catalyst. Again, $[(C_6F_5)_3PBr][B(C_6F_5)_4]$ and $[(C_6F_5)_3PCl][B(C_6F_5)_4]$ were ineffective at room temperature but gave mixtures of imine **6a** and amine **7a** after 24 h at 100 °C (Table 2, entries 10–13).

Mechanistic considerations

^{11}B and ^{19}F NMR spectroscopic analyses of reaction mixtures consistently indicated that the $[B(C_6F_5)_4]^-$ anion remained intact after the hydrosilylation reactions were complete, ruling out any possibility that a borane generated in situ may have catalysed this process. We also considered a mechanism whereby fluoride liberated from $[(C_6F_5)_3PF][B(C_6F_5)_4]$ might enable fluoride ion-catalysed hydrosilylation. To probe this possibility, mesityl nitrile was treated with Et_3SiH (2.4 equiv) and $[Bu_4N]F$ (30 mol%) in C_6D_5Br, and the mixture was heated to 100 °C for 3 d. In this case, no reaction was observed. Given this observation, and considering that the analogous $[(C_6F_5)_3PF][B(C_6F_5)_4]$-catalysed hydrosilylation described herein is complete in only 1 d, with much less catalyst under the same conditions, we were able to rule out the occurrence of such a mechanism.

To determine the precise mechanism of hydrosilylation catalysis, a state-of-the-art DFT study using B2PLYP-D3/def2-QZVP calculations together with TPSS-D3/def2-TZVP (COSMO) thermal corrections and COSMO-RS solvation corrections in toluene was performed (see the Supporting Information). This level of theory was used successfully by Grimme and co-workers for several years to obtain mechanistic information relating to processes involving a variety of FLP systems,[23] and provided extensive thermochemical benchmarking.[24] Free energies and optimised geometries were computed, and the reliability of this method was confirmed by comparison with results from both TPSS-D3 and PW6B95 DFT functionals and highly correlated local CCSD(T) methods.

The origin of Lewis acidity within $[(C_6F_5)_3PF]^+$ is interesting. TPSS-D3-optimised geometries of this cation reveal its C_3 symmetry with a F-P-C angle of 105.4°. This value indicates that the P centre is less pyramidal than that of the parent Lewis base $(C_6F_5)_3P$, which exhibits a clearly sp^3-hybridised P centre, despite larger steric repulsion expected when replacing the electron lone pair on P centre by fluoride. Upon addition of fluoride or hydride to $[(C_6F_5)_3PF][B(C_6F_5)_4]$, the resulting neutral compounds, $(C_6F_5)_3PF_2$ or $(C_6F_5)_3PFH$, show bipyramidal geometries with respective linear F-P-F and F-P-H arrangements about the C_3 axis (Figure 2), consistent with idealised sp^3d hybridisation. The computed d-orbital Mulliken population at the P centre of related compounds increases in the order $(C_6F_5)_3P$ (0.30) < $[(C_6F_5)_3PF]^+$ (0.73) < $(C_6F_5)_3PFH$ (0.75) < $(C_6F_5)_3PF_2$ (0.79) < PF_5 (1.04), depending on the electronegativity and number of ligands. These d populations are approaching the value of unity expected for true sp^3d hybridisation at a neutral five-coordinate P centre, and are larger than values for boron-containing species such as $[(C_6F_5)_3BH]^-$ (0.14), $(C_6F_5)_3B$ (0.15) or $[(C_6F_5)_3BF]^-$ (0.24). Therefore, a plausible conceptualisation of

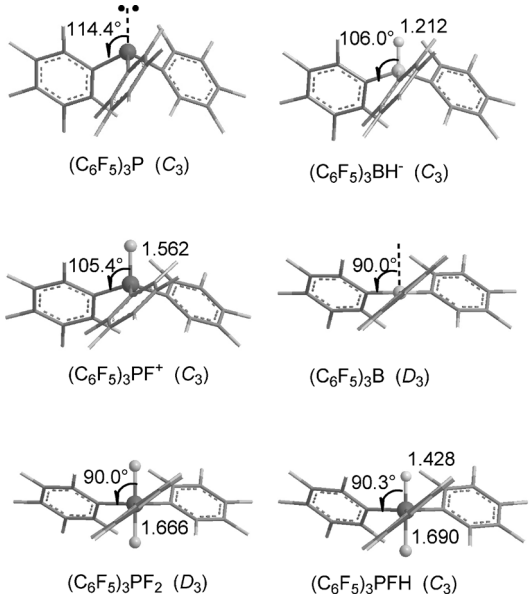


Figure 2. Optimised geometries of some P- and B-containing Lewis acids and bases. Bond lengths are given in Å angles in degrees.

the high Lewis acidity of $[(C_6F_5)_3PF]^+$ should involve the term "strongly 3d-polarised 3p orbital"[25] or alternatively "sp^3d-hybridised orbital as base acceptor." For comparison, the well-known sp^2-hybridised Lewis acid $(C_6F_5)_3B$ uses the vacant 2p orbital as base acceptor, but with a 20.8 kcal mol^{-1} smaller hydride affinity (free energy at TPSS-D3 level). The hydride affinities of $[(C_6F_5)_3PBr]^+$ and $[(C_6F_5)_3PCl]^+$ are 2.3 and 2.7 kcal mol^{-1} smaller than that of $[(C_6F_5)_3PF]^+$, respectively, consistent with relatively lower experimentally observed reactivities. Despite the higher electronegativity of Cl, the hydride affinity of $[(C_6F_5)_3PCl]^+$ is found to be slightly smaller than that of $[(C_6F_5)_3PBr]^+$, likely due to over-compensation of electron back-donation along the comparatively (ca. 0.2 Å) shorter P–Cl bond into the empty 3d orbitals at the Lewis acidic P-centre.

