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## Antimony(v) cations for the selective catalytic transformation of aldehydes into symmetric ethers, $\alpha,\beta$ -unsaturated aldehydes, and 1,3,5-trioxanes†

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1-Diphenylphosphinonaphthyl-8-triphenylstibonium triflate ([2][OTf]) was prepared in excellent yield by treating 1-lithio-8-diphenylphosphinonaphthalene with dibromotriphenylstiborane followed by halide abstraction with AgOTf. This antimony(v) cation was found to be stable toward oxygen and water, and exhibited exceptional Lewis acidity. The Lewis acidity of [2][OTf] was exploited in the catalytic reductive coupling of a variety of aldehydes into symmetric ethers of type **L** in good to excellent yields under mild conditions using Et<sub>3</sub>SiH as the reductant. Additionally, [2][OTf] was found to selectively catalyze the Aldol condensation reaction to afford  $\alpha$ - $\beta$  unsaturated aldehydes (**M**) when aldehydes with 2  $\alpha$ -hydrogen atoms were used. Finally, [2][OTf] catalyzed the cyclotrimerization of aliphatic and aromatic aldehydes to afford the industrially-useful 1,3,5 trioxanes (**N**) in good yields, and with great selectivity. This phosphine–stibonium motif represents one of the first catalytic systems of its kind that is able to catalyze these reactions with aldehydes in a controlled, efficient manner. The mechanism of these processes has been explored both experimentally and theoretically. In all cases the Lewis acidic nature of the antimony(v) cation was found to promote these reactions.

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### Introduction

The development of novel main group element-derived catalysts has entered into a renaissance in recent years.<sup>1</sup> While group 13 Lewis acids represent a well-established area of catalysis,<sup>2</sup> the emergence of group 15 reagents as catalysts has recently garnered much attention. In particular, Stephan<sup>3,4</sup> and Radosevich<sup>5</sup> have utilized P(III) Lewis acids in a number of catalytic transformations, and more recently, Gabbaï and co-workers have investigated Sb(III) and Sb(V) species in sensing and catalytic applications.<sup>6,7</sup> Indeed, Gutmann and Olah have demonstrated that antimony-based Lewis acids rival traditional boron complexes.<sup>8</sup> On the other hand, the corrosive nature of antimony halides such as SbCl<sub>3</sub> and SbCl<sub>5</sub>,<sup>9</sup> has led several groups to develop novel antimony(v) derivatives decorated by organic substituents. These Lewis acids have been shown to exhibit greater stability toward air and water.

Lewis acidic systems are also involved in several important organic and biochemical transformations, including organic

substrates containing carbonyl moieties.<sup>10</sup> For example, the synthesis of aliphatic or aromatic ethers, which are found in many useful natural products,<sup>11</sup> are valuable building blocks for fine chemicals, polymers and dyes,<sup>12</sup> relies primarily on the Williamson synthesis whereby an alkoxide is coupled to an alkyl halide/sulfonate under basic conditions.<sup>13,14</sup> However the large amount of chemical waste, specifically the salt by-product,<sup>15</sup> has been associated with environmental soil and ground water contamination.<sup>16</sup> Alternative methodologies that involve the direct reductive homocoupling of aldehydes was recently reported using organosilicon reagents such as Et<sub>3</sub>SiH, Me<sub>3</sub>SiH, PhSiH<sub>3</sub>, polymethosilhydrosilane, (PMHS) and tetramethyldisiloxane (TMDS) as reducing agents in the presence of Lewis acid catalysts, including BiBr<sub>3</sub>,<sup>17</sup> I<sub>2</sub>,<sup>18</sup> Triflic acid,<sup>19</sup> Cu(OTf)<sub>2</sub>,<sup>20</sup> In(OTf)<sub>3</sub>.<sup>21</sup> However, these methods suffer from poor selectivity, substrate scope, and the catalysts are sensitive to air and moisture. The only example to date of such chemistry with antimony utilized SbI<sub>3</sub>,<sup>22</sup> however the reaction was not catalytic in antimony, and the expensive reducing agent PhSiH<sub>3</sub> was needed.

Another important chemical transformation that involves the carbonyl moiety is the Aldol condensation reaction, used widely for the formation of C–C bonds.<sup>23</sup> The products of Aldol condensation reactions,  $\alpha$ - $\beta$  unsaturated carbonyl derivatives, are present in numerous biologically active com-

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pounds,<sup>24</sup> and find important applications in the fields of pharmaceutical, fragrance, plasticizer, detergent and cosmetic chemistry.<sup>25</sup> Typically, these reactions are performed under basic or acidic conditions<sup>26</sup> that are not environmentally friendly, owing to the higher concentration of corrosive by-products generated. More environmentally benign alternatives have been described in the literature including the use of pyrrolidine or benzoic acid,<sup>27</sup> or (*p*-dimethylamino)benzoate as cocatalyst for aliphatic aldehydes,<sup>28</sup> diphenylboron perchlorate ( $\text{Ph}_2\text{BClO}_4$ ),<sup>29</sup> secondary-amines immobilized on silica support,<sup>30</sup> heteropolyacids,<sup>31</sup> chlorinated silica gel,<sup>32</sup> a solid Lewis basic catalyst containing aminopropyl-trimethoxysilane-functionalized chitosan,<sup>33</sup> lysine,<sup>34</sup> and  $\text{Et}_3\text{N-LiClO}_4$  activated by microwave irradiation.<sup>35</sup> In general, these synthetic methodologies are applicable to only a small range of systems that tolerate only very specific functional groups. Ideally, a selective, inexpensive, and effective catalyst with a broad substrate scope is still needed.

Additionally, the cyclotrimerization of aldehydes to form the corresponding 1,3,5-trioxanes has become a highly-studied transformation as trioxanes play an important role in many industrial applications including stabilizers in color photography, burning regulators in fumigants, flavoring materials, carriers for scents, repellents, deodorants, and insecticides.<sup>36</sup> To date, there is a paucity of reports that describe the synthesis of these materials, and although moderate to high yields have been achieved,<sup>37</sup> there is much room for optimization as the selectivities of these systems are poor.<sup>38</sup> Recently, Findlater *et al.*, demonstrated that  $\text{FeCl}_3$  could selectively catalyze the Aldol condensation or cyclotrimerization of aldehydes under discrete, mild conditions.<sup>39</sup> Inspired by these recent results, we questioned if we could exploit the high Lewis acidity and relative stability of tetraaryl antimony(v) stibonium cations for the selective and catalytic transformations of aldehydes described above.

The use of naphthalene and acenaphthalene scaffolds for supporting group 15 moieties through *peri*-substitution continues to be an area of active investigation as these architectures position the main group elements in close proximity allowing for applications in molecular and anion exchange as well as catalysis.<sup>3,40</sup> Herein, we report the synthesis of an unknown phosphino-stibonium salt that is *peri*-substituted on a naphthalene framework ( $[\mathbf{2}][\text{OTf}] = [\text{Sb}]^+\text{TfO}^-$ , Fig. 1), and describe the ability of this cation to selectively catalyze the conversion of aldehydes into: symmetrical ethers L, (Fig. 1, Pathway I),  $\alpha$ - $\beta$  unsaturated aldehydes M, (Fig. 1, Pathway II), and 1,3,5 trioxanes N (Fig. 1, Pathway III).

The ability of  $[\mathbf{2}]^+$  to selectively catalyze these three independent transformation represents an important contribution to main group element-mediated catalysis and in particular to antimony chemistry.

