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Carbonyl and olefin hydrosilylation mediated by an air-stable phosphorus(III) dication under mild conditions†

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The readily-accessible, air-stable Lewis acid [(terpy)PPh][B(C_6F_5)$_4$]$_2$ 1 is shown to mediate the hydrosilylation of aldehydes, ketones, and olefins. The utility and mechanism of these hydrosilylations are considered.

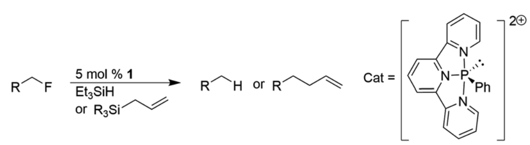
Lewis acids have become an increasingly important class of compounds for their ability to act as catalysts towards various chemical transformations.[1] Many classical group 13 Lewis acids, such as BX_3 (X = H, F, Cl), BPh_3, and $AlCl_3$ are highly reactive as a result of an accessible, vacant p orbital. An analogous situation is also seen for group 14 cations such as [Ph_3C][B(C_6F_5)$_4$] and [Et_3Si][B(C_6F_5)$_4$] where the combination of the vacant p-orbital and the cationic charge makes these species even more Lewis acidic and thus more reactive. Such Lewis acids have found numerous stoichiometric and catalytic applications.[2–11]

In recent years, our group has explored highly electrophilic phosphonium cations such as [(C_6F_5)$_3$PF][B(C_6F_5)$_4$]. In these cations, the Lewis acidity resides in a low-lying σ* orbital principally oriented opposite the P–F bond.[12] Such Lewis acidic cations have proved quite versatile, being used to mediate a variety of reactions including hydrodefluorination,[12] Friedel–Crafts arylation of fluoroalkanes,[13,14] dehydrocoupling of silanes and amines;[15] hydrosilylation of ketones, alkynes, and olefins;[16] deoxygenation of ketones,[17] amides,[18] and phosphine oxides;[19] hydrogenation of olefins,[20] and the hydroarylation of alkynes.[21]

Targeting enhanced stability and improved ease of manipulation of such cations, a number of avenues have been explored. Alteration of the aryl substituents so as to provide steric protection, or replacement of the P–F fragment with phenoxide, trifluoromethyl or methyl groups have been reported.[22–28] Most recently, we have uncovered that dicationic phosphorus(III) coordination complexes are also highly effective Lewis acids but provide the additional benefit in some instances of air-stability. Specifically, the cations [(terpy)PPh]$^{2+}$ (terpy = 2,2′;6′,2″-terpyridine) and [(bipy)PPh]$^{2+}$ (bipy = 2,2′-bipyridine) have been shown to be effective catalysts for hydrodefluorination and carbodefluorination of a series of fluoroalkanes (Scheme 1).[29,30] While the latter dication is more reactive and more sensitive, the species [(terpy)PPh][B(C_6F_5)$_4$]$_2$ **1** provides both reactivity and air stability allowing the above reactions to be done on the benchtop in wet solvents. The reactivity of **1** is attributed to the hemilability of the terpy ligand,[31–44] where dissociation of one arm is required to reveal the Lewis acidic site on the P atom. In the present study, we expand the utility of this P(III) dication demonstrating its ability to mediate the hydrosilylation of aldehydes, ketones, and olefins. The utility and mechanism of these hydrosilylations are considered.

The reaction of 4-methylbenzaldehyde in the presence of 1.1 equivalents of Et_3SiH and 5 mol% of **1** in CH_2Cl_2 led to quantitative formation of the corresponding silyl ether after 13 hours. The impact of solvent was assessed (Table 1). The reactions were equally successful in the halogenated aromatic solvents *o*-dichlorobenzene and *o*-difluorobenzene, but were unsuccessful in diethyl ether, acetonitrile-d$_3$, and tetrahydrofuran (THF). These latter observations were attributed either to the poor solubility of **1** or the interaction of a donor solvent with the Lewis acidic P(III) dication. This notion is further supported by the observation of polymerization of THF upon exposure to **1** after 48 h, typical of Lewis acidic behavior.[45–47] Surprisingly, the reaction can also be performed without solvent, using 5 equivalents of silane as the reaction medium.