Considering the hydrosilylation mechanism, several pathways were considered with the necessity of $[(C_6F_5)_3PF]^+$ established. Indeed, computations show that the direct hydrosilylation of ketone is prevented by a very high free-energy barrier (43.1 kcal mol^{-1}) under ambient conditions (see the Supporting Information, Figure S1, Path C). Turning attention to the crucial role of the Lewis acid, the cation, $[(C_6F_5)_3PF]^+$ (**A$^+$**; Figure 3) was shown to form weak donor–acceptor complexes with the Lewis basic silane **B** and acetophenone **C** via P···H–Si (Figure 3) and P···O=C interactions, respectively, with the former silane complex being slightly more stable. At room temperature, both complexes can easily dissociate, and thus may act effectively as a "frustrated Lewis pair" (FLP) for bond activation. Indeed, the transition structure **TS A$^+$/D** reveals the cooperative action of ketone and phosphonium to heterolytically activate the Si–H bond, resulting in simultaneous transfer of hydride to the P centre and binding of the carbonyl oxygen to the Si cation (Figure 3). This process generates a five-coordinate neutral phosphorane complex and a carbocation. This termolecular reaction encounters a low free-energy barrier (14.2 kcal mol^{-1}), which originates mainly from entropic effects. Stabilised by adjacent phenyl and siloxy groups, the carbocation **E$^+$** is not very reactive but abstracts hydride with a higher free-energy barrier (19.0 kcal mol^{-1}) via transition structure **TS E$^+$/F** to produce the hydrosilylation product while regenerating the catalytically active cation, $[(C_6F_5)_3PF]^+$.

Consideration was also given to the alternative pathway in which $[(C_6F_5)_3PF]^+$ and silane cooperatively act on the ketone. However, this route (see the Supporting Information, Figure S1, Path B) includes a higher free-energy barrier of 21.5 kcal mol^{-1}. At the corresponding transition structure **TS A$^+$/G**, initial hydride transfer from silane generates a reactive silicon cation in an endergonic step. As same-side Si···O attack is likely to occur, this would produce the same adduct as path A. In addition, it is noted that the potential Si···F fluoride abstraction, involving a free cation intermediate, is highly exergonic and thus may represent an undesirable catalyst deactivation pathway.

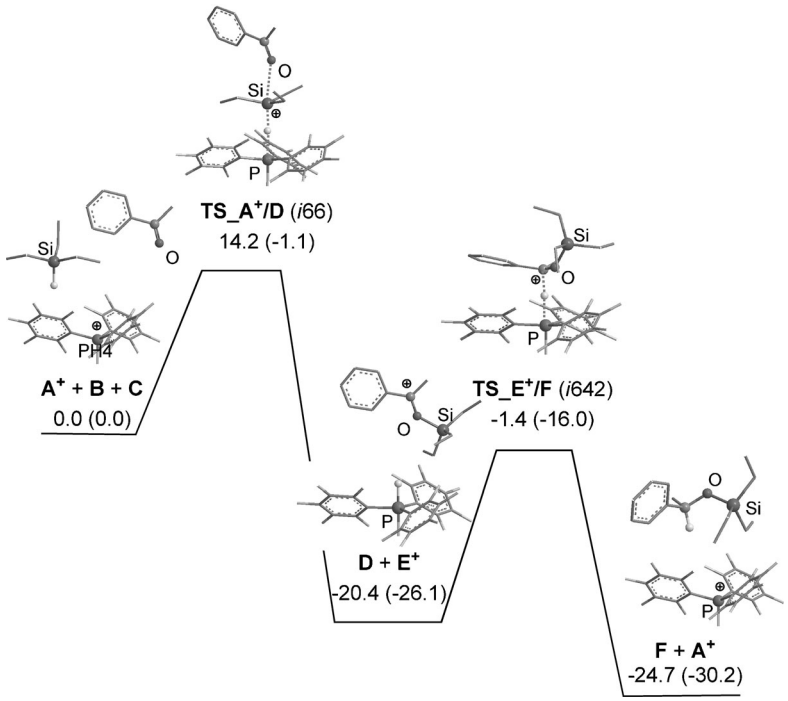
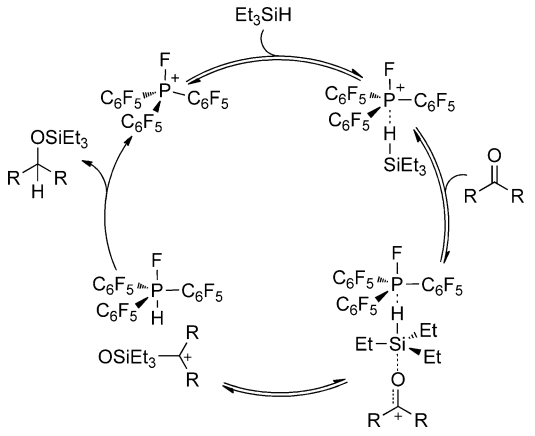


Figure 3. Reaction pathway for the hydrosilylation of ketones catalysed by **A$^+$**. Relative free energies were calculated using B2PLYP-D3 and are given in kcal mol^{-1}; enthalpies given in parentheses. Hydrogen atoms on substituents are omitted for clarity.