## Results and discussion

### Synthesis, structures, and properties

Two stibonium salts ( $[\mathbf{2}][\text{OTf}]$  and  $[\mathbf{4}][\text{OTf}]$ ) were synthesized for this study using the straightforward protocol described in

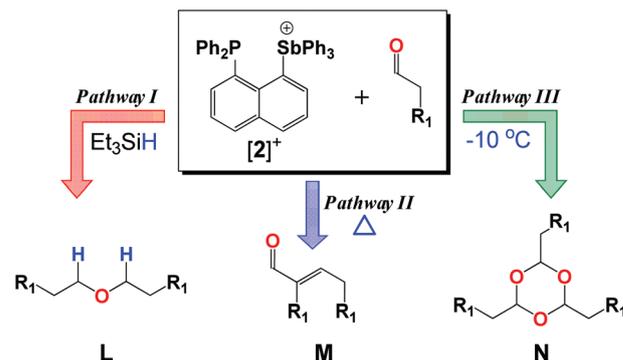
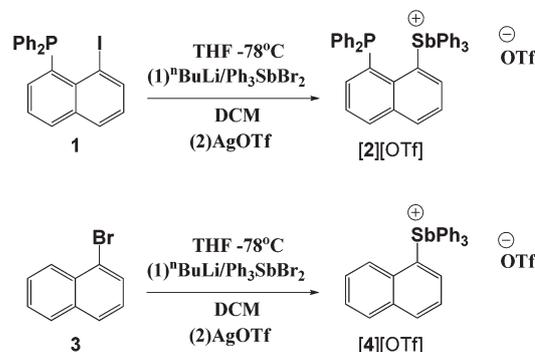


Fig. 1 Multiple transformation of aldehydes selectively catalyzed by the phosphino-stibonium cation  $[\mathbf{2}][\text{OTf}]$ .

Scheme 1. The phosphino-stibonium salt,  $[\mathbf{2}][\text{OTf}]$ , was prepared in excellent yield (70%) by lithium-iodide exchange starting from the known compound, 1-iodo-8-(diphenylphosphino)naphthalene (**1**), followed by addition of dibromotriphenylstiborane to the *in situ*-generated lithium reagent. In a second step, the bromide counter anion was exchanged for triflate using silver(i) triflate. As a control study, the tetraarylstibonium cation  $[\mathbf{4}][\text{OTf}]$  was prepared to determine if the diphenylphosphino substituent in  $[\mathbf{2}]^+$  was necessary for the catalytic activity observed (*vide infra*). Similar to  $[\mathbf{2}]^+$ ,  $[\mathbf{4}][\text{OTf}]$  was prepared by lithium-bromide exchange starting from 1-bromonaphthalene followed by treatment with  $(\text{Ph}_3\text{P})_3\text{SbBr}_2$  and subsequent bromide abstraction with  $\text{AgOTf}$ . Both salts are highly soluble in polar organic solvents (*i.e.* chloroform, dichloromethane, and acetonitrile) and are completely insoluble in apolar hydrocarbons and ethers such as pentane and diethyl ether.

The phosphine-stibonium salt  $[\mathbf{2}][\text{OTf}]$  was fully characterized by multinuclear NMR spectroscopy, DFT computational analyses, and single-crystal XRD, and the identity of  $[\mathbf{4}][\text{OTf}]$  was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy ( $\text{CDCl}_3$ ) as well as by elemental analysis (see ESI<sup>†</sup>). Prior to the anion exchange step, intermediate  $[\mathbf{2}][\text{Br}]$  was isolated, and a minor difference in the identity of  $[\mathbf{2}][\text{OTf}]$  and  $[\mathbf{2}][\text{Br}]$  could be observed by  $^1\text{H}$  NMR (Fig. 2,  $\text{CDCl}_3$ ). Specifically, the *ortho*-



Scheme 1 Synthesis of stibonium salts  $[\mathbf{2}][\text{OTf}]$  and  $[\mathbf{4}][\text{OTf}]$ .

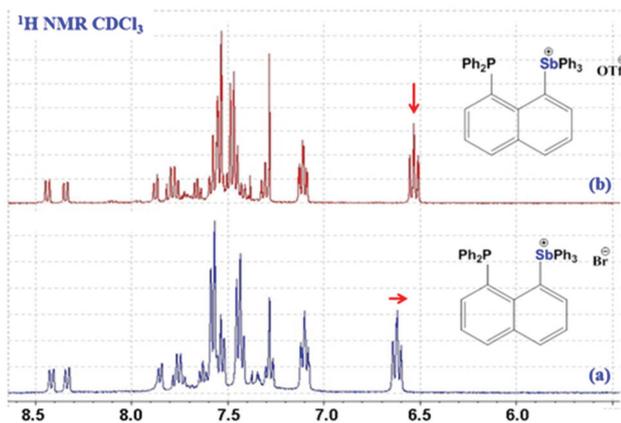


Fig. 2  $^1\text{H}$  NMR spectra comparing  $[2][\text{OTf}]$  (top) to  $[2][\text{Br}]$  (bottom).

protons of the diphenylphosphino moiety were shifted upfield by approximately 0.15 ppm in  $[2][\text{OTf}]$  when compared to  $[2][\text{Br}]$ . In addition, a small downfield shift was observed in the  $^{31}\text{P}$  NMR of  $[2][\text{OTf}]$  ( $-36.1$  ppm) when compared to  $[2][\text{Br}]$  ( $-38.5$  ppm). This small difference may be due to a weak interaction between the triflate anion and the cationic antimony center in solution.

The most striking feature of the single crystal XRD structure of  $[2][\text{OTf}]$  (Fig. 3), was the P1–Sb1 distance of 2.9138(11) Å which is well within the sum of the van der Waals radii. This indicated to us that there is a strong interaction between the phosphorus and antimony centers owing to the high Lewis acidity of the cationic antimony atom. In agreement with this assessment, we note that the P1–Sb1–C21 angle of  $170.18(14)^\circ$  is consistent with donation of the phosphorus atom lone pair into a low-lying Sb1–C21  $\sigma^*$  orbital. In addition, we noticed that the triflate counter ion is weakly coordinated to the P1–Sb1 unit as evidenced by the Sb1–O1 distance (2.812 Å), the O1–Sb1–C31 angle ( $166.8^\circ$ ), the P1–O1 distance (3.661 Å), and the O1–P1–C51 angle ( $158.6^\circ$ ). Even though it is clear that the cationic antimony center engages the oxygen atom of the triflate anion in a stronger interaction, the P1–O1 distance is and the O1–P1–C51 angle are consistent with a weak interaction between the anion and phosphorus atom. While we are uncertain if these unusual interactions persist in solution, they may be the source of the observed upfield chemical shift in the  $^1\text{H}$  NMR of compound  $[2][\text{OTf}]$  when compared to  $[2][\text{Br}]$ . Despite our best efforts, single crystals of  $[2][\text{Br}]$  and  $[4][\text{OTf}]$  that were suitable for an X-ray diffraction could not be obtained to compare to  $[2][\text{OTf}]$ .

To better understand the solid state structure, a natural bond order (NBO) analysis<sup>41</sup> was performed on the crystal structure geometry of  $[2][\text{OTf}]$  (see ESI† for full computational details). In agreement with the crystal structure, a donor acceptor interaction between a phosphorus lone pair and a Sb–C<sub>Ph</sub>  $\sigma^*$  orbital (Fig. 4A) was found in the NBO output file. The energy of this interaction was estimated to be approximately  $23 \text{ kcal mol}^{-1}$  by using the NBO deletion protocol.<sup>42</sup> We also found multiple interactions between the triflate oxygen

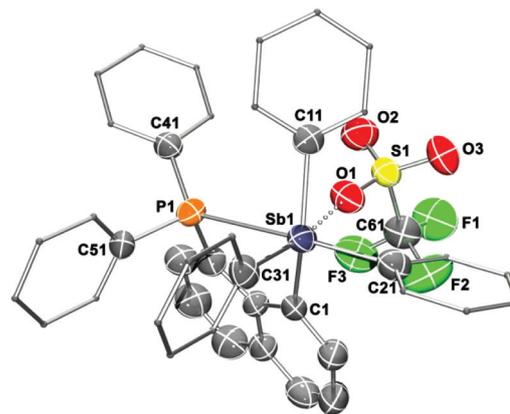


Fig. 3 XRD Crystal structure of  $[2][\text{OTf}]$  (50% thermal ellipsoids, phenyl substituents have been drawn as thin lines for clarity). Pertinent metrical parameters are provided in the text.

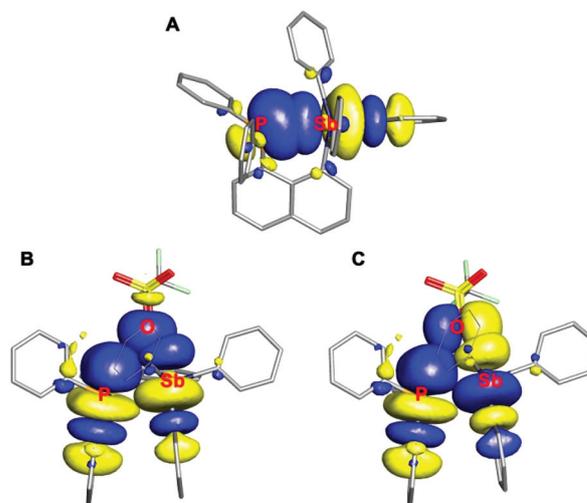


Fig. 4 NBO plots (isovalue 0.03) of A:  $\text{lp}(\text{P}) \rightarrow \sigma^*(\text{Sb}-\text{C}_{\text{Ph}})$ , B and C: four representative  $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{Sb}-\text{C}_{\text{Ph}})$  and  $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{P}-\text{C}_{\text{Ph}})$  donor–acceptor interactions.

