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Catalytic reductive deoxygenation of esters to ethers driven by a hydrosilane activation through non-covalent interactions with a fluorinated borate salt

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Abstract: We report a catalytic and transition metal-free reductive deoxygenation of esters to ethers through the use of a hydrosilane and a fluorinated borate BARF salt as catalyst. Experimental and theoretical studies support the role of noncovalent interactions between the fluorinated catalyst, the hydrosilane and the ester substrate in the reaction mechanism.

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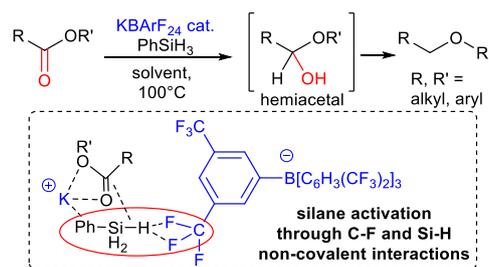
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Electronic Supplementary Information (ESI) available on the web (free of charges).

Introduction

Ethers are ubiquitous in natural products, building blocks or targets for fine chemicals, farming-related chemicals and biologically active compounds.¹ The synthesis of ethers can be achieved following different synthetic routes. Among the stoichiometric methods are the Williamson ether synthesis² and the related alkylation of alcohols³ as well as the direct and stoichiometric reduction of esters.⁴ Regarding catalysed reactions, ethers are prepared by condensation of alcohols,⁵ reductive etherification of aldehydes or ketones with alcohols,^{6,7} direct reduction of carboxylic acid derivatives through hydrogenation⁸ or hydrosilylation.^{9,10} In addition, aromatic ethers are frequently prepared using Buchwald-Hartwig cross-coupling reactions.¹¹ Along the past years, the reductive etherification of carbonyl compounds using hydrogen or a hydrosilane has received more attention applying catalysts based on metals, Brønsted acids or frustrated Lewis pairs (FLP). This bimolecular reaction can lead to symmetric ethers by the reductive coupling of two carbonyl compounds⁶ or to unsymmetric ethers by the reaction of carbonyl compounds with alcohols in the presence of a reducing agent.⁷ By comparison, the reductive deoxygenation of esters is a more direct, straightforward and unimolecular synthetic route to alkyl and aryl-ethers (Scheme 1). This reaction has been developed either using hydrogen and Ru based catalysts,⁸ or combining a hydrosilane with several transition metal⁹ or metal based catalysts.¹⁰ Though catalysed reductions using frustrated Lewis pairs, main-group Lewis acids¹² or Lewis bases¹³ have attracted a great attention, none of these transition metal-free approaches have been applied to the reductive deoxygenation of esters yet.¹⁴ Along our studies of the hydrosilylation reaction using Ir(III) chloride metallacycles¹⁵ or Co(II) salts,^{15h} we noticed the hydrosilylation of esters could lead to variable amounts of ethers depending on the substrate or the nature of the dehalogenation agent such as BARF salts.^{15d,e} While seeking for the origin of these ethers, we have found a new catalytic and selective reduction route of esters to ethers (Scheme 1). This hydrosilylation reaction implies the use of a fluorinated borate BARF salt, i.e. potassium tetrakis[(3,5-trifluoromethyl)phenyl]borate, as catalyst and of phenylsilane reagent. By comparison to the known silane activation modes operating through oxidative addition, metal-ligand cooperation, metal-substrate double activation and heterolytic polar electrophilic activation¹⁶ or through the use of frustrated Lewis pairs,^{12,14,17} our catalytic reaction relies on a silane activation through C-F...H-Si non-covalent interactions between the C-F and Si-H bonds of the fluorinated borate catalyst and the silane.



Scheme 1 Catalysed reductive deoxygenation of esters and lactones through non-covalent interactions.