Collectively, these data are consistent with an FLP hydrosilylation mechanism, in which the silane and phosphonium ion act cooperatively on the ketone (Scheme 4). In principle, other heteroatomic Lewis bases may also participate in analogous termolecular reactions. Thus, the mechanism is thought to be general for ketones, imines and nitriles. Moreover it is directly analogous to the mechanism of hydrosilylation previously established for the boron-based Lewis acid catalyst, $B(C_6F_5)_3$.[12] Interestingly, Piers and co-workers have recently established experimental support for the initial interaction of a B-based Lewis acidic boro-indole with silane[26] In this regard, it is noteworthy that we have previously established that the cation $[(C_6F_5)_3PF]^+$ exhibits greater Lewis acidity than $B(C_6F_5)_3$.

Conclusion

The electrophilic phosphonium cation $[(C_6F_5)_3PF][B(C_6F_5)_4]$ mediates the efficient catalytic hydrosilylation of ketones, imines and nitriles. Competition experiments demonstrate that these reactions can be performed in the presence of other functional



Scheme 4. Proposed mechanism for hydrosilylation catalysis by $[(C_6F_5)_3PF]^+$.

groups and that the preferred reactivity follows the order ketone > nitrile > imine > olefin. In addition, the halophosphonium cations $[(C_6F_5)_3PCl][B(C_6F_5)_4]$ and $[(C_6F_5)_3PBr][B(C_6F_5)_4]$ were prepared and their ability to catalyse a variety of hydrosilylation reactions was studied. These results uncovered the following reactivity trend: $[(C_6F_5)_3PF]^+ > [(C_6F_5)_3PBr]^+ > [(C_6F_5)_3PCl]^+$. Computational studies are consistent with an FLP hydrosilylation mechanism whereby the silane is activated by the phosphonium cation, and the resulting complex acts cooperatively on the substrate. The reactivity of these readily accessible and highly reactive phosphonium-based Lewis acids is the subject of ongoing study in our laboratories.

Experimental Section

General procedures

All preparations and manipulations were carried out under an anhydrous N_2 atmosphere using standard Schlenk and glove box techniques. All glassware was oven-dried and cooled under vacuum before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals or Apollo Scientific, and were used without further purification unless indicated otherwise. The compound, $[(C_6F_5)_3PF][B(C_6F_5)_4]$ was prepared by the reported procedure.[20,27] Solvents, CH_2Cl_2, Et_2O, *n*-pentane, and toluene, were dried using an Innovative Technologies solvent purification system, whereas CD_2Cl_2 and $CDCl_3$ (Aldrich) were deoxygenated, distilled over CaH_2, then stored over 4 Å molecular sieves before use. The solvent, C_6D_5Br (Aldrich), was deoxygenated and stored over 4 Å molecular sieves before use. Reactions were monitored by NMR spectroscopy or thin-layer chromatography (TLC) on EMD Silica Gel 60 F254 plates. TLC visualisation of the developed plates was performed under UV light (254 nm) using either $KMnO_4$ or anisaldehyde stains. Neutral silica (Silica-P, 40–63 μm, Silicycle, Québec, Canada) for flash column chromatography was used as received. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer. ^1H NMR data, referenced to external Me_4Si, are reported as follows: chemical shift (δ/ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextuplet, m = multiplet, dm = doublet of multiplets, br = broad), coupling constant (Hz), normalised integrals. $^{13}C\{^1H\}$ NMR chemical shifts (δ/ppm) are referenced to external Me_4Si. High-resolution mass spectra (HRMS) were obtained using either a micro mass 70S-250 (EI) spectrometer, an ABI/Sciex QStar Mass (DART) spectrometer, or a JOEL AccuTOF-DART spectrometer.

Syntheses

$(C_6F_5)_3PCl_2$: In a 20 mL vial, $(C_6F_5)_3P$ (100 mg, 188 μmol) was dissolved in CH_2Cl_2 (1 mL) and then a 2.0 M solution of SO_2Cl_2 in CH_2Cl_2 (0.19 mL, 190 μmol) was added dropwise via syringe. After 30 min the solvent was removed under reduced pressure and the remaining solid was washed with *n*-pentane (3×2 mL). The solid was dried under vacuum, producing the product as a white powder (90 mg, 79% yield). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 147.45 (br d, J = 256.5 Hz), 144.20 (br d, J = 257.4 Hz), 137.98 (br d, J = 254.3 Hz), 119.45 ppm (br d, J = 181.0 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = −104.50 ppm (s); $^{19}F\{^1H\}$ NMR (377 MHz, CD_2Cl_2): δ = −128.35 to −128.63 (m, 6F), −146.20 to −146.40 (m, 3F), −158.68 to −158.95 ppm (m, 6F); elemental analysis calcd (%) for $C_{18}F_{15}PCl_2$: C 35.85; found: C 36.09.

