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Catalytic Ketone Hydrodeoxygenation Mediated by Highly Electrophilic Phosphonium Cations**

Meera Mehta, Michael H. Holthausen, Ian Mallov, Manuel Pérez, Zheng-Wang Qu, Stefan Grimme, and Douglas W. Stephan**

***Abstract:** Ketones are efficiently deoxygenated in the presence of silane using highly electrophilic phosphonium cation (EPC) salts as catalysts, thus affording the corresponding alkane and siloxane. The influence of distinct substitution patterns on the catalytic effectiveness of several EPCs was evaluated. The deoxygenation mechanism was probed by DFT methods.*

Lewis acids are an important class of reagents in synthetic chemistry and mediate a wide variety of stoichiometric and catalytic transformations.[1] Indeed, such compounds find applications across a broad cross-section of the chemical community. Quintessential examples of Lewis acids, such as the classically simple group XIII compounds BH_3, BF_3, and $AlMe_3$, possess a vacant acceptor p orbital. More recently, electron-withdrawing groups, such as perfluorinated arenes in boranes, have been installed to increase Lewis acidity, thus facilitating Lewis acid catalysis and frustrated Lewis pair (FLP) reactivity.[2] Strong Lewis acids based on group XIV cations, such as $[Ph_3C]^+$ or $[R_3Si]^+$,[3] were mainly used stoichiometrically, as their high reactivity often hampers application in catalysis. In contrast, group XV cations are generally more chemically robust and the tendency of, for example, P^V phosphonium cations $[R_4P]^+$ to form neutral phosphoranes R_4PX, is evidence for certain Lewis acidity. This property has been exploited in the development of fluoride ion sensors[4] as well as catalysts for (cyclo)addition reactions to polar or activated unsaturated substrates.[5] More recently, we have focused on enhancing this Lewis acidity by preparing more electrophilic phosphonium cations (EPCs) such as $[(C_6F_5)_3PF]^+$ (**1**), $[(C_6F_5)_2PhPF]^+$ (**2**), and $[(C_6F_5)Ph_2PF]^+$ (**3**). We have demonstrated that the low-lying antibonding orbital[6] permits these species to act as highly effective catalysts for the hydrodefluorination of fluoroalkanes,[6] hydrosilylation of olefins, ketones, and alkynes,[7] and the dehydrocoupling of amines, acids, and thiols with silanes.[8] In the latter case, tandem transfer hydrogenation can also be effective with concurrent dehydrocoupling reactions.[8] The scope of these EPCs has been broadened to include dicationic phosphonium species $[(SIMes)PPh_2F]^{2+}$ (**5**)[9] and bifunctional bis(phosphonium) compounds.[10] The additional charge is manifested in even greater Lewis acidity.

Hydrodeoxygenation of ketones has garnered increasing attention given its many applications in biofuels and fine-chemical syntheses.[11] Classic protocols for deoxygenation include the Barton–McCombie (R_3SnH),[12] Clemmensen (Zn/Hg, HCl),[13] or Wolff–Kishner reductions (H_4N_2, KOH),[14] and these methods generally require harsh reaction conditions, use stoichiometric amounts of toxic reagents, and show poor functional-group tolerance. Heterogeneous catalysis employing, for example, PtO_2[15] and Ni/Al_2O_3[16] and H_2 as the reducing agent is known, while a recent report has described the use of Pd/C[17] with polymethylhydrosiloxane (PMHS) for the reduction of aromatic ketones.

Herein, we probe the ability of a range of EPCs (**1**–**9**; Figure 1) to effect ketone reduction. In the presence of silane, the P^V Lewis acids **1**–**3** and **5**–**8** are shown to be effective catalysts for the deoxygenation of ketones under mild reaction conditions, thus affording the corresponding alkane and siloxane.