Results and discussion

The screening of catalysts and reaction conditions was performed on the reductive deoxygenation of ester **1a** (Tables 1, S1, S2 and S3). At 100 °C, in TCE (1,1',2,2'-tetrachloroethane) and in the presence of 2 equivalents of phenylsilane, ether **2a** was formed in a quantitative yield while using 5 or 2 mol% of potassium tetrakis[(3,5-trifluoromethyl)phenyl]borate under water-free conditions (Table 1, entries 1-2). A decrease of the catalyst loading to 1 mol% or of the reaction time to 6 hours led to lower yields of **2a** (entries 3-4). While the use of 5 mol% of sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate resulted in a reduced yield of **2a** (entry 5), a catalyst change to trityltetra(pentafluorophenyl)borate $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ or *N,N*-dimethylanilinium tetra(pentafluorophenyl)borate $\text{Me}_2\text{PhHNB}(\text{C}_6\text{F}_5)_4$ did not allow the reductive deoxygenation of **1a** (Table 1, entries 6-7, Table S1). Though the Lewis acid tris(pentafluorophenyl)borate $\text{B}(\text{C}_6\text{F}_5)_3$ was previously reported as an effective catalyst for the deoxygenation of alcohols, ethers and carbonyl compounds,¹² no catalytic activity was noticed herein (entry 8).

Table 1 Development of the catalytic reaction.

Entry	Catalyst	Time (h)	Yield (%) ^[a]
1	KBArF_{24} (5) ^[b]	15	>99
2	KBArF_{24} (2) ^[b]	15	>99
3	KBArF_{24} (1) ^[b]	15	78
4	KBArF_{24} (5) ^[b]	6	95
5	NaBArF_{24} (5) ^[b]	15	95
6	$\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (5) ^[c]	15	0
7	$(\text{CH}_3)_2\text{NHPhB}(\text{C}_6\text{F}_5)_4$ (5) ^[d]	15	0
8	$\text{B}(\text{C}_6\text{F}_5)_3$ (5) ^[e]	15	0
9	$\text{NaB}(\text{Ph})_4$ (5)	15	0
10	none	15	0 ^[f]
11	KBArF_{24} (2) + 18-Crown-6 (4)	15	0

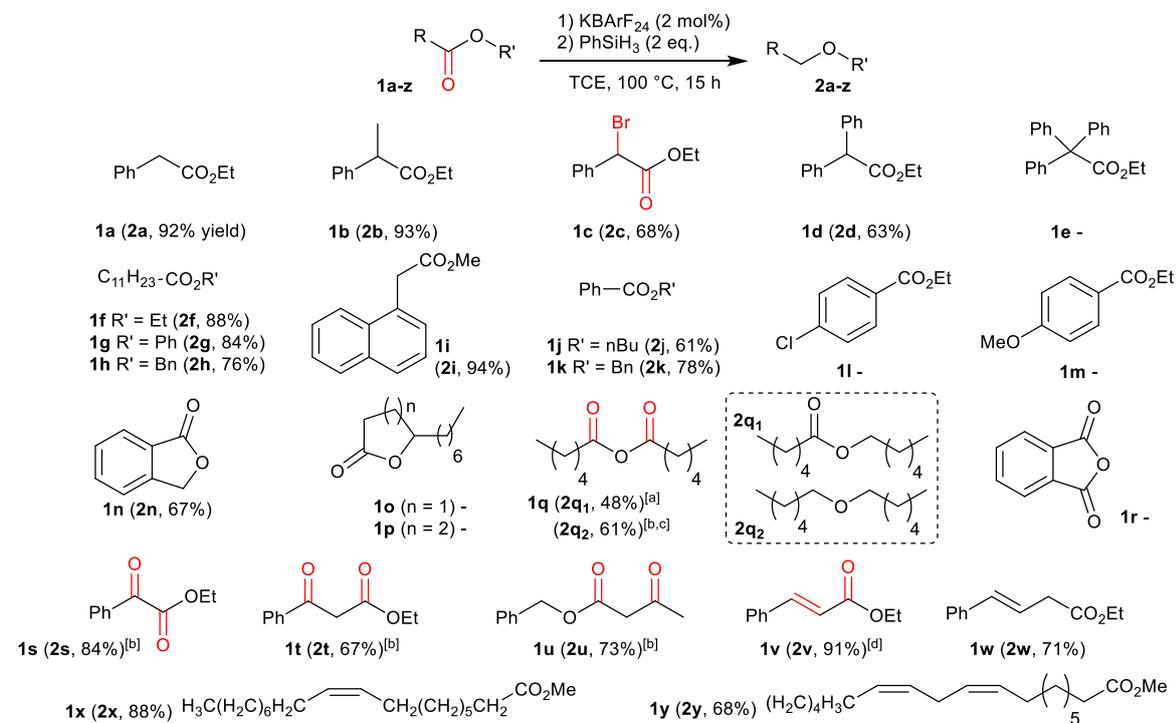
[a] Determined by GC. [b] BArF_{24} : tetrakis[(3,5-trifluoromethyl)phenyl]borate.