$[(C_6F_5)_3PCl][B(C_6F_5)_4]$: In a 20 mL vial, $(C_6F_5)_3PCl_2$ (63 mg, 105 μmol) was fully dissolved in toluene (2 mL). A stir-bar was added and the solution was placed in cold-well (ca. −35 °C). $[Et_3Si{\cdot}tol][B(C_6F_5)_4]$ (86 mg, 100 μmol) was added, and the solution turned a slight yellow colour over time. The solution was taken out of the cold well and allowed to stir for 30 min. Toluene was then pipetted off, and the solution was washed with toluene (2×1 mL) before removing the solvent under reduced pressure. The resulting solid was isolated as a white powder (106 mg, 85% yield). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ = 148.40 (br d, J = 272.0 Hz), 148.05 (br d, J = 241.8 Hz), 139.35 (br d, J = 255.4 Hz), 138.12 (br d, J = 261.3 Hz), 136.22 ppm (br d, J = 238.3 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 27.35 ppm (s); $^{19}F\{^1H\}$ NMR (377 MHz, CD_2Cl_2): δ = −124.81 to −125.04 (m, 6F), −125.05 to −125.28 (m, 3F), −133.44 (br s, 8F), −150.47 to −150.71 (m, 6F), −163.89 (t, J = 20.4 Hz, 4F), −167.90 ppm (br t, J = 18.3 Hz, 8F); ^{11}B NMR (128 MHz, CD_2Cl_2): δ = −16.69 (s). elemental analysis calcd (%) for $C_{42}F_{35}PClB$: C 40.47; found: C 40.45.

$(C_6F_5)_3PBr_2$: In a 20 mL vial, $(C_6F_5)_3P$ (100 mg, 188 μmol) was fully dissolved in CH_2Cl_2 (1 mL), and then a 1.0 M solution of Br_2 in CH_2Cl_2 (0.19 mL, 190 μmol) was added dropwise via syringe. The solution turned a dark orange colour and after a few minutes a precipitate formed. After 30 min, the solvent was removed under reduced pressure and the remaining solid was washed with *n*-pentane (3×2 mL). The solid was dried under vacuum and isolated as a light yellow powder (121 mg, 93% yield). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ = 146.65 (br d, J = 248.2 Hz), 144.39 (br d, J = 260.5 Hz), 138.01 (br d, J = 257.5 Hz), 107.49 ppm (br d, J = 57.2 Hz); $^{31}P\{^1H\}$ NMR (203 MHz, CD_2Cl_2): δ = −86.68 ppm (s); $^{19}F\{^1H\}$ NMR (377 MHz, CD_2Cl_2): δ = −128.59 (br t, 6F, J = 19.1 Hz), −145.21 (br t, 3F, J = 20.2 Hz), −158.72 ppm (br t, 6F, J = 20.1 Hz); elemental analysis calcd (%) for $C_{18}F_{15}PBr_2$: C 31.24; found: C 25.20, N 0.44.

$[(C_6F_5)_3PBr][B(C_6F_5)_4]$: In a 20 mL vial, $(C_6F_5)_3PBr_2$ (106 mg, 153 μmol) was partially dissolved in toluene (2 mL) with the aid of a stir-bar. The orange suspension was placed in a cold well (ca. −35 °C), and $[Et_3Si{\cdot}tol][B(C_6F_5)_4]$ (126 mg, 146 μmol) was added. After 30 min, the suspension was taken out of the cold well. The top layer of toluene was pipetted off, and the orange solid was then washed with toluene (2×1 mL) before removing the solvent under reduced pressure. The resulting solid was isolated as an off-white powder (138 mg, 73% yield). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ = 148.30 (br d, J = 250.1 Hz), 148.05 (br d, J = 236.7 Hz), 139.21 (br d, J = 255.8 Hz), 138.19 (br d, J = 235.6 Hz), 136.22 (br d, J = 243.8 Hz), 124.02 ppm (br s); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ =

−5.73 ppm (s); $^{19}F\{^1H\}$ NMR (377 MHz, CD_2Cl_2): $\delta = -124.69$ (br s, 6F), −126.30 (br s, 3F), −133.34 (br s, 10F), −150.94 (br s, 6F), −163.82 (t, $J = 20.21$ Hz, 5F), −167.82 ppm (br t, $J = 17.45$ Hz, 10F); ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta = -16.71$ ppm (s); elemental analysis calcd (%) for $C_{42}F_{35}PBrB$: C 39.07; found: C 36.69, N 0.65. CCDC-1037077 contains the crystallographic data for $[(C_6F_5)_3PBr][B(C_6F_5)_4]$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Representative protocol for hydrosilylation reactions

All hydrosilylation experiments were performed in a similar manner, and therefore only one reaction is described in detail. Isolated product yields determined for several products were compared with those determined by ^1H NMR spectroscopy. To a solution of the catalyst $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (6 mg, 5 μmol) in CD_2Cl_2, $CDCl_3$ or C_6D_5Br (2.5 mL) was added Et_3SiH (98 mg, 850 μmol) followed by heptan-4-one **1b** (40 mg, 350 μmol) at 25 °C. Monitoring the reaction by NMR spectroscopy and TLC showed that the ketone had been completely consumed within 1 h. To the reaction mixture was then added CH_3CN (0.02 mL). The mixture was diluted with CH_2Cl_2 (10 mL), filtered over silica gel and the solvent evaporated to afford a mixture of the hydrosilylated compound **2b** and 8% of $(Et_3Si)_2O$ as a colourless oil (73 mg , 86% yield).