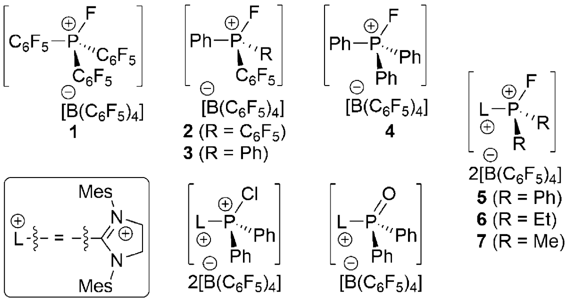

Figure 1. The electrophilic phosphonium cations **1**–**9**.

In our initial efforts, reactions of dialkyl- and diarylketones, 2-methylpentanone (**10a**) and benzophenone (**11a**), respectively, and Et_3SiH were performed in the presence of a catalytic amount of one of the Lewis acidic EPCs (**1**–**9**; Figure 1). By using 1.0 mol% of **1**[6] and 2.1 equivalents of Et_3SiH in CD_2Cl_2, quantitative deoxygenation of both sub-

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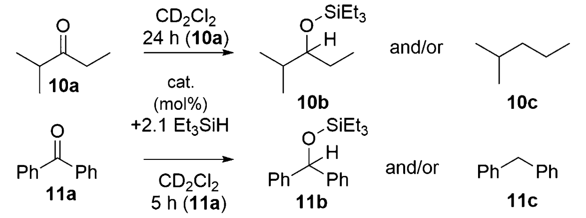
strates was observed, thus yielding the corresponding $Me_2CHCH_2CH_2CH_3$ (**10c**) and Ph_2CH_2 (**11c**, Table 1). The reduction of **10a** required heating to 50 °C for 24 hours, whereas **11a** was reduced after five hours at room temperature. The corresponding reaction using **10a** and Et_3SiH in a 1:1 ratio gave selective formation of the hydrosilylated intermediate $Me_2CHCH(OSiEt_3)CH_2CH_3$ (**10b**), whereas a 1:1 ratio of **11a** and Et_3SiH gave 50 % conversion to **11c** with 50 % of unreacted **11a**.

Table 1: Deoxygenation/hydrosilylation of the alkyl- and aryl-substituted ketones **10a** and **11a**, respectively.



Catalyst (mol %)[a]	**10a** T [°C]	**10a** Conv. [%][b]	**11a** T [°C]	**11a** Conv. [%][b]
$B(C_6F_5)_3$ (1.0)	RT	> 99 (**10b**)	RT	> 99 (**11b**)
$B(C_6F_5)_3$ (5.0)	50	> 99 (**10b**)	50	91/9 (**11b**/**11c**)
$B(C_6F_5)_3$ (10)	50	> 99 (**10b**)	50	80/20 (**11b**/**11c**)
1 (1.0)	50	> 99 (**10c**)	RT	> 99 (**11c**)
2 (1.0)	50	> 99 (**10c**)	RT	> 99 (**11c**)
3 (1.0)	50	> 99 (**10b**)	50	15 (**11b**)/85 (**11c**)
4 (1.0)	50	0	RT	0
5 (1.0)	50	> 99 (**10c**)	RT	> 99 (**11c**)
6 (1.0)	50	> 99 (**10c**)	RT	> 99 (**11c**)
7 (1.0)	50	> 99 (**10c**)	RT	> 99 (**11c**)
8 (1.0)	50	> 99 (**10c**)	RT	> 99 (**11c**)
9 (1.0)	50	0	RT	0

[a] Et_3SiH (2.1 equiv) was added to a solution of the catalyst (1 mol %) in CD_2Cl_2 and then the substrate (1.0 equiv) was added. [b] Determined by ^1H NMR spectroscopy.