O1 and the cation  $[2]^+$ . Surprisingly, the two filled O1 p orbitals behave as donor orbitals to vacant  $\sigma^*$  Sb–C<sub>Ph</sub> and P–C<sub>Ph</sub> acceptor orbitals (Fig. 4B and C). Collectively, these interactions were estimated to be approximately  $10.6 \text{ kcal mol}^{-1}$  (NBO deletion) with the O1–Sb and the O1–P interactions accounting for *ca.*  $9.3$  and  $1.3 \text{ kcal mol}^{-1}$ , respectively. Close inspection of the natural charges on the P and Sb centers (0.97 and 1.89, respectively) indicates that the positive charge of the cation may be delocalized over the two group 15 elements. We ascribe this phenomenon to the differing catalytic properties of  $[2]^+$  when compared to  $[4]^+$  (*vide infra*).

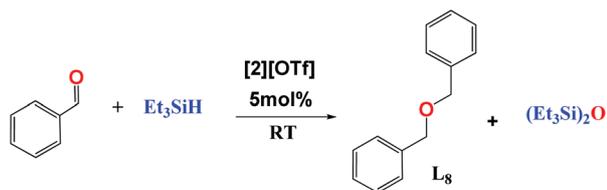
### Catalytic activity studies

We have explored the ability of the stibonium cations  $[2]^+$  and  $[4]^+$  to catalyze the reductive coupling of aldehydes (Fig. 1,

Pathway I), the Aldol condensation of aldehydes (Fig. 1, Pathway II), and the cyclotrimerization of aldehydes (Fig. 1, Pathway III). In general, it was found that cation  $[2]^+$  was a superior catalyst when compared to  $[4]^+$  in Pathway I and exhibited greater catalytic activity and selectivity. In contrast, both cations were found to be excellent catalysts for Pathways II and III (see ESI† for specific results regarding cation  $[4]^+$ ).

We initially explored the ability of  $[2]^+$  or  $[4]^+$  to catalyze the hydrosilylation of aldehydes with  $\text{Et}_3\text{SiH}$ , and used benzaldehyde as a model substrate. During the course of our work, Gabbaï and coworkers demonstrated that the bifunctional dication  $1,2\text{-}[(\text{Ph}_2\text{MeSb})_2\text{C}_6\text{H}_4]^{2+}$  catalyzed the hydrosilylation of benzaldehyde and 4-fluorobenzaldehyde, however they also showed that the monofunctional analogue  $[\text{Ph}_3\text{SbMe}]^+$  exhibited no catalytic activity.<sup>7</sup> Interestingly, when 5 mol% of  $[2]^+$  was used as a catalyst, we did not observe the expected hydrosilylated species, benzyloxytriethylsilane ( $\text{Ph-CH}_2\text{-O-SiEt}_3$ , **5**, *vide infra*), but instead found that dibenzyl ether (**L**<sub>8</sub>) along with the symmetric siloxane ( $(\text{Et}_3\text{Si})_2\text{O}$ ) were the only products (Scheme 2). We have extended this reactivity to include a wide substrate scope including aliphatic, aromatic, and haloaromatic aldehydes (Table 1). For all cases, we found excellent catalytic activity and selectivity for the conversion of these aldehydes into the corresponding symmetric ethers (**L**). This method also allowed for the synthesis of the unknown ether, 3,3'-oxybis(methylene)-bis(fluorobenzene) (**L**<sub>12</sub>) in good isolated yield.

From these results we have observed that  $[2]^+$  is a potent catalyst for both aliphatic and aromatic aldehydes, however longer reactions times were required to convert aromatic aldehydes into the corresponding ethers (Table 1, entries 8–15). The activity and the selectivity of this reaction suffered when aldehydes with aromatic substituents featuring strongly electron-withdrawing groups were used (Table 1, entries 9, 13, and 14). Indeed, pentafluorobenzaldehyde (entry 9) resulted in much lower selectivity for the formation of ether **L**<sub>9</sub> (50%), and also required higher temperatures (70 °C) and longer reaction times, similar to *p*-trifluoromethylbenzaldehyde (entry 13) and *p*-nitrobenzaldehyde (entry 14). Interestingly, when reactions with aliphatic aldehydes were heated, the selectivity for the formation of ethers **L** was lost and mixtures of unidentified products were observed by <sup>1</sup>H and <sup>13</sup>C NMR. This loss of selectivity was not observed when reactions with aromatic aldehydes were heated. Catalyst  $[4][\text{OTf}]$  was also



**Scheme 2** Reductive coupling of benzaldehyde to afford ether **L**<sub>8</sub> catalyzed by  $[2]^+$  in  $\text{CH}_2\text{Cl}_2$ .

**Table 1** Substrate scope for the reductive coupling of aldehydes to give symmetric ethers **L**<sup>a</sup>

Entry	Aldehyde (R)	Time (h)	Product	Selectivity (%)	Yield <sup>b,c</sup> (%)
1	$\text{CH}_2\text{CH}_2\text{CH}_3$	1	<b>L</b> <sub>1</sub>	100	100 <sup>e</sup>
2	$(\text{CH}_2)_8\text{CH}_3$	1	<b>L</b> <sub>2</sub>	100	100(90)
3	$\text{CH}_2\text{CH}_2\text{Ph}$	2	<b>L</b> <sub>3</sub>	100	100(90)
4	<sup>i</sup> Pr	1	<b>L</b> <sub>4</sub>	100	100 <sup>e</sup>
5	$\text{CH}(\text{CH}_2\text{CH}_3)_2$	2	<b>L</b> <sub>5</sub>	100	100(90)
6	Cyclohexyl	1	<b>L</b> <sub>6</sub>	100	100(90)
7	$\text{CH}(\text{Ph})_2$	1	<b>L</b> <sub>7</sub>	80	90(70)
8	Ph	12	<b>L</b> <sub>8</sub>	100	100(90)
9	$\text{C}_6\text{F}_5$	48 <sup>d</sup>	<b>L</b> <sub>9</sub>	50	50 <sup>e</sup>
10	2-Br- $\text{C}_6\text{H}_4$	12	<b>L</b> <sub>10</sub>	100	100(50)
11	3-Br- $\text{C}_6\text{H}_4$	12	<b>L</b> <sub>11</sub>	100	100(50)
12	3-F- $\text{C}_6\text{H}_4$	12	<b>L</b> <sub>12</sub> (New)	100	100(70)
13	4- $\text{CF}_3$ - $\text{C}_6\text{H}_4$	12 <sup>d</sup>	<b>L</b> <sub>13</sub>	100	100(90)
14	4- $\text{NO}_2$ - $\text{C}_6\text{H}_4$	24 <sup>d</sup>	<b>L</b> <sub>14</sub>	100	100(80)
15	4- $\text{CH}_3$ - $\text{C}_6\text{H}_4$	12	<b>L</b> <sub>15</sub>	100	100(90)

<sup>a</sup> Reactions conditions: aldehyde :  $\text{Et}_3\text{SiH}$  (1 : 3), RT,  $[2][\text{OTf}]$  (3 mol%),  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup> Yields: based on <sup>1</sup>H NMR. <sup>c</sup> Isolated yield after purification (in parenthesis). <sup>d</sup> Reactions heated to 70 °C. <sup>e</sup> Final products were compared with literature values but not isolated.

found to catalyze the reaction shown in Scheme 2 (ESI, Table S1†). For butyraldehyde (entry 1, Tables 1 and S1†)  $[4]^+$  was found to catalyze the conversion to **L**<sub>1</sub> much faster than  $[2]^+$ . However, when bulkier aliphatic or aromatic aldehydes were used the selectivity of  $[4]^+$  for the conversion to the corresponding ethers **L** was found to be much lower (<20%).