Reaction conditions and product characterisations

$Et_3SiOCH(Me)Cy$, **2a**: 2.0 equivalents of Et_3SiH were used relative to **1a**, and the reaction was conducted for 1 h at 25 °C. (82 mg of a mixture of the hydrosilylated compound **2a** and 15% of $(Et_3Si)_2O$, 83% yield of **2a**, colourless oil). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 3.57$ (quint, $J = 6.3$ Hz, 1H), 1.80 (m, 1H), 1.74 (m, 2H), 1.66 (m, 2H), 1.29–1.12 (m, 4H), 1.08 (d, $J = 6.3$ Hz, 3H), 1.05–0.90 (m, 2H), 0.96 (t, $J = 8.2$ Hz, 9H), 0.59 ppm (q, $J = 7.9$ Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): $\delta = 73.1$, 45.4, 29.4, 29.3, 27.4, 27.2, 27.1, 21.2, 7.4 (3C), 5.7 ppm (3C); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): $\delta = 15.1$ ppm (s); MS (DART ionisation): *m/z*, (%): 247.2 (50), 243.2 ($[M+H]^+$, 20), 133.2 ($[HOSiEt_3]^+$, 50), 111.1 ($[M-OSiEt_3]^+$, 100).

$Et_3SiOCHPr_2$, **2b**: 2.0 equivalents of Et_3SiH were used relative to **1b**, and the reaction was conducted for 1 h at 25 °C (73 mg of a mixture of the hydrosilylated compound **2b** and 8% of $(Et_3Si)_2O$, 86% yield of **2b**, colourless oil). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 3.63$ (quint, $J = 5.5$ Hz, 1H), 1.38 to 1.22 (m, 8H), 0.91 (t, $J = 7.9$ Hz, 9H), 0.85 (t, $J = 7.1$ Hz, 6H), 0.55 ppm (q, $J = 7.7$ Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): $\delta = 72.7$, 40.3 (2C), 19.3 (2C), 14.8 (2C), 7.4 (3C), 5.8 ppm (3C); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): $\delta = 14.9$ ppm (s); MS (DART ionisation): *m/z* (%): 231.2 ($[M]^+$, 75), 133.1; HRMS (DART ionisation): *m/z* calcd for $C_{13}H_{31}OSi$, $[M+H]^+$: 231.21442; found: 231.21496.

$Et_3Si(N(tBu)CH_2Ph)$, **4a**: 1.2 equivalents of Et_3SiH were used relative to **3a**, and the reaction was conducted for 12 h at 25 °C. The crude product was diluted with CH_2Cl_2 (10 mL), filtered through silica gel and evaporated (46 mg, 97% yield, colourless oil). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.35$ (d, $J = 7.9$ Hz, 2H), 7.25 (t, $J = 7.9$ Hz, 2H), 7.12 (t, $J = 7.9$ Hz, 1H), 4.10 (s, 2H), 1.17 (s, 9H), 0.97 (t, $J = 8.0$ Hz, 9H), 0.66 ppm (q, $J = 8.0$ Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): $\delta = 147.00$, 128.3 (2C), 126.9 (2C), 126.0, 55.4, 49.4, 31.2 (3C), 8.2 ppm (3C), 7.9 (3C); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): $\delta = 9.5$ ppm (s); MS (DART ionisation): *m/z* (%): 164.1 ($[M-Et_3Si+2H]^+$, 100); HRMS (DART ionisation): *m/z* calcd for $C_{11}H_{18}N$ $[M-Et_3Si+2H]^+$: 164.14392; found: 164.14415.

$Et_3SiN(tBu)CH_2(C_6H_4\text{-}4\text{-}Br)$, **4b**: 1.2 equivalents of Et_3SiH were used relative to **3b**, and the reaction was conducted for 72 h at 25 °C (99% yield as determined by NMR spectroscopy). ^1H NMR (400 MHz, C_6D_5Br): $\delta = 7.31$ (d, $J = 8.8$ Hz, 2H), 7.12 (d, $J = 8.9$ Hz, 2H), 3.90 (s, 2H), 1.06 (s, 9H), 0.93 (t, $J = 8.0$ Hz, 9H), 0.60 ppm (q, $J = 7.8$ Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): $\delta = 144.7$, 130.4 (2C), 127.6 (2C), 118.8, 54.2, 47.9, 30.2 (3C), 7.5 (3C), 6.9 ppm (3C); ^{29}Si NMR (79.5 MHz, C_6D_5Br): $\delta = 9.5$ ppm (s); MS (DART ionisation): *m/z* (%): 242.1 ($[M-Et_3Si+2H]^+$, 100), 244.1 ($[M-Et_3Si+2H]^+$, 90); HRMS (ESI): *m/z* calcd for $C_{11}H_{17}BrN$ $[M-Et_3Si+2H]^+$: 242.0539 and 244.0544; found: 242.0540 and 244.0518, respectively.