We note that hydrosilylation of ketones has been previously reported using the Lewis acid catalyst $B(C_6F_5)_3$.[18] For comparative purposes, the substrates were treated with silane in the presence of the catalyst $B(C_6F_5)_3$ (Table 1). Quantitative hydrosilylation of **10a**, thus yielding exclusively **10b**, was observed. In the case of **11a**, 1.0 mol % of $B(C_6F_5)_3$ effected hydrosilylation of **11a**, while 5 mol % $B(C_6F_5)_3$ gave a 91:9 mixture of **11b** and **11c**, and 10 mol % $B(C_6F_5)_3$ gave an 80:20 mixture of **11b** and **11c**. The data demonstrate that with $B(C_6F_5)_3$ as the catalyst, significantly increased catalyst loading gave poor yields of the deoxygenated product **11c** compared to EPCs. The impact of reduced Lewis acidity of the EPC was also probed. Whereas **2**[6] effects complete deoxygenation of **10a** and **11a**, the catalyst **3**[19] effects only the hydrosilylation of substrate **10a** to **10b**. Nonetheless, **3** does catalyze the reduction of **11a**, thus affording **11c** in 85 % yield. Further reduction of the Lewis acidity, for example in the phosphonium ion $[Ph_3PF]^+$ (**4**),[10,20] eliminated catalytic activity completely and neither hydrosilylation nor deoxygenation was observed. The previously reported dicationic phosphonium ion **5**[9] is an effective catalyst for the deoxygenation of **10a** and **11a** in the presence of two equivalents of silane, thus affording quantitative formation of **10c** and **11c**, respectively.

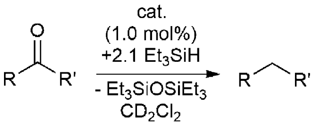
The alkyl-substituted dicationic analogues $[(SIMes)Et_2PF]^{2+}$ (**6**) and $[(SIMes)Me_2PF]^{2+}$ (**7**) were prepared in a fashion analogous to **5**. To this end, the chlorophosphines R_2PCl (R = Et, Me) were reacted with 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidine (SIMes) in the presence of $[Et_3Si][B(C_6F_5)_4]\cdot 2(C_7H_8)$,[21] thus yielding the phosphenium cation $[(SIMes)R_2P][B(C_6F_5)_4]$. Subsequent oxidation by XeF_2, followed by fluoride abstraction gave **6** and **7** in good overall yields.

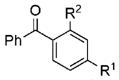
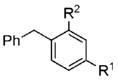
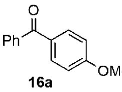
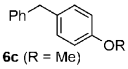
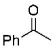
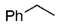
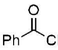
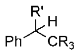
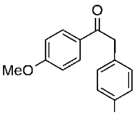
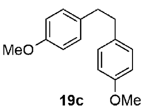
The compounds **6** and **7** also proved to be effective catalysts for **10a** and **11a**, thus yielding the corresponding products **10c** and **11c** quantitatively (Table 1). In a similar vein, oxidation of $[(SIMes)Ph_2P][B(C_6F_5)_4]$ with SO_2Cl_2 and subsequent chloride abstraction afforded the salt $[(SIMes)Ph_2PCl][B(C_6F_5)_4]_2$ (**8**), which also proved to be effective for the deoxygenation of **10a** and **11a**. It is important to point out that while the monocationic species $[(SIMes)Ph_2PO][B(C_6F_5)_4]$ (**9**) is ultimately observed as a catalyst degradation product, independent synthesis confirmed it is completely ineffective as a catalyst. In addition, several commercially available silanes were screened for the hydrodeoxygenation of **11a** (see the Supporting Information), and Et_3SiH was selected as the hydride source for the catalysis described herein.