To further understand how the stibonium cation catalyzed the reaction shown in Scheme 2, we probed the interaction of various aldehydes with  $[2]^+$  using <sup>1</sup>H NMR spectroscopy ( $\text{CDCl}_3$ ). Unfortunately, when an excess benzaldehyde was treated with  $[2]^+$  (3 mol%), we were unable to observe the formation of any intermediates in solution even when heating to 70 °C. In contrast, when a 3 : 1 solution of butyraldehyde :  $[2][\text{OTf}]$  in  $\text{CDCl}_3$  was heated to 70 °C, the formation of an orange color and an upfield shift of the resonances corresponding to  $[2]^+$  were observed (Fig. 5). We attribute the observed upfield shift with lone-pair donation from the Lewis basic oxygen atom of the aldehyde into a  $\text{Sb-C}_{\text{Ph}}$   $\sigma^*$  orbital that is localized on the Lewis acidic stibonium center. This aldehyde–stibonium interaction (**A**<sub>c</sub>) has been further corroborated computationally (*vide infra*).

When the solution shown in Fig. 5 was heated for 12 hours, the butyraldehyde was found to disappear concomitant with the appearance of new peaks that corresponded to an olefin-containing product. The identity of this new compound was verified to be (*E*)-2-ethyl-2-hexenal by heating a solution of butyraldehyde in  $\text{CDCl}_3$  to 70 °C for 12 hours in the presence of 3 mol% of  $[2]^+$  (Fig. 6). The conversion of butyraldehyde into (*E*)-2-ethyl-2-hexenal demonstrated that without the redu-

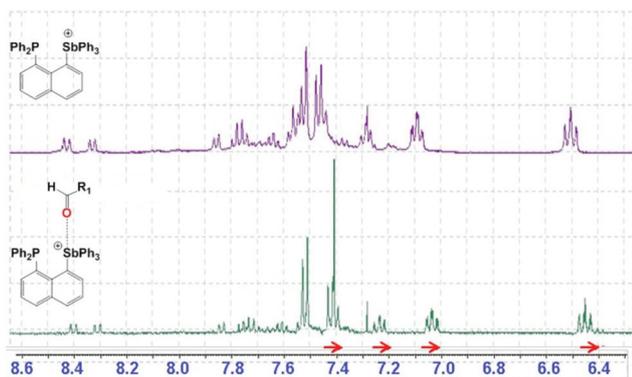


Fig. 5  $^1\text{H}$  NMR spectra showing the interaction of butyraldehyde and stibonium salt  $[2][\text{OTf}]$  when mixed at  $70\text{ }^\circ\text{C}$  in  $\text{CDCl}_3$  (3 : 1 ratio).

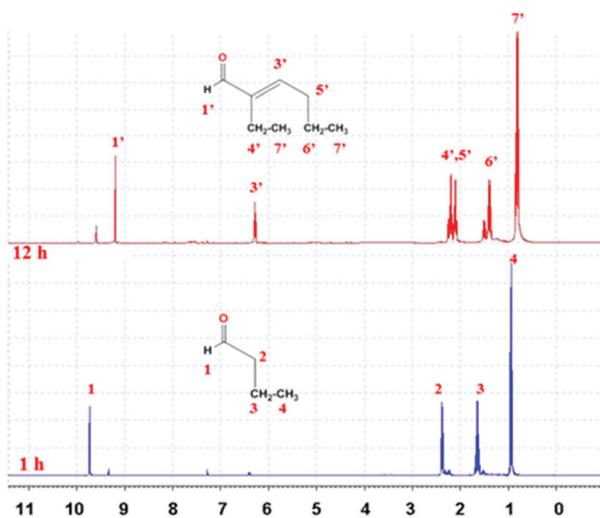


Fig. 6  $^1\text{H}$  NMR spectra showing the conversion of butyraldehyde into (*E*)-2-ethyl-hexenal, ( $\text{M}_1$ ) over a period of 12 h, using 3 mol%  $[2][\text{OTf}]$  in  $\text{CDCl}_3$  at  $70\text{ }^\circ\text{C}$ .

cing agent  $\text{Et}_3\text{SiH}$  present,  $[2]^+$  could also catalyze the Aldol condensation of aldehydes according to Fig. 1, Pathway II.

Substrate scope studies revealed that these reactions were limited to aldehydes with two  $\alpha$ -hydrogen atoms, and suggested to us that steric bulk at the  $\alpha$ -position may impede the formation of the intermediate  $\beta$ -hydroxy aldehyde Aldol product. Additionally, under our experimental conditions dehydration to the corresponding  $\alpha,\beta$ -unsaturated aldehydes ( $\text{M}$ ) as shown in Table 2 was observed exclusively. We were able to further optimize this reaction, and found that with lower catalyst loading (0.5 mol%) the same activity and selectivity for the formation of  $\text{M}$  was observed (Table 2). Importantly, after these reactions were completed, we were able to recycle the stibonium salt by the addition of hexanes to the reaction mixture which resulted in the precipitation of the catalyst and allowed for separation by decanting the supernatant solution.

Table 2 Substrate scope for the Aldol condensation reactions catalyzed by  $[2][\text{OTf}]$  to give  $\alpha,\beta$ -unsaturated aldehydes  $\text{M}^a$

Entry	Aldehyde (R)	Time (h)	Product	Selectivity (%)	Yield <sup>b/c</sup> (%)
1	$\text{CH}_2\text{CH}_2\text{CH}_3$	24	$\text{M}_1$	100	100 (90)
2	$(\text{CH}_2)_8\text{CH}_3$	24	$\text{M}_2$	100	100 (90)
3	$\text{CH}_2\text{CH}_2\text{Ph}$	24	$\text{M}_3$	100	100 (90)
4	$\text{CH}_2\text{Ph}$	24	$\text{M}_4$	100	100 (90)

<sup>a</sup> Reactions conditions: aldehyde,  $[2][\text{OTf}]$  (0.5 mol%)  $70\text{ }^\circ\text{C}$ ,  $\text{CH}_2\text{Cl}_2$ .  
<sup>b</sup> Yields: based on  $^1\text{H}$  NMR. <sup>c</sup> Isolated yield after column chromatography in parenthesis.

The observed selectivity for the formation of the  $\alpha,\beta$ -unsaturated aldehydes over the  $\beta$ -hydroxy aldehydes is highly desired, and our catalytic system surpasses the majority of known systems reported in the literature which typically suffer from the production of mixtures of products.<sup>38</sup> Surprisingly, no difference in catalytic activity or selectivity was observed when these Aldol condensation reactions were catalyzed with  $[4][\text{OTf}]$ . Indeed, when carried out under identical conditions to that of  $[2]^+$ , Aldol condensation reactions catalyzed by  $[4]^+$  gave identical results. While we currently have no explanation for this observation, we believe that the highly Lewis acidic nature of the antimony(v) cationic center in these catalysts precludes any disparate reactivity between  $[2]^+$  and  $[4]^+$  that may arise due to the  $\text{Ph}_2\text{P}$  moiety in  $[2]^+$ .

Previous reports have found that water plays important role in Aldol condensation reactions, and can serve to either speed up the reaction or to improve selectivity.<sup>14,43</sup> In this context, we have also found that water plays an important role the Aldol condensation reaction catalyzed by  $[2]^+$ . Specifically, we believe that the water acts as a Lewis base in this reaction. Indeed, when these reactions were carried out under identical conditions, but in the presence of molecular sieves, the formation of the Aldol condensation product was suppressed from 100 to 6% (see ESI, Fig. S4†). These findings corroborated the need for water in the reaction, and from a mechanistic standpoint, suggested that water may act as a Lewis base in these reactions (*vide infra*). While it may also be possible that exogenous water may serve as a source of protons which may in fact catalyze Pathway II, we find this unlikely given the presence of the Lewis basic phosphino group in  $[2]^+$ . With that said, we have not been able to rule out this possibility at this time.

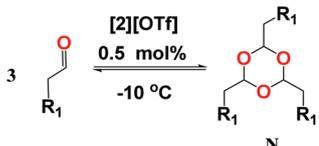
Inspired by recent work from Findlater *et al.*,<sup>39</sup> that demonstrated the ability of the Lewis acid  $\text{FeCl}_3$  to catalyze the cyclo-trimerization of aldehydes to give 1,3,5-trioxanes, we next

questioned if our stibonium cations could similarly serve as catalysts for this transformation. Given that judicious water in the solvent favors the Aldol condensation reaction (Pathway II), whereas the presence of a reducing silane favors the formation of the symmetric ethers (Pathway I), we hypothesized that the removal of both the solvent and the reducing agent in these reactions may enhance the interaction of the aldehyde with the  $[\text{Sb}]^+$  center, and thus increase the electrophilic character of the acyl carbon.