[c] $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$: trityl tetra(pentafluorophenyl)borate.

[d] $(\text{CH}_3)_2\text{NHPhB}(\text{C}_6\text{F}_5)_4$: *N,N*-Dimethylaniliniumtetra(pentafluorophenyl)borate.

[e] $\text{B}(\text{C}_6\text{F}_5)_3$: tris(pentafluorophenyl)borate.

[f] at 100 or 150 °C.



Similarly, no reaction was observed using 5 mol% NaB(Ph)₄ (entry 9) or no catalyst at 100 or 150 °C (entry 10). Interestingly, while using an additional 4 mol% of 18-Crown-6, a crown ether known for its ability to engage cation–crown interactions, the reaction did not proceed (entry 11). This last result highlighted the role of K cation in the reaction process.

In addition, the use of Ph₃CB(C₆F₅)₄ as catalyst was further studied with other organic solvents or additives and we noticed the reaction proceeded only with CPME in a 19% yield (Table S1, entries 1-8). Moreover, though bases were reported as effective catalysts in various hydrosilylation reactions,¹⁸ we did not observe any reaction of **1a** applying 5 mol% of KOH, KH or others within our experimental conditions (Table S1, entries 9-16). The best hydrosilanes for the reaction proved to be phenylsilane and to some extent diphenylsilane and n-hexylsilane (Table S2, entries 1-5). The use of phenyldimethylsilane, 1,1,3,3-tetramethyldisiloxane (TMDS) and triethylsilane led to much lower yields and catalytic activities (Table S2, entries 6-8) and no reaction was observed using triethoxysilane and triphenylsilane (Table S2, entries 9, 10). Though the disproportionation of phenylsilane is likely to occur along our catalytic reactions,¹⁹ we did not observe any release of flammable SiH₄ gas during our catalyses, nor the formation of Ph₂SiH₂ and Ph₃SiH. At the end, the screening of various solvents demonstrated the reaction was only working using TCE (1,1',2,2'-tetrachloroethane) (Table S3). Such dependence would suggest the solvent polarity controls the ion pairing between the potassium cation and the BArF₂₄ anion, the resulting solvent shared ion pairs being the necessary catalytic active species.²⁰

The scope of the catalytic reductive deoxygenation reaction was subsequently studied for a series of aliphatic and aromatic esters (Scheme 2). Ethyl-phenylacetate reactants **1a** and **1b** led to the corresponding ethers in high yields. It was worth to note the reduction of **1c** resulted in the loss of the bromine substituent. If phenyl- and naphthyl- derivatives **1d** and **1i** were reduced in fair yields, the bulky triphenylacetate **1e** didn't react due to steric hindrance. Dodecanoates **1f-h** offered the corresponding ethers in good yields, independently of the ester substituent. A similar trend was observed for benzoate derivatives **1j-k** but no reaction occurred when the phenyl moiety of ethyl benzoates **1l** and **1m** was functionalized by a chloride or a methoxy. While saturated cyclic lactones **1o-p** did not react, the reduction of phthalide **1n** into the corresponding ether underlined the need of an activating group. By comparison, this trend was reversed for anhydrides as phthalic derivative **1r** was unreactive and hexanoic anhydride **1q** had either one carbonyl function reduced, either two depending on the equivalents of phenylsilane used. Interestingly, when a carbonyl group was present on position 2 or 3 from the ester function like in reactants **1s-u**, we observed a double reduction provided 4 equivalents of phenylsilane were used. By comparison, an additional alkene function was only reduced while being conjugated with the ester. Indeed, this reactivity was observed for ethyl cinnamate **1v** but not for ester **1w**, methyl oleate **1x** or methyl linoleate **1y** which led after reaction to the related unsaturated ethers.