$Et_3SiN(tBu)CH_2(C_6H_4\text{-}3\text{-}Br)$, **4c**: 1.2 equivalents of Et_3SiH were used relative to **3c**, and the reaction was conducted for 24 h at 25 °C (99% yield as determined by NMR spectroscopy). ^1H NMR (400 MHz, C_6D_5Br): $\delta = 7.56$ (s, 1H), 7.19 (m, 2H), 6.99 (t, $J = 7.8$ Hz, 1H), 3.93 (s, 2H), 1.06 (s, 9H), 0.94 (t, $J = 7.9$ Hz, 9H), 0.59 ppm (q, $J = 7.7$ Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): $\delta = 148.3$, 129.0, 128.9, 128.2, 124.2, 121.9, 54.1, 47.9, 30.1 (3C), 7.5 (3C), 6.8 ppm (3C); ^{29}Si NMR (79.5 MHz, C_6D_5Br): $\delta = 9.7$ ppm (s); MS (ESI): *m/z* (%): 168.9 ($[M-Et_3SiNtBu]^+$, 100), 170.9 ($[M-Et_3SiNtBu]^+$, 90), 242.1 ($[M-Et_3Si+2H]^+$, 60), 244.1 ($[M-Et_3Si+2H]^+$, 55); HRMS (ESI) *m/z* calcd for $C_{11}H_{17}BrN$ $[M-Et_3Si+2H]^+$: 242.0539 and 244.0544; found: 242.0541 and 244.0520.

$Et_3SiN(tBu)CH_2(C_6H_4\text{-}4\text{-}tBu)$, **4d**: 1.2 equivalents of Et_3SiH were used relative to **3d**, and the reaction was conducted for 24 h at 25 °C (99% yield as determined by NMR spectroscopy). ^1H NMR (400 MHz, C_6D_5Br): $\delta = 7.32$ (s, 4H), 4.04 (s, 2H), 1.23 (s, 9H), 1.11 (s, 9H), 0.96 (t, $J = 8.4$ Hz, 9H), 0.64 ppm (q, $J = 8.4$ Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): $\delta = 147.5$, 142.5, 125.5 (2C), 124.2 (2C), 54.2, 48.0, 33.6, 31.0 (3C), 30.4 (3C), 7.6 (3C), 7.0 ppm (3C); ^{29}Si NMR (79.5 MHz, C_6D_5Br): $\delta = 8.7$ ppm (s); MS (DART ionisation): *m/z* (%): 220.2 ($[M-Et_3Si+2H]^+$, 100); HRMS (ESI) *m/z* calcd for $C_{15}H_{26}N$ $[M-Et_3Si+2H]^+$: 220.2060; found: 220.2061.

$Et_3SiN{=}CHPh$, **6a**: 1.2 equivalents of Et_3SiH were used relative to **5a**, and the reaction was conducted for 24 h at 25 °C. The crude product was diluted with CH_2Cl_2 (10 mL), filtered through silica gel and evaporated (32 mg, 88% yield, colourless oil). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 9.08$ (s, 1H), 7.83 (m, 2H), 7.47 (m, 3H), 1.04 (t, $J = 8.0$ Hz, 9H), 0.80 ppm (q, $J = 7.8$ Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): $\delta = 169.3$, 139.8, 131.6, 129.1 (2C), 128.9 (2C), 7.4 (3C), 4.2 ppm (3C); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): $\delta = 7.6$ ppm (s); MS (DART ionisation): *m/z* (%): 220.2 ($[M+H]^+$, 100); HRMS (DART ionisation): *m/z* calcd for $C_{13}H_{22}NSi$, $[M+H]^+$: 220.15215; found: 220.15305.

$(Et_3Si)_2NCH_2Ph$, **7a**: 2.4 equivalents of Et_3SiH were used relative to **5a**, and the reaction was conducted for 24 h at 100 °C. The crude product was diluted with CH_2Cl_2 (10 mL), filtered through silica gel and evaporated (55 mg, 98% yield, colourless oil). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.34$ to 7.23 (m, 4H), 7.18 (t, $J = 6.9$ Hz, 1H), 4.17 (s, 2H), 0.96 (t, $J = 7.8$ Hz, 18H), 0.64 ppm (q, $J = 7.6$ Hz, 12H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): $\delta = 145.3$, 128.3 (2C), 127.1 (2C), 126.5, 49.5, 8.1 (6C), 6.6 ppm (6C); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): $\delta = 12.2$ ppm (s); MS (DART ionisation): *m/z* (%): 336.2 ($[M+H]^+$, 100); HRMS (DART ionisation): *m/z* calcd for $C_{19}H_{38}NSi_2$, $[M+H]^+$: 336.25428; found: 336.25475.