Indeed, we found that treating the aldehydes shown in Table 3 (entries 1–7) with 1 mol% of  $[\text{2}][\text{OTf}]$  without solvent or  $\text{Et}_3\text{SiH}$  at  $-10^\circ\text{C}$  resulted in the formation of the 1,3,5-trioxanes (**M**) according to the reaction shown in Table 3. In comparison to previous work from Findlater *et al.*,<sup>39</sup> water does not play an important role in this reaction, however the reversibility of the process is strongly temperature dependent, analogous with the previous finding that utilized  $\text{FeCl}_3$  as the catalyst.<sup>39</sup> We further optimized this reaction and found that as low as 0.5 mol% loading of  $[\text{2}]^+$  in an inert solvent such as hexamethyldisiloxane could catalyze the formation of trioxanes **N** at  $-10^\circ\text{C}$  (Table 3). We also found that higher temperatures favored the reverse reaction, and if the reaction was carried out at room temperature the conversion to **N** was negligible even in the presence of 5 mol% of  $[\text{2}]^+$ .

Even though the reaction can be performed under solvent free conditions, the solubility of  $[\text{2}]^+$  in some of the viscous aldehydes (entries 1, 5, 6, and 7) was low and necessitated the addition of  $\sim 50\ \mu\text{L}$  of  $(\text{Me}_3\text{Si})_2\text{O}$ . The reaction is limited to aldehydes with 1 or 2  $\alpha$ -hydrogen atoms, but despite this limitation, we utilized this methodology to prepare the unknown trioxane, 2,4,6-tri(isopentyl)-1,3,5-trioxane (**N**<sub>5</sub>). Similar to the Aldol condensation reaction,  $[\text{4}]^+$  was also found to exhibit similar catalytic activity for the formation of the trioxanes **N** when compared to the phosphine-substituted cation  $[\text{2}]^+$ .

**Table 3** Substrate scope for the cyclotrimerization of aldehydes catalyzed by  $[\text{2}][\text{OTf}]$  to give 1,3,5-trioxanes **N**<sup>a</sup>



Entry	Aldehyde (R)	Time (h)	Product	Selectivity (%)	Yield <sup>b</sup> (%)
1	$\text{CH}_2\text{CH}_2\text{CH}_3$	12 <sup>c</sup>	<b>N</b> <sub>1</sub>	100	90
2	$(\text{CH}_2)_8\text{CH}_3$	12	<b>N</b> <sub>2</sub>	100	90
3	$\text{CH}_2\text{Ph}$	12	<b>N</b> <sub>3</sub>	100	90
4	$\text{CH}_2\text{CH}_2\text{Ph}$	12	<b>N</b> <sub>4</sub>	100	90
5	$\text{CH}(\text{CH}_2\text{CH}_3)_2$	12 <sup>c</sup>	<b>N</b> <sub>5</sub> (New)	100	50
6	Cyclohexyl	2 <sup>c</sup>	<b>N</b> <sub>6</sub>	100	90
7	$\text{CH}(\text{Ph})_2$	12 <sup>c</sup>	<b>N</b> <sub>7</sub>	90	70

<sup>a</sup> Reactions conditions: aldehyde,  $[\text{2}][\text{OTf}]$  (0.5 mol%),  $(\text{Me}_3\text{Si})_2\text{O}$ ,  $-10^\circ\text{C}$ . <sup>b</sup> Isolated yield after purification. <sup>c</sup> No solvent was used.

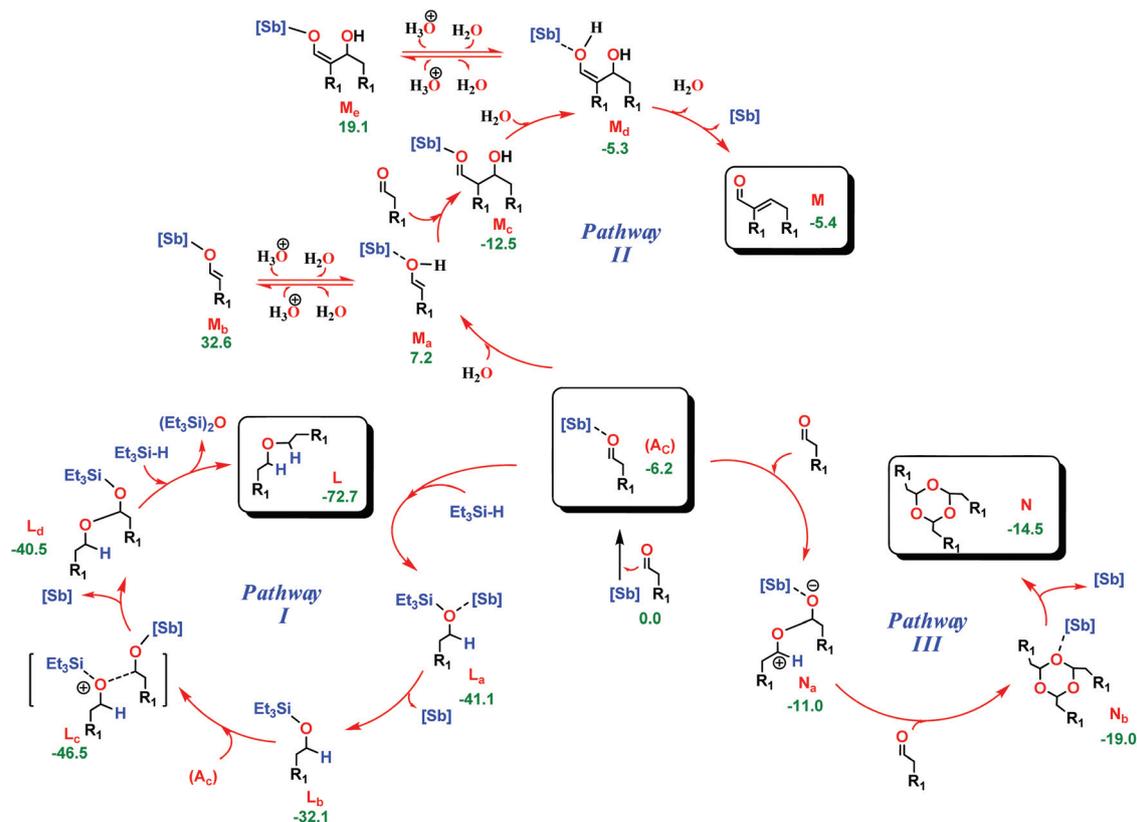
## Computational mechanistic studies

To gain a further understanding into these reactions catalyzed by  $[\text{2}]^+$ , we have optimized the geometries of proposed intermediates that could potentially form in each reaction using density functional (DFT) methods. For these reactions, we propose three distinct catalytic pathways for each reaction that all stem from a single intermediate (denoted as **A**<sub>c</sub>). Indeed, it was found that the interaction of the aldehyde oxygen atom with the cationic Sb(v) center (**A**<sub>c</sub>), was favorable by  $-6.2\ \text{kcal mol}^{-1}$  (Scheme 3.) These calculations are in agreement with a recent review from Davis,<sup>5a</sup> which claims that  $\sigma$ -donation from the aldehyde oxygen atom to the Lewis acidic atom is the most common mode of activation seen in main group Lewis acid catalysis.

