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Carbonyl and Olefin Hydrosilylation Mediated by an Air-Stable Phosphorus(III) Dication Under Mild Conditions

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Abstract. 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 is 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 BX₃ (X = H, F, Cl), BPh₃, and AlCl₃ 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 $[(C_6F_5)_3PF][B(C_6F_5)_4]$. 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 Freidel-Crafts arylation of fluoroalkanes,¹³⁻¹⁴ dehydrocoupling of silanes and amines;¹⁵ hydrosilylation of ketones, alkynes, and olefins;¹⁶ deoxygenation 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⁺ and [(bipy)PPh]²⁺ 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 ligand³¹⁻⁴⁴, 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 is considered.



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

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-d₃, 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 48h, 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.

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Table 1 Impact of solvent on hydrosilylation a



No.	Solvent ^a	т	Conv. ^b	No.	Solvent ^a	т	Conv.⁵
		(h)	(%)			(h)	(%)
1	CH_2CI_2	13	>99	6	o-C ₆ H ₄ Cl ₂	13	>99
2	Toluene	24	<1	7	$O-C_6H_4F_2$	13	>99
3	C ₆ H₅Cl	24	41	8	Et ₂ O	13	<1
4	THF℃	13	26	9	CD₃CN	24	<10
5	CDCl ₃	24	80	10	None ^d	13	>99

^astandard conditions: 25 °C, 1.1 eq. Et₃SiH, 0.05 mmol 4-methyl benzaldehyde, 0.7 mL solvent, 5 mol % of 1. ^bConversion monitored by ¹H NMR spectroscopy. ^cSome oligomerization observed after 13 hours. ^d5 eq. of Et₃SiH.

Table 1. Impact of silicon hydride on hydrosilylation.^a



No	Silicon-	Т	Conv.	No	No Silicon-Hydride ^a		Conv.
	Hydride ^a	(h)	(%) [⊾]			(h)	(%)⁵
1	Et₃SiH	24	>99	7	(C ₆ F₅)₃SiH ^c	24	<1
2	(<i>n</i> Hex)₃SiH	24	26	8	(EtO)₃SiH	24	<1
З	(Me₃Si)₃SiH	24	< 1	9	(Me₃SiO)₃SiH	24	<1
4	Ph₂MeSiH	24	59	10	Me ₃ SiOSiMe ₂ OSiMe ₂ H	0.5	>99
5	Ph₃SiH	24	<1	11	Me ₃ SiOSiMe ₂ OSiMe ₂ H ^d	24	75
6	Ph_2SiH_2	24	<1	12	(MeSiHO) _n (PMHS) ^c	24	23

^astandard conditions: 25 °C, 1.1 eq. Si-H, 0.05 mmol MeC₆H₄C(O)H, 0.7 mL CH₂Cl₂, 5 mol % of 1. ^bConversion monitored by ¹H NMR spectroscopy. ^cSilane exhibits poor solubility in the solvent ^dReaction set up under ambient conditions on the benchtop, with dry solvent.

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). Use of $(n-hex)_3SiH$ 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-assem aldehyde bly in solution.

A series of aldehydes were hydrosilylated using Et₃SiH and 5 mol% of **1** affording generally high yields (Table 3). Arylaldehydes were used that included both electron-withdrawing substituents groups (eg. NO₂, halides, entry 2-ride group in the *para*-position, led to reduced conversion (56%, 24 h) (Table 3, entries 1-12), while sterically demanding arenes (Table 3, entries 13, 14) led to a significant decrease in activity. In contrast, aliphatic aldehydes were readily reduced (Table 3, entries 15,16). This re8), or electron-donating groups (eg OMe, Table 3, entries 9-12). A fluoactivity was extended to ketones. While electron-withdrawing substituents (Table 3, entries 17, 20) gave modest yields of the hydrosily ated products, as off 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, 23) was attributed to the hydrolysis of the silylether.