These results establish that EPCs are highly effective catalysts for deoxygenation of ketones. To probe the generality of this observation, the EPCs **1** and **5** were used as catalysts for the deoxygenation of a series of ketones (Tables 2 and 3). *Para*-fluoro-substituted benzophenone (**12a**), as well as *para*-bromo- (**13a**), *ortho*-chloro- (**14a**), and *ortho*-methyl-substituted derivatives (**15a**) were converted in high yields into the respective deoxygenated products **12c**–**15c** by both catalysts within five hours at ambient temperature. The *para*-methoxy-substituted benzophenone (**16a**) is selectively deoxygenated in the presence of 2.1 equivalents of Et_3SiH, thus yielding the compound **16c**. By using longer reaction times and 3.2 equivalents of silane, the reduction proceeds further with methoxy ether cleavage, thus affording $PhCH_2(C_6H_4OSiEt_3)$ (**16d**). Acetophenone (**17a**) is quantitatively reduced to ethyl benzene (**17c**), while the deactivated α-CF_3-acetophenone derivative **18a** is selectively hydrosilylated by either **1** and **5** with Et_3SiH in a 1:1 stoichiometry to give the silyl ether **18b** in high yield. Interestingly, increasing the catalyst loading to 5.0 mol % and the use of seven equivalents of Et_3SiH effects hydrodefluorination,[2,5] thus yielding ethyl benzene. Finally, the ketone **19a** is quantitatively converted into **19c** with 2.1 equivalents Et_3SiH. It is interesting to note that for ketones **11a**–**17a** and **19a**, reactions with Et_3SiH in a 1:1 stoichiometry gave 1:1 mixtures of the starting material and the corresponding deoxygenation products **11c**–**17c** and **19c**. The respective hydrosilylated intermediates were not observed.

In contrast to aryl-substituted ketones, the dialkyl ketones **20a**–**27a** are selectively hydrosilylated to give **20b**–**27b** at room temperature after one hour in the presence of either **1** or **5** as the catalyst (Table 3). Longer reaction times (24 h) and heating of the reaction mixtures to 50 °C results in

Table 2: Catalytic deoxygenation of alkyl- and aryl-substituted ketones.



Substrate	Cat.	T [°C]	t [h]	Conv. [%][a]	Product
 **12a** (R^1 = F, R^2 = H) **13a** (R^1 = Br, R^2 = H) **14a** (R^1 = H, R^2 = Cl) **15a** (R^1 = H, R^2 = CH_3)	1	RT	5	84 (**12c**)	 **12c** (R^1 = F, R^2 = H) **13c** (R^1 = Br, R^2 = H) **14c** (R^1 = H, R^2 = Cl) **15c** (R^1 = H, R^2 = CH_3)
	5	RT	5	89 (**12c**)	
	1	RT	5	>99 (**13c**)	
	5	RT	5	>99 (**13c**)	
	1	RT	5	>99 (**14c**)	
	5	RT	5	>99 (**14c**)	
	1	RT	5	>99 (**15c**)	
	5	RT	5	88 (**15c**)	
 **16a**	1	RT	5	71 (**16c**)	 **16c** (R = Me) **16d** (R = SiEt$_3$)
	5	RT	5	>99 (73; **16c**)	
	5	RT	12	>99 (60; **16d**)[b]	
 **17a**	1	RT	5	>99 (**17c**)	 **17c**
	5	RT	5	>99 (**17c**)	
 **18a**	1	RT	5	76 (**17c**)[c]	 **18b** (R/R' = F/OSiEt$_3$) **17c** (R/R' = H)[c]
	5	RT	5	>99 (74; **18b**)	
	5	RT	5	81 (**17c**)[c]	
 **19a**	1	RT	5	>99 (**19c**)	 **19c**
	5	RT	5	>99 (35; **19c**)	

Reaction conditions: Et$_3$SiH (2.1 equiv) was added to a solution of the catalyst (1 mol%) in CD$_2$Cl$_2$ and then the substrate (1.0 equiv) was added. [a] Determined by ^{1}H NMR spectroscopy. Yields of the isolated product are given within parentheses. [b] 3.2 equiv of Et$_3$SiH were used. [c] 7 equiv of Et$_3$SiH and 5.0 mol% catalyst loading were used.