$Et_3SiN{=}CH(C_6H_2\text{-}2,4,6\text{-}Me_3)$, **6b**: 2.4 equivalents of Et_3SiH were used relative to **5b**, and the reaction was conducted for 24 h at 100 °C (96% yield as determined by NMR spectroscopy). ^1H NMR (400 MHz, C_6D_5Br): $\delta = 9.42$ (s, 1H), 6.71 (s, 2H), 2.42 (s, 6H), 2.16 (s, 3H), 1.03 (t, $J = 8.0$ Hz, 9H), 0.73 ppm (q, $J = 7.9$ Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br): $\delta = 169.1$, 138.2, 137.2 (2C), 129.3 (2C), 128.6, 20.7, 20.2 (2C), 6.8 (3C), 3.4 ppm (3C); ^{29}Si NMR (79.5 MHz,

C_6D_5Br): $\delta = 7.7$ ppm (s); MS (DART ionisation): *m/z* (%): 280.2 ([$M+NH_4$]$^+$, 100), 149.2 ([$MesCHNH_2$]$^+$, 75).

(Et_3Si)$_2$NHBu, **7c**: 2.4 equivalents of Et_3SiH were used relative to **5c**, and the reaction was conducted for 48 h at 100 °C (99% yield as determined by NMR spectroscopy). ^{1}H NMR (400 MHz, C_6D_5Br): $\delta =$ 2.72 (m, 2H), 1.40 (m, 2H), 1.17 (sex, $J = 7.5$ Hz, 2H), 0.96 (t, $J =$ 8.0 Hz, 18H), 0.87 (t, $J = 7.5$ Hz, 3H), 0.61 ppm (q, $J = 8.0$ Hz, 12H); ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br): $\delta = 44.9$, 37.5, 20.1, 13.7, 7.3 (6C), 5.4 ppm (6C); ^{29}Si NMR (79.5 MHz, C_6D_5Br): $\delta = 10.4$ ppm (s); MS (DART ionisation): *m/z* (%): 273.2 ([$M-Et$]$^+$, 20), 259.2 (20), 217.2 (25), 203.2 (30), 193.2 (40), 144.1 (60), 130.1 ([$M-Bu-SiEt_3$]$^+$, 100).

$Et_3SiOCHMe(CH_2)_3CH{=}CH_2$, **2c**: 2.0 equivalents of Et_3SiH were used relative to **1c**, and the reaction was conducted for 6 h at 25 °C (95% yield as determined by NMR spectroscopy). ^{1}H NMR (400 MHz, C_6D_5Br): $\delta = 5.78$ (m, 1H), 4.97 (m, 2H), 3.74 (sex. $J =$ 6.1 Hz, 1H), 2.08 (m, 2H), 1.46 (m, 2H), 1.09 (d, $J = 6.5$ Hz, 3H), 0.95 (m, 9H), 0.54 ppm (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br): $\delta =$ 138.2, 113.8, 126.9 (2C), 67.3, 38.5, 29.6, 23.5, 6.6 (3C), 4.7 ppm (3C); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): $\delta = 15.42$ ppm (s); MS (DART ionisation): *m/z* (%): 232.2 ([$M+NH_4$]$^+$, 80), 215.2 ([$M+H$]$^+$, 35), 187.2 (45), 133.1 (100).

$Et_3SiOC{=}C(Me)(C_4H_8)$, **2d**: 2.0 equivalents of Et_3SiH were used relative to **1d**, and the reaction was conducted for 12 h at 25 °C (96% yield as determined by NMR spectroscopy). ^{1}H NMR (400 MHz, C_6D_5Br): $\delta = 1.99$ (m, 2H), 1.89 (m, 2H), 1.61 (s, 3H), 1.56 (m, 2H), 1.47 (m, 2H), 0.98 (t, $J = 8.0$ Hz, 9H), 0.61 ppm (q, $J = 8.0$ Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br): $\delta = 142.6$, 109.9, 29.9 (2C), 29.8 (2C), 23.5 (2C), 22.7 (2C), 16.0, 6.6 (3C), 5.4 ppm (3C); ^{29}Si NMR (79.5 MHz, C_6D_5Br): $\delta = 15.9$ ppm (s); MS (DART ionisation): *m/z* (%): 226.2 ([M]$^+$, 30), 211.2 ([$M-Me$]$^+$, 60), 209.2 (75), 113.1 (100).

$Et_3SiOCHMe(C_6H_4$-4-CN), **2e**: 2.0 equivalents of Et_3SiH were used relative to **1e**, and the reaction was conducted for 12 h at 25 °C (99% yield as determined by NMR spectroscopy). ^{1}H NMR (400 MHz, C_6D_5Br): $\delta = 7.27$ (d, $J = 8.3$ Hz, 2H), 7.20 (d, $J = 8.2$ Hz, 2H), 4.71 (q, $J = 6.3$ Hz, 1H), 1.26 (d, $J = 6.5$ Hz, 3H), 0.88 (t, $J =$ 8.0 Hz, 9H), 0.51 ppm (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br): $\delta =$ 151.3, 131.3 (2C), 125.2 (2C), 118.1, 110.3, 69.4, 26.5, 6.5 (3C), 4.4 ppm (3C); ^{29}Si NMR (79.5 MHz, C_6D_5Br): $\delta = 18.9$ ppm (s); MS (DART ionisation): *m/z* (%): 279.2 ([$M+NH_4$]$^+$, 100), 262.2 ([$M+H$]$^+$, 75), 165.1 (50); HRMS (DART ionisation): *m/z* calcd for $C_{15}H_{23}NOSi$, [$M+H$]$^+$: 262.16272; found: 262.16289.