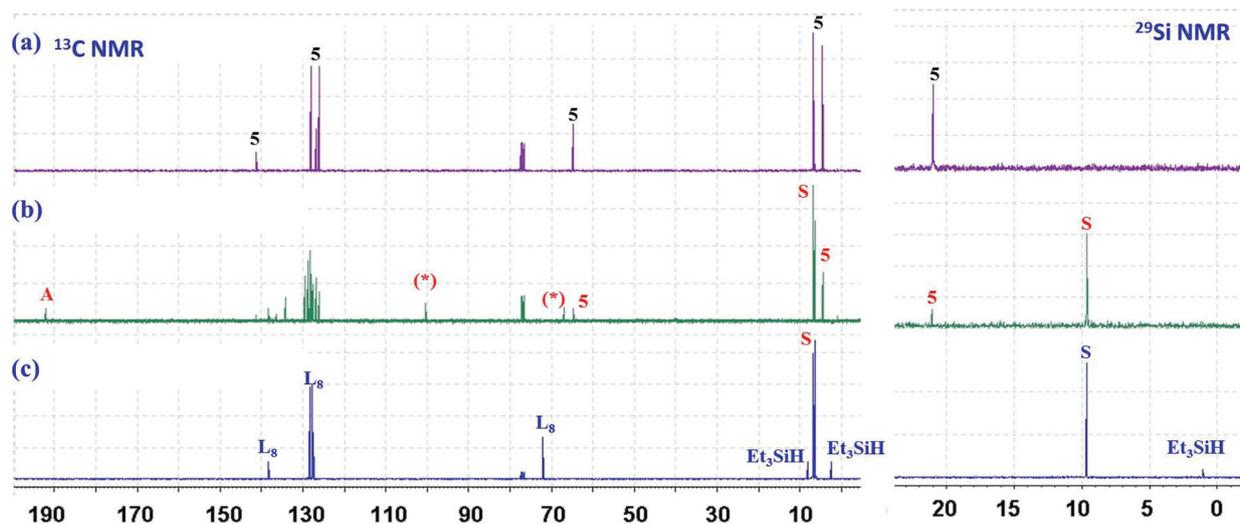
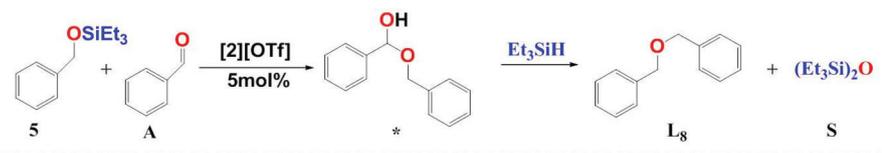
**Pathway I:** This pathway details the proposed catalytic cycle for the formation of the symmetric ethers **L** (Scheme 3). The formation of intermediate **A**<sub>c</sub> results in a more polarized  $\text{C}=\text{O}$  double bond and facilitates the addition of a  $\text{Si}-\text{H}$  bond across the  $\text{C}=\text{O}$  bond to give intermediate **L**<sub>a</sub> which spontaneously releases  $[\text{2}]^+$  to give hydroxylated product **L**<sub>b</sub>. The formation of **L**<sub>b</sub>, was calculated to be exothermic by  $-32.1\ \text{kcal mol}^{-1}$ . Unfortunately we have not been able to observe **L**<sub>b</sub>, however we have independently synthesized the hydroxylated compound benzyloxytriethylsilane (**5**, see Fig. 7a for  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR,  $\text{CDCl}_3$ ),<sup>44</sup> to determine if our experimental conditions resulted in the immediate conversion to ether **L** in the presence of another activated aldehyde species (**A**<sub>c</sub>) as shown in Scheme 3. Interestingly when  $\text{Et}_3\text{SiH}$  was added to **5** in the presence of  $[\text{2}]^+$  (5 mol%), no reaction was observed even upon heating. This suggested that the formation of intermediates of type **A**<sub>c</sub> is critical to these reactions. Additional supportive evidence showed that the addition of benzaldehyde and  $\text{Et}_3\text{SiH}$  to **5** in the absence of  $[\text{2}]^+$  did not afford dibenzyl ether (**L**<sub>8</sub>).

To confirm that the hydroxylated products (**L**<sub>b</sub>) react with activated aldehyde complexes (**A**<sub>c</sub>), we next treated **5** with benzaldehyde (**A**) and  $[\text{2}]^+$  (5 mol%) in the absence of  $\text{Et}_3\text{SiH}$  (Fig. 7). This reaction was monitored by  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ). After a period of 12 h, the appearance of a new species (\*) was observed by  $^{13}\text{C}$  NMR (Fig. 7b) with a peak at 105 ppm that is characteristic of a hemiacetal. The conversion of **5** into a new species was also observed in the  $^{29}\text{Si}$  NMR with the disappearance the hydroxylated product (21 ppm) and the appearance of a new signal at 9.8 ppm. This new signal was attributed to the formation of the siloxane  $(\text{Et}_3\text{Si})_2\text{O}$ , which may have formed by hydrolysis of a silyl-hemiacetal precursor. The addition of a slight excess of  $\text{Et}_3\text{SiH}$  to this reaction resulted in the immediate formation of **L**<sub>8</sub> and  $(\text{Et}_3\text{Si})_2\text{O}$  as shown by the crude  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR (Fig. 7c).

These results clearly demonstrated that once the hydroxylated product **L**<sub>b</sub> is formed, it may react immediately with **A**<sub>c</sub> to form the hemiacetal **L**<sub>d</sub> through **L**<sub>c</sub>. However under our experimental conditions, we suggest that **L**<sub>d</sub> is rapidly reduced by  $\text{Et}_3\text{SiH}$  to form the final symmetric ether **L**. Indeed, our computational studies revealed that this final reduction was exothermic by more than  $30\ \text{kcal mol}^{-1}$  ( $-40.5$  for **L**<sub>d</sub>, and



**Scheme 3** Proposed mechanism for the catalytic transformation of aldehydes into symmetric ethers (Pathway I),  $\alpha,\beta$  unsaturated aldehydes (Pathway II), and 1,3,5-trioxanes (Pathway III). Numbers correspond to calculated DFT energies ( $\text{kcal mol}^{-1}$ ).



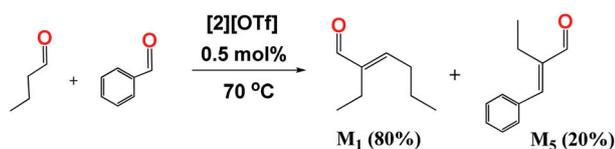
**Fig. 7**  $^{13}C$  and  $^{29}Si$  NMR spectra of: (a) benzoyloxytriethylsilane (5), (b) the reaction of 5 with benzaldehyde (A) and  $[2][OTf]$  (5 mol%), and (c) the formation of dibenzyl ether ( $L_8$ ) and hexaethyldisiloxane (S) upon addition of  $Et_3SiH$ . Spectra recorded at RT,  $CDCl_3$ .

$-72.7 \text{ kcal mol}^{-1}$  for L). The large exothermic nature of these steps may explain why we are unable to observe or isolate the hydrosilylated compounds  $L_b$  or hemiacetal derivatives  $L_d$  using our method. Importantly, we are currently investigating the potential for this methodology to be expanded toward the preparation of unsymmetric ethers starting from hydrosilylated compounds of type  $L_b$  and aldehydes.

**Pathway II:** This pathway details the proposed catalytic cycle for the formation of the Aldol condensation products  $M$  (Scheme 3). In this pathway, we propose that the activated species  $A_c$  is isomerized to the enol derivative  $M_a$  in the presence water. Even though formation of the enol is uphill by  $7.2 \text{ kcal mol}^{-1}$ , we believe it to be largely favored over complete deprotonation of the aldehyde to give the enolate  $M_b$  as this species was calculated to be  $32.6 \text{ kcal mol}^{-1}$  higher in energy. The endothermic formation of enol  $M_a$  is also consistent with the need to heat these reactions (*vide supra*). Regardless,  $M_a$  is sufficiently nucleophilic to add to another equivalent of the aldehyde in an exothermic reaction ( $-12.5 \text{ kcal mol}^{-1}$ ) to give the Aldol product  $M_c$ . Unlike  $A_c$ ,  $M_c$  is more susceptible to tautomerization in the presence of water and is isomerized to  $M_d$  by an energetically favored process ( $-5.3 \text{ kcal mol}^{-1}$ ). We also calculated that the enol  $M_d$  is enthalpically favored over the enolate  $M_e$  ( $-5.3$  versus  $19.1 \text{ kcal mol}^{-1}$ ) analogous to the  $M_a/M_b$  equilibrium. Instead, it was found that deprotonation of  $M_d$  by water favored elimination of the  $\beta$ -hydroxy substituent to give the  $\alpha,\beta$ -unsaturated condensation product  $M$ . Our calculations also favored the formation of compound  $M$  over  $M_e$  by more than  $30 \text{ kcal mol}^{-1}$ .