The impact of the silane employed on the efficacy of hydrosilylation was also probed (Table 2). Again, the hydrosilylation of 4-methylbenzaldehyde was used as the test case (Table 2).



Scheme 1 C–C coupling mediated by a P(III) dication: [(terpy)PPh][B(C_6F_5)$_4$]$_2$ **1**.

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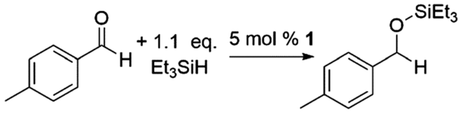
Table 1 Impact of solvent on hydrosilylation[a]



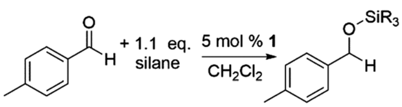
No.	Solvent[a]	T (h)	Conv.[b] (%)	No.	Solvent[a]	T (h)	Conv.[b] (%)
1	CH_2Cl_2	13	>99	6	o-$C_6H_4Cl_2$	13	>99
2	Toluene	24	<1	7	o-$C_6H_4F_2$	13	>99
3	C_6H_5Cl	24	41	8	Et_2O	13	<1
4	THF[c]	13	26	9	CD_3CN	24	<10
5	$CDCl_3$	24	80	10	None[d]	13	>99

[a] Standard conditions: 25 °C, 1.1 eq. Et_3SiH, 0.05 mmol 4-methyl benzaldehyde, 0.7 mL solvent, 5 mol% of **1**. [b] Conversion monitored by ^{1}H NMR spectroscopy. [c] Some oligomerization observed after 13 hours. [d] 5 eq. of Et_3SiH.

Use of (n-hex)$_3$SiH or Ph_2MeSiH as well PMHS proved much less effective, while $(Me_3Si)_3SiH$, Ph_3SiH, Ph_2SiH_2, $(C_6F_5)_3SiH$, $(EtO)_3SiH$ or $(Me_3SiO)_3SiH$ gave no reaction. It is noteworthy that the catalytic hydrosilylation of 4-methylbenzaldehyde is also observed when **1** is generated *in situ* by adding a mixture of the and Et_3SiH into a stirring solution 10 mol% terpyridine, $PhPCl_2$ and $Na[B(C_6F_5)_4]$ in dry CH_2Cl_2, indicating catalyst self-assembly in solution.

A series of aldehydes were hydrosilylated using Et_3SiH and 5 mol% of **1** affording generally high yields (Table 3). Aryl-aldehydes containing both electron-withdrawing substituents groups (*e.g.* NO_2, halides, entry 2–8), or electron-donating groups (*e.g.* OMe, entries 9–12) were used. A fluoride group in the *para*-position, led to reduced conversion (56%, 24 h) (Table 3, entries 1–12). Sterically demanding arenes (Table 3, entries 13 and 14) led to a significant decrease in activity. In contrast, aliphatic aldehydes and electron-rich aromatic aldehydes were readily reduced (Table 3, entries 9–12, 15, 16). This activity was extended to ketones. While electron-withdrawing substituents (Table 3, entries 17–20) gave modest yields of the hydrosilylated products, use of more electron rich ketones resulted in quantitative reduction (Table 3, entries 21–28). Diminished isolated yields in a few cases (Table 3, entries 4, 6 and 23) were attributed to the hydrolysis of the silylether.