Larger scale hydrosilylation reactions

$Et_3SiOCHPr_2$, **2b**: To a solution of the catalyst [$(C_6F_5)_3PF$][$B(C_6F_5)_4$] (30 mg, 0.024 mmol) in CD_2Cl_2 (2.5 mL) was added Et_3SiH (394 mg, 3.4 mmol) followed by heptan-4-one **1b** (194 mg, 1.7 mmol) at 25 °C. Monitoring the reaction by NMR spectroscopy showed that the ketone had been completely consumed within 1 h. (95% yield as determined by NMR spectroscopy).

$Et_3Si(N(t$Bu)$CH_2Ph)$, **4a**: To a solution of the catalyst [$(C_6F_5)_3PF$][$B(C_6F_5)_4$] (30 mg, 0.024 mmol) in CD_2Cl_2 (2.5 mL) was added Et_3SiH (209 mg, 1.8 mmol) followed by **3a** (274 mg, 1.7 mmol) at 25 °C. The reaction was monitored by NMR spectroscopy, which showed that the reaction was completed after 24 h at 25 °C or 2 h at 50 °C. The crude product was diluted with CH_2Cl_2 inside of glove box, filtered through silica gel and evaporated (430 mg, 91% yield, colourless oil).

Computational details

The quantum chemical DFT calculations were performed with the TURBOMOLE 6.4 suite of programs.[28] The structures were fully optimised at the TPSS-D3/def2-TZVP + COSMO level of theory, which combines the TPSS *meta*-GGA density functional[29] with the BJ-damped DFT-D3 dispersion correction[30] and the def2-TZVP basis set,[31] using the Conductor-like Screening Model (COSMO) continuum solvation model[32] for CH_2Cl_2 solvent (dielectric constant $\varepsilon =$ 8.93, refractive constant $n = 1.424$, $R_{solv} = 2.94$ Å). For the present $\mathbf{A}^+ + \mathbf{C} + Et_3SiH$ reaction system with 75 atoms, it leads to 1737 basis functions (35, 23, 17 atoms and 1091, 319, 327 basis functions, respectively) in our DFT calculations. The density-fitting RI-J approach[33] was used to accelerate the geometry optimisation and numerical harmonic frequency calculations in solution. The optimised structures were characterised by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections according to a modified ideal gas-rigid rotor-harmonic oscillator model.[34]

The final solvation energies in toluene solvent were computed with the COSMO-RS solvation model in the COSMOtherm program package[35] on the above TPSS-D3-optimised structures. To check the effects of the chosen DFT functional on the reaction energies and barriers, gas-phase single-point calculations using the TPSS-D3, hybrid PW6B95-D3[36] and double-hybrid B2PLYP-D3[37] were performed using a larger def2-QZVP basis set.[38] The final reaction enthalpies (ΔH) and Gibbs free energies (ΔG) were determined from the gas-phase single-point energies plus thermal corrections plus COSMO-RS solvation energies. The results from different DFT functionals are in good mutual agreement. In our discussion, the B2PLYP-D3 Gibbs free energies (in kcal mol^{-1}, at 298.15 K, 1 atm) were used unless specified otherwise.

Further ab initio calculations were also performed using the ORCA 3.0.1 suite of programs.[39] MP2/CBS calculations were performed using the frozen core and RI approximations (def2-TZVP/C and def2-QZVP/C auxiliary basis sets, respectively) and Halkier CBS extrapolation using def2-TZVP and def2-QZVP basis sets.[40] Highly correlated DLPNO-CCSD(T) calculations[41] using the large and diffuse aug-cc-pVTZ basis set[42] and default setup for the thresholds were also performed to benchmark our B2PLYP-D3 calculations, resulting in systematically lower free-energy barriers by about 4 kcal mol^{-1} (The computed relative free energies for TS 1/2$^+$, TS 2/3$^+$, and TS 1/4$^+$ were 9.8, −5.0 and 16.3 kcal mol^{-1}, respectively). This agreement between high-level wavefunction theory and DFT methods further supports the reliability of the applied theory.

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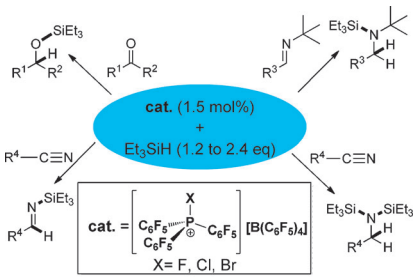
FULL PAPER

Proceed with cation: The electrophilic phosphonium salt, $[(C_6F_5)_3PF][B(C_6F_5)_4]$, catalyses the efficient hydrosilylation of ketones, imines and nitriles at room temperature. In the presence of this catalyst, adding one equivalent of hydrosilane to a nitrile yields a silylimine product, whereas adding a second equivalent produces the corresponding disilylamine.



Hydrosilylation

M. Pérez, Z.-W. Qu, C. B. Caputo, V. Podgorny, L. J. Hounjet, A. Hansen, R. Dobrovetsky, S. Grimme, D. W. Stephan**

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Hydrosilylation of Ketones, Imines and Nitriles Catalysed by Electrophilic Phosphonium Cations: Functional Group Selectivity and Mechanistic Considerations