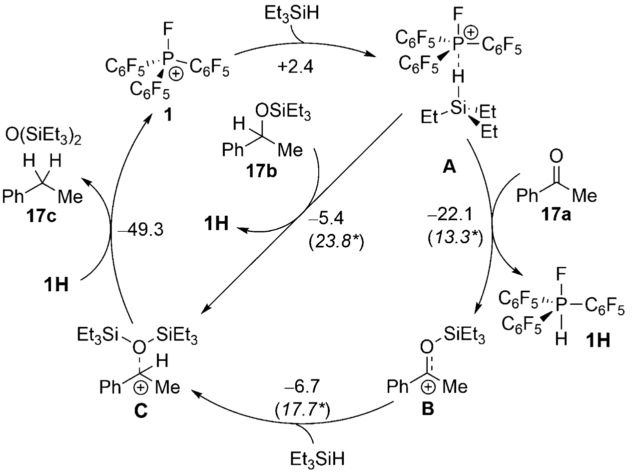


Figure 2. Possible mechanisms for deoxygenation of ketones. The EPC **1** was considered as the catalyst and the $[B(C_6F_5)_4]^-$ anions are not depicted. The level of theory used was B2PLYP-D3/def2-QZVP (in CH$_2$Cl$_2$) and the values reported are reaction Gibbs free energies in kcal mol^{-1}. Barriers are indicated by an asterisk.

quantitative deoxygenation. Ketones featuring one methyl substituent (**20a**–**23a**) were reduced to the corresponding **20c**–**23c**. The presence of a chloro substituent on the α-carbon atom, as in **24a**, deactivates the carbonyl function and only allows hydrosilylation to yield **24b**, even upon heating for a longer reaction time. After 24 hours, instead of deoxygenation, formal elimination of Et$_3$SiOH occurs for substrates **25a** and **26a**, thus yielding the alkenes **25c** and **26c**, respectively. For dicyclohexylketone (**27a**) both the deoxygenated product **27c** and the elimination product **27d** were observed.

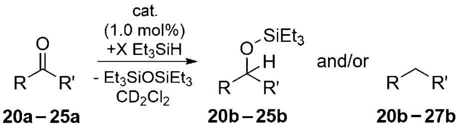
As mentioned above, the hydrosilylation of alkenes, alkynes,[7] imines, ketones, and nitriles catalyzed by **1** has been previously reported[6–8] and computational and experimental data supported a mechanism involving interaction of the EPC with the silane (Figure 2; **A**). This hydrosilylation is mechanistically analogous to the long-established $B(C_6F_5)_3$-mediated hydrosilylation of carbonyl compounds established by the groups of Piers[18,22] and Oestreich.[23] We now have probed the mechanism of the deoxygenation reactions by DFT calculations[24,25] (Figure 2) employing the B2PLYP-D3/def2-QZVP level of theory and using acetophenone and Et$_3$SiH in the presence of the cation **1**. Two pathways for deoxygenation were considered. One possible mechanism involves the S$_N$2-like nucleophilic attack by the silyl ether oxygen in **17b** at the Si center of **A**. This reaction generates $(C_6F_5)_3PFH$ (**1H**) and $[(Et_3Si)_2OCHPhMe]^+$ (**C**), and is exergonic by 5.4 kcal mol^{-1} with a free energy barrier of 23.8 kcal mol^{-1}. Subsequent hydride delivery from **1H** prompts elimination of $(Et_3Si)_2O$ thus giving **17c** and regenerating **1**.

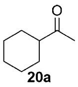
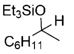
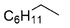
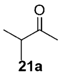
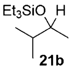
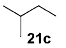
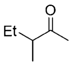
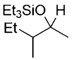
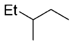
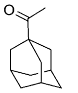
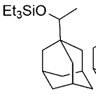
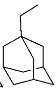
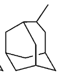
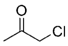
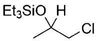
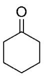
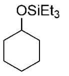
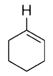
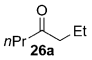
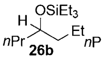
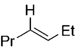
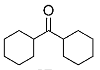
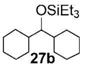
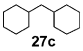
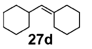
An alternative pathway involves reaction of the transiently generated $[(Et_3Si)OCPhMe]^+$ (**B**) with the silane to generate **C**, which again abstracts hydride from **1H** to yield the product alkane, siloxane, and **1** (Figure 2). Calculations predict the transformation of **B** into **C** is exergonic by 6.7 kcal mol^{-1} with an activation barrier of 17.7 kcal mol^{-1}. From these computations, the latter pathway is energetically favorable, however, it may well be that variations in the substrate, catalyst or silane could reverse the energetic preference and thus either reaction mechanism may be operative.