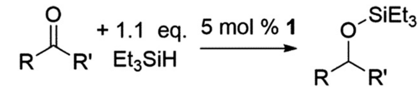
Table 2 Impact of silicon hydride on hydrosilylation[a]



No.	Silicon-hydride[a]	T (h)	Conv.[b] (%)	No.	Silicon-hydride[a]	T (h)	Conv.[b] (%)
1	Et_3SiH	24	>99	7	$(C_6F_5)_3SiH$[c]	24	<1
2	(nHex)$_3$SiH	24	26	8	$(EtO)_3SiH$	24	<1
3	$(Me_3Si)_3SiH$	24	<1	9	$(Me_3SiO)_3SiH$	24	<1
4	Ph_2MeSiH	24	59	10	$Me_3SiOSiMe_2OSiMe_2H$	0.5	>99
5	Ph_3SiH	24	<1	11	$Me_3SiOSiMe_2OSiMe_2H$[d]	24	75
6	Ph_2SiH_2	24	<1	12	$(MeSiHO)_n$(PMHS)[c]	24	23

[a] Standard conditions: 25 °C, 1.1 eq. Si–H, 0.05 mmol $MeC_6H_4C(O)H$, 0.7 mL CH_2Cl_2, 5 mol% of **1**. [b] Conversion monitored by ^{1}H NMR spectroscopy. [c] Silane exhibits poor solubility in the solvent. [d] Reaction set up under ambient conditions on the benchtop, with dry solvent.

Table 3 Summary of the hydrosilylation of aldehydes and ketones[a]



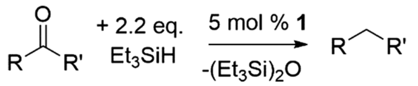
No.[a]	R, R[1]	T (h)	Conv.,[b] % (yield%)
1	Ph, H	24	>99 (93)
2	4-$(NO_2)C_6H_4$, H	24	>99 (99)
3	4-BrC_6H_4, H	24	>99 (84)
4	4-ClC_6H_4, H	24	>99 (33)
5	2-ClC_6H_4, H	24	>99 (87)
6	2-BrC_6H_4, H	24	>99 (50)
7	4-FC_6H_4, H	24	56 (56)
8	3,4-$Cl_2C_6H_3$	1	99 (95)
9	4-MeC_6H_4, H	24	>99 (96)
10	3-$(MeO)C_6H_4$, H	24	>99 (97)
11	3,5-$(MeO)_2C_6H_3$, H	24	>99 (99)
12[c]	4-$(C(O)H)C_6H_4$, H	24	94 (94)
13	2-MeC_6H_4, H	24	25 (24)
14	2,4,6-$Me_3C_6H_4$, H	24	<1
15	$(C_6H_5)_2CH$, H	24	>99 (98)
16	i-$PrCH_2$, H	24	>99 (99)
17	C_6H_5, CF_3	24	66 (61)
18	Me, CH_2CF_3[c]	24	16 (16)
19	4-$(SO_2Me)C_6H_4$, Me	6	>99 (97)
20	4-$(NO_2)C_6H_4$, Me	14	>99 (92)
21[d]	Me, Me[d]	24	>99 (98)
22[d]	Cyclohexanone[d]	24	>99 (99)
23[d]	Me, t-Bu[d]	24	>99 (79)
24	CH_2Ph, Et	6	>99 (95)
25[c]	CH_2Ph, Et[c]	6	>99 (95)
26	CH_2CH_2Ph, Me	1	>99 (96)
27	4-Heptanone	24	>99 (99)
28	2-Adamantanone	14	>99 (99)

[a] Conditions: 1.1 eq. Et_3SiH, 0.05 mmol aldehyde, 0.7 mL CH_2Cl_2, 5 mol% of **1**. [b] Conversion (based on substrate) monitored by ^{1}H NMR spectroscopy. [c] Reaction performed at 50 °C. [d] Reaction set up under ambient conditions on the benchtop, with dry solvent.