Given that our calculations predicted that the formation of enol  $M_a$  was only slightly endothermic, we questioned if this enol could be used in a cross Aldol condensation reaction. To address this question, we treated butyraldehyde, an aldehyde with enolizable protons, with benzaldehyde, an aldehyde with no  $\alpha$ -protons, in the presence of  $[2]^+$  (0.5 mol%) at  $70^\circ\text{C}$  (Scheme 4).

While we were able to successfully trap the purported enol of type  $M_a$ , formed from butyraldehyde,  $[2]^+$  and water, the major product obtained from this reaction was the butyraldehyde self-condensation product ( $M_1$ , 80% yield) with only minor formation of the desired cross-condensation product (*E*)-2-benzylidenebutanal ( $M_5$ , 20% yield), even in the presence of a large excess of benzaldehyde. To confirm these results, both compounds were isolated and fully characterized by NMR spectroscopy (see ESI, Fig. S5 and S6<sup>†</sup>). Despite the poor selectivity for the formation of  $M_5$ , we believe that future optimization may be possible. We also plan to design and



**Scheme 4** Cross-Aldol condensation reaction catalyzed by  $[2][\text{OTf}]$  in  $\text{CH}_2\text{Cl}_2$ .

study second generation catalysts derived from  $[2]^+$  as the direct coupling of aldehydes to afford symmetric and asymmetric products continues to be an important synthetic approach and current topic of interest in organic chemistry.<sup>38b,45</sup>

**Pathway III:** This pathway details the proposed catalytic cycle for the cyclotrimerization of aldehydes to afford 1,3,5-trioxanes of type  $N$  (Scheme 3). As described earlier, we could favor the formation of 1,3,5-trioxanes by eliminating the triethyl silane and suppressing the temperature of the reaction. By avoiding these conditions, our computational analyses revealed that nucleophilic attack from another aldehyde on the acyl carbon atom of  $A_c$  to give the intermediate  $N_a$  is energetically favored by  $11.0 \text{ kcal mol}^{-1}$ . The computations also revealed a buildup of positive charge on one of the former acyl carbons in compound  $N_a$  as shown in Scheme 3. For this reason, the addition of a third aldehyde molecule to  $N_a$  followed by intramolecular cyclization to give the 1,3,5-trioxane coordinated to the cationic antimony center ( $N_b$ ) is exothermic ( $-19.0 \text{ kcal mol}^{-1}$ ). Finally, the dissociation of the stibonium cation back into the catalytic cycle to release the free trioxane ( $N$ ) was also found to be downhill by another  $14.5 \text{ kcal mol}^{-1}$ . These calculations are not only in good agreement with our optimized reactions conditions which demonstrated that these trioxanes could be readily prepared at low temperature, but also affirm that the reversibility of each step in this process could potentially hamper product formation at elevated temperatures.<sup>39</sup>

## Experimental

### General considerations

**Note: Antimony compounds are potentially toxic and should be handled accordingly.** Unless otherwise noted, these procedures were all carried out using typical Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glove box. Solvents were dried and degassed by an Innovative Technology solvent purification system and stored over  $3 \text{ \AA}$  molecular sieves in a nitrogen-filled glove box. Dichloromethane and hexanes were dried under nitrogen over CaH and Na/K, respectively and distilled prior to use. Aldehydes with 95 to 98% purity have been purchased either from Sigma Aldrich or Alfa Aesar and were used as received. The starting material, 1-diphenylphosphino-8-iodonaphthalene, was synthesized according to a literature report.<sup>46</sup> Melting points were recorded on a Mel-Temp apparatus in sealed capillary tubes and are uncorrected. All other reagents were used as received. NMR spectra were recorded on Bruker Avance 400 MHz/52 mm spectrometer. Chemical shifts ( $\delta$ ) are given in ppm and are referenced to the residual solvent:  $^1\text{H}$ : 7.26 ppm;  $^{13}\text{C}$ :  $\text{CDCl}_3$ , 77.0 ppm;  $^{31}\text{P}$  NMR:  $\text{H}_3\text{PO}_4$  0 ppm. All column chromatography was performed using small columns ( $5 \times 60 \text{ mm}$ ) with silica gel (Aldrich), 700–230 mesh,  $60 \text{ \AA}$ , and pore volume of  $0.75 \text{ cm}^3 \text{ g}^{-1}$  as the stationary phase. Electrospray Ionization mass spectra were obtained on a Waters Synapt G2 ESI-Q-TOF

mass spectrometer. Elemental analyses were performed at Midwest Microlabs, LLC (Indianapolis, IN).

### Crystallography

All crystallographic measurements were carried out on a Rigaku Mini CCD area detector diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 223 K using an Oxford Cryostream low-temperature device. A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using Crystal Clear Expert 2.0. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinements on  $F_2$  using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen. Colorless, single crystals of [2][OTf] were obtained by slow vapor diffusion of diethyl ether into a dichloromethane solution saturated with the compound. This compound crystallized in the monoclinic space group  $P2_1/m$ , and key details of the crystal and structure refinement data are summarized in Table S2.† Further crystallographic details may be found in the respective CIF files which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference number for [2][OTf] was assigned as 1453179.

### Computational details

All geometries were optimized using the M06<sup>47</sup> density functional method with LANL2DZ basis/pseudopotential for antimony and 6-31G(d,p) basis set for other atoms. Stationary points were characterized as minima by vibrational frequency analysis from the Hessian matrix. Solvent effect was included using the SMD implicit solvent model for dichloromethane. This method was chosen for geometry optimization since the computed bond parameters of the catalyst [Sb]<sup>+</sup> are in good agreement with the experimental values (Fig. S70†). The energies were further refined using M06/6-31+G(2d,2p) [LANL2DZdp] electronic energies. All calculations were performed using Gaussian 09.<sup>48</sup> In the catalytic Pathway II dimeric H<sub>2</sub>O species was included, in order to correctly model the hydrogen bonding interactions and solvation effects of the hydronium ion and water molecules in the solution. Propanal was used as the model aldehyde in the computational study. The enthalpy energies in the main articles were reported in kcal mol<sup>-1</sup>.

### Synthetic details

#### Synthesis of dibromo triphenylstiborane (Ph<sub>3</sub>SbBr<sub>2</sub>).

A 250 mL Schlenk flask was charged with triphenylstibine (5 g, 14.16 mmol), 20 mL of diethyl ether, and a magnetic stirbar. Under an atmosphere of nitrogen, bromine (2.48 g, 0.80 mL, 15.57 mmol) diluted in 2 mL of ether was added drop wise. Immediately, the precipitation of a white solid was observed. After all of the bromine had been added, the reaction mixture was stirred for 30 minutes at room temperature, after which time mother liquor was decanted away from the resulting solid. The solid product was then washed with diethyl ether

(5 × 50 mL), until the washings were colorless. No further purification was needed in subsequent reactions, and Ph<sub>3</sub>SbBr<sub>2</sub> was isolated in 90% yield as a white solid. Spectroscopic data was in agreement with known values.<sup>49</sup>

**Synthesis of [2][Br].** A 100 mL Schlenk flask was charged with 1-diphenylphosphino-8-iodonaphthalene (1 g, 2.28 mmol) a magnetic stirring bar and 40 mL of tetrahydrofuran. The solution was degassed and cooled to -78 °C followed by the drop wise addition of *n*BuLi (2.2 M in hexanes, 1.55 mL, 3.42 mmol). After the addition was completed, the solution was stirred for an additional 2 hours at -78 °C during which time the color became dark red. The reaction mixture was then cooled to -110 °C (LN<sub>2</sub>/acetone slurry) and a solution of Ph<sub>3</sub>SbBr<sub>2</sub> (1.28 g, 2.51 mmol) in THF (5 mL) was added drop wise. The resulting solution was stirred at -110 °C for two hours and was then allowed to warm to room temperature overnight. After that time the color of the solution turned to pale orange. The solvent was then removed *in vacuo* to yield a brown solid which was washed with a 1 : 3 DCM : hexanes solvent mixture (3 + 15 mL) to remove traces of any unreacted starting materials and salt byproducts. The residue then was dissolved in DCM and filtered over Celite. The filtrate was then concentrated to afford [2][Br] as a yellow solid in 70% yield which was used in the next step without further purification. Note: [2][Br] very air and moisture sensitive, and should be stored under an atmosphere of nitrogen at all times. m.p. 120–122 °C. <sup>1</sup>H NMR (400 MHz) (CDCl<sub>3</sub>):  $\delta$  6.56–6.61, 7.08–7.13, 7.3 (m, 10H, PPh), 7.44–7.88(m, 19H, SbPh + H<sub>3</sub> + H<sub>4</sub>), 8.33–8.34(d, 1H, H<sub>2</sub>,  $J = 8.4$  Hz), 8.41–8.44(d, 1H, H<sub>1</sub>,  $J = 8.4$  Hz). <sup>13</sup>C NMR (100.61 MHz):  $\delta$  128.85, 128.94, 129.81, 130.68, 131.95, 132.40, 132.53, 134.14. <sup>31</sup>P NMR (161.9755 MHz) (CDCl<sub>3</sub>):  $\delta$  -38.50. Elemental analysis calculated (%) for C<sub>42</sub>H<sub>35</sub>BrCl<sub>4</sub>PSb ([2][Br] + 2 (CH<sub>2</sub>Cl<sub>2</sub>)): C: 51.31, H: 3.38. Found: C: 51.42, H: 3.65. C<sub>40</sub>H<sub>31</sub>PSb<sup>+</sup> HRMS(ESI<sup>+</sup>)  $m/z$ : (M - Br) calculated: 663.1202. Found: 663.1201.