Table 2. Summary of the hydrosilylation of aldehydes and ketones. ^a							
	$R \xrightarrow{O} + 1.1 \text{ eq.} \xrightarrow{5 \text{ mol } \% 1} R \xrightarrow{O} \xrightarrow{\text{SiEt}_3} R \xrightarrow{F} R$						
	No ^a	R, R ¹	T (h)	Conv. ^b % (Yield %)			
	1	Ph, H	24	>99 (93)			
	2	4-(NO ₂)C ₆ H ₄ , H	24	>99 (99)			
	3	4-BrC ₆ H ₄ , H	24	>99 (84)			
	4	4-CIC ₆ H ₄ , H	24	>99 (33)			
	5	2-CIC ₆ H ₄ , H	24	>99 (87)			
	6	2-BrC ₆ H ₄ , H	24	>99 (50)			
	7	4-FC ₆ H ₄ , H	24	56 (56)			
	8	3,4-Cl ₂ C ₆ H ₃	1	99 (95)			
	9	4-MeC ₆ H ₄ , H	24	>99 (96)			
	10	3-(MeO)C ₆ H ₄ , H	24	>99 (97)			
	11		24	>00 (>00)			

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2	4-(NO ₂)C ₆ H ₄ , H	24	>99 (99)
3	4-BrC ₆ H ₄ , H	24	>99 (84)
4	4-CIC ₆ H ₄ , H	24	>99 (33)
5	2-CIC ₆ H ₄ , H	24	>99 (87)
6	2-BrC ₆ H ₄ , H	24	>99 (50)
7	4-FC ₆ H ₄ , H	24	56 (56)
8	3,4-Cl ₂ C ₆ H ₃	1	99 (95)
9	4-MeC ₆ H ₄ , H	24	>99 (96)
10	3-(MeO)C ₆ H ₄ , H	24	>99 (97)
11	3,5-(MeO) ₂ C ₆ H ₃ , H	24	>99 (>99)
12 ^c	4-(C(O)H)C ₆ H ₄ , H	24	94 (94)
13	2-MeC ₆ H ₄ , H	24	25 (24)
14	2,4,6-Me ₃ C ₆ H ₄ , H	24	<1
15	(C ₆ H ₅)₂CH, H	24	>99 (98)
16	<i>i</i> -PrCH₂, H	24	>99 (99)
17	C_6H_{5} , CF_3	24	66 (61)
18	Me, CH ₂ CF ₃ ^c	24	16 (16)
19	4-(SO ₂ Me)C ₆ H ₄ , Me	6	>99 (97)
20	4-(NO ₂)C ₆ H 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	CH₂Ph, Et	6	>99 (95)
25°	CH₂Ph, Et c	6	>99 (95)
26	CH ₂ CH ₂ Ph, Me	1	>99 (96)
27	4-heptanone	24	>99 (99)
28	2-adamantanone	14	>99 (99)

^aconditions: 1.1 eq. Et₃SiH, 0.05 mmol aldehyde, 0.7 mL CH₂Cl₂, 5 mol % of 1. ^bConversion (based on substrate) monitored by ¹H NMR spectroscopy. ^cReaction performed at 50°C. ^dReaction 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 an approximately 50% yield of diphenylmethane and bis(triethylsilyl)ether as observed by ¹H 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 Et₃SiH 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 Journal Name

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electron rich diaryl ketones, $(tBuC_6H_4)_2CO$, and $(Me_2NC_6H_4)_2CO$ minimal and no reactions were observed (Table 4, entries 10, 11). Similarly, the sterically encumbered ketone *i*Pr₃C₆H₄C(O)Me (Table 4, entry 12) and the electron-deficient ketone (C₆F₅)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, 2adamantanone quantitative reduction to adamantane (Table 4, entry 22) was achieved although heating to 120° C was required.

Table 4. Summary of the deoxygenation of ketones.