It is noteworthy that in closely related chemistry, $B(C_6F_5)_3$ has been shown to catalyze the deoxygenation of unsaturated cyclic ethers and silyl ethers,[23] thus affording allylic and homoallylic alcohols[26] and siloxanes, respectively.[27] In addition $B(C_6F_5)_3$ has also been used to dehydrocouple silanes with alcohols[28] to give silylethers.

In summary, EPCs act as catalysts for the hydrosilylation and deoxygenation of a broad range of aryl and alkyl ketones, thus affording silyl ethers and alkanes. This reactivity further affirms that EPCs are more reactive Lewis acid catalysts than $B(C_6F_5)_3$ and broadens the range of applications of these metal-free phosphorus-based Lewis acid catalysts. Ongoing efforts are targeting synthetic applications of this deoxygenation chemistry, as well as further exploration of the rich chemistry of EPC derivatives.

Table 3: Catalytic hydrosilylation/deoxygenation of alkyl-substituted ketones.



Substrate	Cat.	Equiv	T [°C]	t [h]	Conv. [%][a]	Product(s)
 **20a**	**1**	3.1	RT	1	> 99 (84; **20b**)	 **20b**  **20c**
	1	3.1	50	24	96 (**20c**)	
	5	3.1	50	24	> 99 (**20c**)	
 **21a**	**1**	3.1	50	24	91 (**21c**)	 **21b**  **21c**
	5	3.1	RT	1	> 99 (**21b**)	
	5	3.1	RT	24	> 99 (**21c**)	
 **22a**	**1**	3.1	RT	1	> 99 (77; **22b**)	 **22b**  **22c**
	1	3.1	RT	24	96 (**22c**)	
	5	3.1	50	1	> 99 (**22c**)	
 **23a**	**1**	3.1	50	24	20/80 (**23c/23d**)	 **23b**  **23c**  **23d** **23b**
	5	3.1	RT	1	> 99 (72; **23b**)	
	5	3.1	50	24	10/90 (**23c/23d**)	
 **24a**	**1**	3.1	50	24	> 99 (**24b**)	 **24b**
	5	3.1	RT	24	> 99 (**24b**)	
 **25a**	**1**	2.1	RT	24	76/20 (**25b/25c**)	 **25b**  **25c**
	5	2.1	RT	1	> 99 (84; **25b**)	
	5	2.1	RT	24	78/16 (**25b/25c**)	
 **26a**	**1**	1.1	RT	24	> 99 (83; **26b**)	 **26b**  **26c**
	1	3.1	RT	1	43/57 (**26b/26c**)	
	5	3.1	RT	1	95/5 (**26b/26c**)	
 **27a**	**1**	3.1	50	24	81/19 (**27c/27d**)	 **27b**  **27c**  **27d**
	5	3.1	RT	1	89/11 (**27b/27d**)	
	5	3.1	50	24	72/28 (**27c/27d**)	

Reaction conditions: Et_3SiH (1.1 to 3.1 equiv) was added to a solution of the catalyst (1.0 mol%) in CD_2Cl_2 and then the substrate (1.0 equiv) was added. [a] Determined by ^1H NMR spectroscopy. Yields of isolated products are given within parentheses.

Keywords: density functional calculations · hydrosilylation · Lewis acids · phosphorus · synthetic methods

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TZVP + COSMO(CH_2Cl_2) computed geometries and thermal corrections and more reliable COSMO-RS(CH_2Cl_2) solvation free energies. For more information, please see the Supporting Information.

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