In the case of benzophenone, efforts to effect hydrosilylation using 1 equivalent of silane resulted in approximately 50% yield of diphenylmethane and bis(triethylsilyl)ether as observed by ^{1}H NMR spectroscopy (Table 4, entry 1). When two equivalents of silane were used, complete conversion to diphenylmethane was observed with 94% yield (entry 2). The same reduction in 66% yield is achieved when this reaction is performed on the benchtop (Table 4, entry 3). This observation was generalized to diaryl ketones (Table 4, entries 4–9), where the treatment with 2 equivalents of Et_3SiH and 5 mol% of **1**, led to the quantitative deoxygenation to the corresponding alkane. While several such reductions proceeded in 1.5 h, in some cases, 24 h was required. In the case of the electron rich diaryl ketones, (4-tBuC$_6$H$_4$)$_2$CO, and $(4\text{-}Me_2NC_6H_4)_2CO$ minimal and no reactions were observed, respectively (Table 4, entries 10 and 11). Similarly, the sterically encumbered ketone 2,4,6-i$Pr_3C_6H_4C(O)Me$ (Table 4, entry 12) and the electron-deficient ketone $(C_6F_5)_2CO$ (Table 4, entry 13) showed no reactivity. On the other hand, alkyl, aryl ketones were reduced (Table 4, entries 14–21). In the case of the diakyl ketone, 2-adamantanone quantitative reduction to adamantane (Table 4, entry 22) was achieved although heating to 120 °C was required.

The hydrosilylation of olefins was also probed using a catalytic amount of **1** (5 mol%). For example, addition of the gas-phase sample of isobutene to a solution of Et_3SiH and **1** prompted the

Table 4 Summary of the deoxygenation of ketones

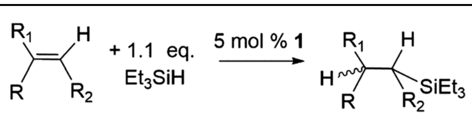


No.[a]	R, R[1]	T (h)	Conv.,[b] % (yield%)
1[c]	Ph, Ph	1.5	>99 (50)
2	Ph, Ph	1.5	>99 (94)
3[d]	Ph, Ph	24	66 (66)
4	4-ClC_6H_4, 4-ClC_6H_4	1.5	>99 (90)
5	2-ClC_6H_4, Ph	1.5	>99 (98)
6	4-BrC_6H_4, Ph	1.5	90 (90)
7	4-MeC_6H_4, 4-MeC_6H_4	24	>99 (97)
8	4-tBuC_6H_4, Ph	24	>99 (98)
9	2-MeC_6H_4, Ph	1.5	>99 (97)
10	4-tBuC_6H_4, 4-tBuC_6H_4	24	16 (16)
11	4-$Me_2NC_6H_4$, 4-$Me_2NC_6H_4$	24	<1
12	2,4,6-i$Pr_3C_6H_2$, Me	24	<1
13	C_6F_5, C_6F_5	24	<1
14	Dibenzocycloheptadienone	8	>99 (99)
15	Cy, Ph	1.5	>99 (97)
16	iPr, Ph	24	>99 (98)
17	4-$MeOC_6H_4$, Ph	24	60 (58)
18	tBu, Ph	24	>99 (91)
19	α-Tetralone	6	>99 (99)
20	4-$F_3CC_6H_4$, Ph	6	>99 (98)
21	Me, Ph	1.5	>99 (96)
22	2-Adamantanone[e]	13	>99 (94)

[a] Conditions: 2.1 eq. Et_3SiH, 0.05 mmol ketone, 0.7 mL CH_2Cl_2, 5 mol% of **1**. [b] Conversion (based on ketone) monitored by ^1H NMR spectroscopy. [c] 1 equiv. of silane. [d] Reaction set up under ambient conditions on the benchtop, with dry solvent. [e] 120 °C.