**Synthesis of [2][OTf].** A 100 mL Schlenk flask was charged with [2][Br] (1 g, 1.34 mmol), silver(i) triflate (370 mg, 1.47 mmol), a magnetic stirring bar, and 50 mL of DCM. The flask was covered with aluminum foil and the reaction was stirred for 5 hours in the dark. The resulting suspension was then filtered over Celite to remove AgBr, and the filtrate was concentrated *in vacuo* to give a brown oily material that solidified after drying under high vacuum overnight (~80% yield). The resultant brown solid was further purified by dissolving in an excess of diethyl ether (5 mL) followed by the addition of hexanes (50 mL) to precipitate [2][OTf] as a white solid that is stable to air and moisture (700 mg, 65% yield). m.p. 94–96 °C <sup>1</sup>H NMR (400 MHz) (CDCl<sub>3</sub>):  $\delta$  6.46–6.51, 7.06–7.10, 7.26–7.29 (m, 10H, PPh), 7.43–7.84(m, 19H, SbPh + H<sub>3</sub> + H<sub>4</sub>), 8.34(d, 1H, H<sub>2</sub>,  $J = 8.4$  Hz), 8.42, 8.44(d, 1H, H<sub>1</sub>,  $J = 8.4$  Hz). <sup>13</sup>C NMR (100.61 MHz):  $\delta$  128.93, 129.01, 130.94, 132.22, 132.29, 132.30, 132.56, 133.97, 133.98. <sup>31</sup>P NMR (161.9755 MHz) (CDCl<sub>3</sub>):  $\delta$  -36.10. <sup>19</sup>F NMR (376.49 MHz):  $\delta$  -78.50(triflate). Elemental analysis calculated (%) for C<sub>42.2</sub>H<sub>33.4</sub>F<sub>3</sub>O<sub>3</sub>PCl<sub>2.4</sub>SSb ([2][OTf] + 1.2 CH<sub>2</sub>Cl<sub>2</sub>): C: 55.37, H: 3.68. Found: C: 55.29, H: 3.61.

$C_{40}H_{31}PSb^+$  HRMS(ESI<sup>+</sup>)  $m/z$ : (M – OTf) calculated: 663.1202. Found: 663.1201.

**Synthesis of [4][OTf].** A 100 mL Schlenk flask was charged with 1-bromonaphthalene (500 mg, 2.4 mmol) a magnetic stirring bar and 40 mL of tetrahydrofuran. The solution was degassed and cooled to  $-78$  °C followed by the drop wise addition of *n*BuLi (2.2 M in hexanes, 2.41 mL, 5.31 mmol). The resulting solution became dark and was stirred for 2 hours at  $-78$  °C after which time  $Ph_3SbBr_2$  (1.36 g, 2.65 mmol) in THF (5 mL) was added drop wise. The solution was allowed to warm to room temperature overnight and the color changed from pale yellow to colorless. The reaction mixture was concentrated *in vacuo* to afford an oily material that was washed with a 1 : 3 DCM : hexanes solvent mixture (3 × 15 mL). The residue was then dissolved in DCM (50 mL) and then filtered over Celite. The filtrate was then concentrated to dryness to give a white semi-solid material which was used without further purification. The solid was then dissolved in DCM (40 mL) and the solution was transferred to a 100 mL Schlenk flask that was wrapped in aluminum foil. To this solution was added AgOTf (510 mg, 1.96 mmol) and the resulting suspension was allowed to stir at room temperature for 12 hours. The suspension was then filtered over Celite and the filtrate was concentrated to dryness *in vacuo* to give a brown oily material which was washed with cold hexanes to give a white solid. After drying under high vacuum overnight, [4][OTf] was obtained as a white solid that is stable to air and moisture (1.06 g, 70% yield). m.p. 90–92 °C. <sup>1</sup>H NMR (400 MHz) (CDCl<sub>3</sub>):  $\delta$  7.53–7.57, 8.10–8.14, 8.30–8.35(m, 3H, H<sub>1</sub>, H<sub>2</sub>, H<sub>5</sub>), 7.63–7.84(m, 19H, ShPh + H<sub>3</sub> + H<sub>4</sub>). <sup>13</sup>C NMR (100.61 MHz): 127.66, 129.23, 130.95, 131.35, 131.73, 133.43, 133.86, 135.52, 135.57. <sup>19</sup>F NMR(376.4983 MHz):  $\delta$  –78.30(triflate). Elemental analysis calculated (%) for:  $C_{31}H_{26}F_3O_3SbCl_4$  ([4][OTf + 2(CH<sub>2</sub>Cl<sub>2</sub>)]): C: 46.59, H: 3.28. Found: C: 46.07, H: 2.80.  $C_{28}H_{22}Sb^+$  HRMS(ESI<sup>+</sup>)  $m/z$ : (M – OTf) calculated: 479.0760. Found: 479.0760.

## Conclusions

We have synthesized two unknown stibonium triflate salts, [2][OTf] and [4][OTf], and have demonstrated for the first time that these cations can serve to catalyze: (1) the reductive coupling of aldehydes to give symmetric ethers (L), (2) the Aldol condensation of aldehydes to give  $\alpha$ - $\beta$  unsaturated compounds (M), and (3) the cyclotrimerization of aldehydes to the corresponding 1,3,5-trioxanes (N). Spectroscopic and computational data have revealed that the highly Lewis acidic cationic anti-mony(v) center engages the Lewis basic oxygen atom of these aldehydes in a strong interaction which ultimately polarizes the C=O bond.

We have evidence which suggested that a transient hydro-silylated product **L<sub>b</sub>** is involved in the formation of ethers L. These results may provide synthetic chemists with new opportunities for the preparation of asymmetric ethers. Likewise we have also determined that water plays an important role in the

Aldol condensation reaction catalyzed by [2]<sup>+</sup> or [4]<sup>+</sup>. We have also explored the potential for [2]<sup>+</sup> to catalyze cross-Aldol condensation reactions, however at this time the selectivity for the crossed product needs improvement. Despite this limitation, we have also found that 1,3,5-trioxanes can be readily produced at low temperature free from solvent, or in the presence of inert solvents such as (Me<sub>3</sub>Si)<sub>2</sub>O, but lower temperatures are required to tune the selectivity and increase the reactivity of the process.

For the latter two reactions, there was no apparent difference in catalytic activity or selectivity between cations [2]<sup>+</sup> and [4]<sup>+</sup>. However, it was found that cation [2]<sup>+</sup> was a far superior catalyst in terms of both activity and selectivity for the preparation of ethers L when compared to [4]<sup>+</sup>. Unfortunately, the computational analyses of this reaction using [2]<sup>+</sup> as a catalyst did not reveal any informative data regarding the presence of the diphenylphosphino moiety. While it may be possible that sterics lie at the heart of the selectivity difference observed between [2]<sup>+</sup> and [4]<sup>+</sup>, we can't rule out the possibility that the phosphine substituent may impart ulterior electronic effects which ultimately govern the formation of the product. Current investigations are guided toward a more detailed mechanistic understanding how of these stibonium cations interact with carbonyl-containing substrates.

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