Mechanistic considerations and theoretical insights

Several attempts were made to obtain experimental evidences of the reaction mechanism by performing stoichiometric reactions. At first, a mixture of KBarF₂₄ with 1, 2 or 9 equivalents of PhSiH₃ in TCE was studied using in-situ infra-red spectroscopy at 100 °C (Figure 1). Upon addition of an excess of PhSiH₃, we observed two symmetric C–F stretching bands at 1143 and 1130 cm⁻¹ having almost the same intensity as well as two anti-symmetric C–F stretching bands at 1283 and 1299 cm⁻¹ with different intensities. The higher and lower frequencies may be assigned respectively to free C–F and to C–F interacting with PhSiH₃, because weak Si···C-F hydrogen bondings usually result in a blue shift of the vibration bands to lower frequency and in the shortening of the Si–H bond.^{21a,b} Because fluorine can be considered as a Hydrogen-bond acceptor with O–H, N–H and C–H donors,^{20c,d} the occurrence of some C–F···Si–H weak interactions may be reasonable in our case.

We pursued our investigations by performing ¹H, ¹³C, ¹⁹F and ²⁹Si NMR experiments on mixtures of NaBArF₂₄ catalyst and PhSiH₃ in TCE-d₂ (see the SI, tables S4 and S5, Figures S1-S5).

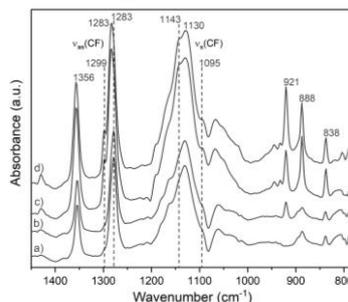


Figure 1 Infra-red spectra at 100 °C of a TCE solution of: a) KBarF₂₄, b) KBarF₂₄ and 1 equivalent of PhSiH₃, c) KBarF₂₄ and 2 equivalents of PhSiH₃, d) KBarF₂₄ and 9 equivalents of PhSiH₃.

Among the two main species we observed, the starting NaBARF_{24} was the most abundant and the second might appear as a possible adduct between NaBARF_{24} and PhSiH_3 . By comparison to the starting NaBARF_{24} , the second species showed the averaged para aromatic carbons and related protons comprised between the CF_3 groups had deshielded chemical shifts respectively of about 10 ppm and 0.65 ppm (Table S5). While averaged ipso aromatic carbons bound to the boron atom were shielded of about 20 ppm, related meta and ortho aromatic carbons as well as ortho protons had higher chemical shifts. Though these NMR features might suggest a NaBARF_{24} - PhSiH_3 adduct with possible interactions between the silane $\sigma(\text{Si-H})$ and the borate $\sigma(\text{C}_{\text{para-H}})$ and $p(\text{C}_{\text{para}})$ orbitals, further interpretations proved to be difficult.