conversion to the corresponding alkyl silane, regioselectively, within one hour at room temperature as observed by ^1H NMR spectroscopy (Table 5, entry 1). Similarly, the silyl-derived olefins, $Ph_3SiCH_2CH{=}CH_2$ and $Ph_3SiCH(Me)CH{=}CH_2$ and the cyclic olefin cyclohexene were hydrosilylated after 24 h at 50 °C (Table 5, entries 2–4). The α-methylstyrene derivatives $(4\text{-}XC_6H_4)C(Me){=}CH_2$ (X = H, Me, Cl) were fully hydrosilylated regioselectively at room temperature in 24 h (Table 5, entries 5–7). In the case of $(4\text{-}FC_6H_4)C(Me){=}CH_2$, hydrosilylation was similarly effective although this required performance at 50 °C (Table 5, entry 8). Bulkier or trisubstituted olefins (*e.g.* 1-methylcyclopentene, triphenylethylene, and trans-α-methylstilbene; Fig. S108–S110, ESI†) showed no reactivity under these conditions. Similarly, both terminal and internal alkynes, (PhCCPh, PhCCH, and 4-CF_3PhCCH) were not hydrosilylated under the above conditions. It is also interesting that minimal hydrodefluorination[29] of 4-CF_3PhCCH (10%) was observed, suggesting that the presence of the alkyne fragment intervenes in C–F activation. Similarly, addition of PhCCH to a hydrosilylation reaction of α-methyl styrene inhibited the reduction completely. Further a mixture of **1** and PhCCPh (10 eq.) shows a small change in the chemical shift and sharpened lines in the $^{31}P\{^1H\}$ NMR spectrum at −50 °C inferring interaction of alkyne with **1**. This suggests alkyne binding to the Lewis acid, **1**, inhibits activation of the silane thus precluding catalysis.

Table 5 Summary of hydrosilylation of olefins[a]



No.	R, R[1], R[2]	T (h)	Conv.,[b] % (yield%)
1[c]	Me, Me, H	1	>99
2[d]	H Ph_3SiCH_2, H	24	>99
3[d]	Me, Me_3SiCH_2, H	24	>99
4[d]	Cyclohexene	24	>99 (99)
5	Ph, Me, H	24	>99 (96)
6	4-MeC_6H_4, Me, H	24	>99 (98)
7	4-ClC_6H_4, Me, H	24	>99 (95)
8[d]	4-FC_6H_4, Me, H	72	79 (73)

[a] Standard conditions: 1.1 eq. Et_3SiH, 0.05 mmol ketone, 0.7 mL CH_2Cl_2, 5 mol% of **1**, 24 h. [b] Conversion monitored by ^1H NMR spectroscopy. [c] Reagent added in the gas phase (1 atm). [d] Reaction performed at 50 °C.

The mechanism of these transformations was considered. We previously reported the use of **1** as a Lewis acid catalyst for hydrodefluorination and C–C coupling reactions. In these cases, we proposed that the activation of Si–H by the Lewis acid site on **1** was permitted by the hemilability of the terpy ligand, prompting C–F activation and hydride transfer. It is tempting to propose an analogous mechanism for the current hydrosilylations, which would mimic the Piers-type FLP hydrosilylation mechanism.[48]

An alternative that was also considered involved the possibility that **1** acts as an initiator, prompting silylium-based catalysis. This pathway would suggest that **1** abstracts hydride from silane. However, we note that **1** proved stable in the presence of silane with no evidence of hydride abstraction. Indeed, independent delivery of a hydride to **1** with Na[$HBEt_3$] led to degradation of **1** affording $PhPH_2$ as the predominant P-containing product as indicated by a triplet at −123 ppm in the ^{31}P NMR spectrum. Given that **1** was also spectroscopically observed post-catalysis, it is unlikely that **1** acts as an initiator. Moreover, the absence of hydrosilylation of alkyne or isomerization or polymerization of 1-hexene or isobutene, is inconsistent with silylium catalysis as such strong Lewis acids[16,49,50] effect these reactions. Collectively, these data support the proposition that **1** mediates the hydrosilylation catalysis.

In summary, we have shown that the air stable phosphorus(III) Lewis acid, [(terpy)PPh][$B(C_6F_5)_4$]$_2$ **1**, is an effective catalyst for the catalytic hydrosilylation reactions of aldehydes, ketones, and olefins. These reactions proceed with the expected regio-selectivity. The facile synthesis of **1** from commercially available materials together with its air stability makes it a readily accessible, easily manipulated catalyst for hydrosilylation. Ongoing efforts continue to probe further catalytic applications of this and related P(III) coordination compounds. The results of these studies will be reported in due course.

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Conflicts of interest

The authors declare no conflict of interest.

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