O	+ 2.2 eq.	5 mol % 1	\sim
	Et ₃ SiH		R´ `R'
	5	-(Et ₃ SI) ₂ O	

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-CIC ₆ H ₄ , 4-CIC ₆ H ₄	1.5	>99 (90)
5	2-ClC ₆ H ₄ , Ph	1.5	>99 (98)
6	4-BrC ₆ H ₄ , Ph	1.5	90 (90)
7	4-MeC ₆ H ₄ , 4-MeC ₆ H ₄	24	>99 (97)
8	4-tBuC ₆ H ₄ , Ph	24	>99 (98)
9	2-MeC ₆ H ₄ , Ph	1.5	>99 (97)
10	4-tBuC ₆ H ₄ , 4-tBuC ₆ H ₄	24	16 (16)
11	4-Me ₂ NC ₆ H ₄ , 4-Me ₂ NC ₆ H ₄	24	<1
12	2,4,6- <i>i</i> Pr ₃ C ₆ H ₄ , Me	24	<1
13	C ₆ F ₅ , C ₆ F ₅	24	<1
14	Dibenzocycloheptadienone	8	>99 (99)
15	Cy, Ph	1.5	>99 (97)
16	iPr, Ph	24	>99 (98)
17	4-MeOC ₆ H ₄ , Ph	24	60 (58)
18	tBu, Ph	24	>99 (91)
19	α-tetralone	6	>99 (99)
20	4-F ₃ CC ₆ H ₄ , Ph	6	>99 (98)
21	Me, Ph	1.5	>99 (96)
22	2-adamantanone ^e	13	>99 (94)

^aconditions: 2.1 eq. Et₃SiH, 0.05 mmol ketone, 0.7 mL CH₂Cl₂, 5 mol % of 1; ^bConversion (based on ketone) monitored by ¹H NMR spectroscopy; ^c1 equiv. of silane, ^dReaction set up under ambient conditions on the benchtop, with dry solvent. ^e120 °C.

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 Et₃SiH and 1 prompted the conversion to the corresponding alkyl silane within one hour at room temperature as observed by ¹H NMR spectroscopy (Table 5, Entry 1). Similarly, the silyl-derived olefins, Ph₃SiCH₂CH=CH₂ and Ph₃SiCH(Me)CH=CH₂ and the cyclic olefin cyclohexene were hydrosilylated after 24 h at 50 °C (Table 5, Entry 2-4). The aromatic derived olefins $(4-XC_6H_4)C(Me)=CH_2$ (X = H, Me, Cl) were fully hydrosilylated at room temperature in 24 h (Table 5, Entries 5-7). In the case of $(4-FC_6H_4)C(Me)=CH_2$, hydrosilylation was similarly effective although this required performance at 50 °C (Table 5 ,Entry 8). Bulkier or trisubstituted olefins (eg 1methylcyclopentene, triphenylethylene, and trans-αmethylstilbene; Figures S108-S110) showed no reactivity under these conditions. Similarly, both terminal and internal alkynes,

(PhCCPh, PhCCH, and 4-CF₃PhCCH) were not hydrosilvlated under the above conditions. It is also interesting that minimal hydrodefluorination²⁹ of 4-CF₃PhCCH (10%) was observed, suggesting that the presence of the alkyne fragment intervenes in C-F activation. Similarly, addition of PhCCH to a hydrosilvlation reaction of α -methyl styrene inhibited the reduction completely. Further a mixture of **1** and PhCCPh (10 eqv) shows a small change in the chemical shift and sharpened lines in the ³¹P{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. Hydrosilylation of olefins^a



No.	R, R ¹ , R ²	T (h)	Conv. ^b % (Yield %)
51 ^c	Me, Me, H	1	>99
52 ^d	H Ph ₃ SiCH ₂ , H	24	>99
53 ^d	Me, Me ₃ SiCH ₂ , H	24	>99
54 ^d	Cyclohexene	24	>99 (99)
55	Ph, Me, H	24	>99(96)
56	4-MeC ₆ H ₄ , Me, H	24	>99 (98)
57	4-ClC ₆ H ₄ , Me, H	24	>99 (95)
58 ^d	4-FC ₆ H ₄ , Me, H	72	79 (73)

^astandard conditions: 1.1 eq. Et₃SiH, 0.05 mmol ketone, 0.7 mL CH₂Cl₂, 5 mol % of 1, 24 h. ^bConversion monitored by ¹H NMR spectroscopy; ^cReagent added in the gas phase (1 atm); ^dReaction 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[HBEt₃] led to degradation of **1** affording PhPH₂ as the predominant P-containing product as indicated by a triplet at -123 ppm in the ³¹P 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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Conflict of Interest

The authors declare no conflict of interest.

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