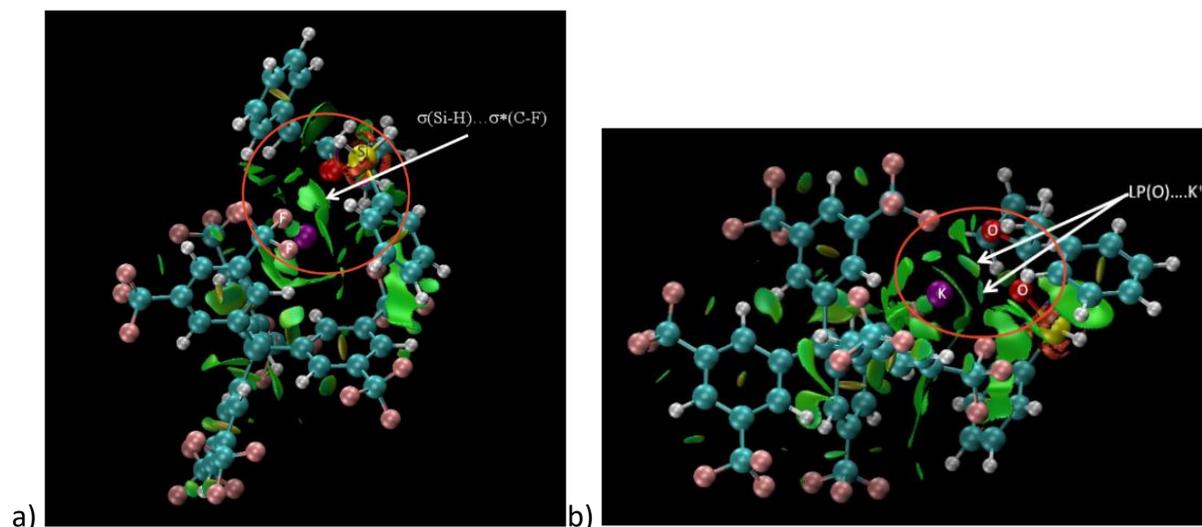


Figure 2 NCI plot of possible intermediates showing non-covalent interactions: a) between the C-F and the Si-H bonds; b) between the K^+ of the catalyst and both the oxygens of the ester reactant.

The observed non-covalent interactions were further supported by full quantum chemical calculations using density functional theory (DFT) at the PBE/TZVP level of theory. Visualization of some results with the NCI plot highlighted two possible intermediates implying either the KBARF_{24} catalyst and PhSiH_3 , either the KBARF_{24} and the ester reagent (Figure 2). In the first, the catalyst showed weak interactions between the Si center of the reagent and the fluoride atoms of the BARF_{24} anion (Figure 2a).²¹ In the second, both oxygens of the ester reactant showed moderate to weak interactions with the potassium cation of the catalyst (Figure 2b).²²

In addition, we have focused on the 2nd order perturbation energy extracted from the NBO analysis to figure out about the nature of the possible non-covalent interactions between the separate moieties (see Figures 3 and 4, Table 2). As already stated, an interaction of interest is between the K^+ ion of the KBARF_{24} catalyst and the oxygen atom of the ester reactant. From the interaction energy values (28.5 kcal/mol and 38.7 kcal/mol shown in Table 2, entries 1 and 2) and the NBO images (shown in Figure 3), it is clear that there is a moderate to high overlap between K^+ and oxygen of the ester reactant.²² Furthermore, the orbital interaction between the Si center of the silane reagent with the fluorine atoms of the KBARF_{24} catalyst showed a weaker interaction (19.0 kcal/mol shown in Table 2, entries 3 and 4) and a comparatively stronger interaction (58.2 kcal/mol) between the Si-H bond of the silane reagent and the C-F bond of the KBARF_{24} catalyst (shown in Figure 4). Finally, the full quantum chemical calculations using density functional theory (DFT) at the PBE/TZVP level of theory also highlighted a possible mechanism for this reductive deoxygenation reaction (see the supporting informations).

Conclusions

In summary, we have reported a highly selective transition metal-free reductive deoxygenation of esters to ethers. This hydrosilylation reaction was effectively performed through the use of potassium tetrakis[(3,5-trifluoromethyl)phenyl]borate as catalyst and of phenylsilane reagent. Experimental and theoretical studies of the reaction mechanism have suggested and supported the role of noncovalent interactions between the fluorinated KBARF catalyst, the phenylsilane reagent and the ester substrate in the reaction mechanism..

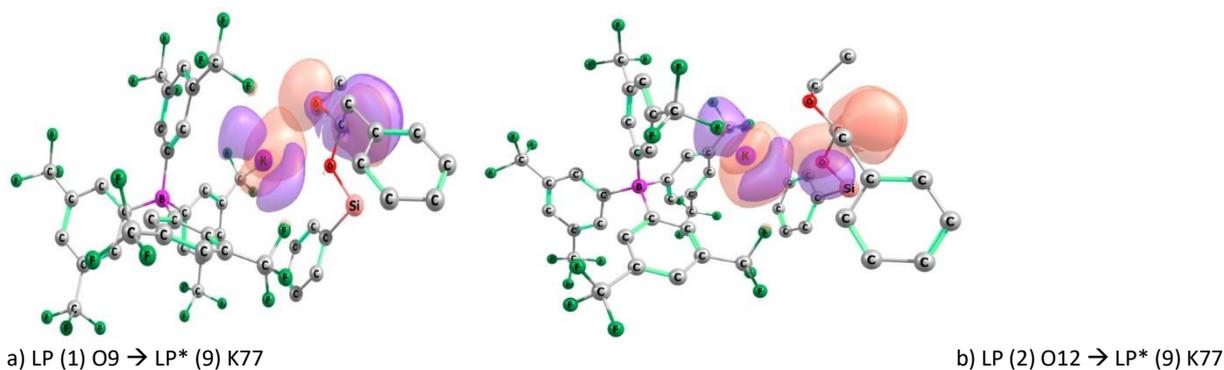


Figure 3. Second order perturbation theory analysis of the Fock matrix in NBO basis showing the important interactions between the K⁺ ion of the catalyst and the oxygen atom of the reactant species: a) LP (1) O9 → LP* (9) K77, b) LP (2) O12 → LP* (9) K77.

Table 2. Interaction energy values from the NBO analysis for: the interaction between the K⁺ ion of the catalyst and the oxygen atom of the reactant species (entries 1, 2) and the interaction between the Si center of the substrate with the fluoride of the catalyst (entries 3, 4).

Entry	Donor(i)	Occupancy	Acceptor(j)	Occupancy	E2 (kcal/mol)
1	LP (1) O9	1.95	LP* (9) K77	0.005	28.5
2	LP (2) O12	1.89	LP* (9) K77	0.005	38.7
3	BD (1) Si13-H78	1.98	BD* (1) C58-F62	1.97	58.2
4	BD (1) Si13-H78	1.98	BD* (1) C58-F61	1.95	19.0

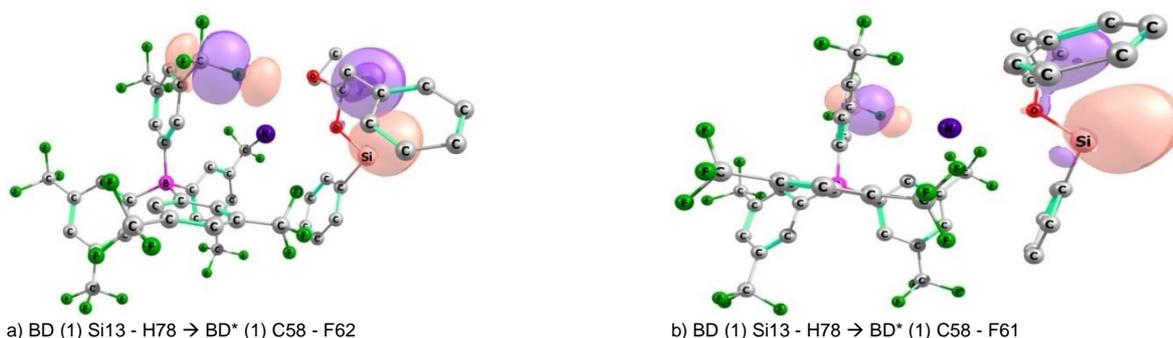


Figure 4. Second order perturbation theory analysis of the Fock matrix in NBO basis showing the important interaction between Si center of the substrate with the fluoride of the catalyst: a) BD (1) Si13 - H78 → BD* (1) C58 - F62 and b) BD (1) Si13 - H78 → BD* (1) C58 - F61.

Conflicts of interest

There are no conflicts to declare

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Catalytic reductive deoxygenation of esters to ethers driven by a hydrosilane activation through non-covalent interactions with a fluorinated borate salt

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A fluorinated borate BArF salt catalyses the reductive deoxygenation of esters to ethers by using hydrosilanes. Experimental and theoretical studies highlight the role of noncovalent interactions in the reaction mechanism.

