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## Phosphonium-stibonium and bis-stibonium cations as pnictogen-bonding catalysts for the transfer hydrogenation of quinolines

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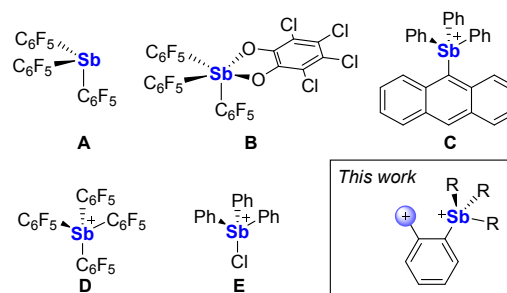
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**Abstract:** Bifunctional Lewis acidic group 15 compounds have emerged as appealing platforms for anion sensing and organocatalysis. As part of our interest in the chemistry of these compounds, we have now compared the catalytic properties of  $[o\text{-}(\text{MePPH}_2)\text{C}_6\text{H}_4\text{SbPh}_2]^+$  (**[3]**<sup>+</sup>),  $[o\text{-}(\text{PPH}_2)\text{C}_6\text{H}_4\text{SbPh}_3]^+$  (**[4]**<sup>+</sup>),  $[o\text{-}(\text{MePPH}_2)\text{C}_6\text{H}_4\text{SbPh}_3]^{2+}$  (**[5]**<sup>2+</sup>), and  $[o\text{-C}_6\text{H}_4(\text{SbMePh}_2)_2]^{2+}$  (**[6]**<sup>2+</sup>) using the transfer hydrogenation of 2-phenyl-quinoline and 3-bromoquinoline with Hantzsch ester as a benchmark reaction. This study, which also involved an evaluation of the catalytic properties of  $[\text{Ph}_4\text{Sb}]^+$  and  $[\text{Ph}_3\text{MeP}]^+$ , shows that antimony cations are generally more active than their phosphorus counterparts. Our results also demonstrate that dicationic systems such as **[6]**<sup>2+</sup> are superior activators.

Antimony halides display elevated Lewis acidity<sup>1</sup> and have been used for numerous applications<sup>2</sup> including the generation of superacids.<sup>3</sup> Organoantimony derivatives, although significantly less acidic than their halide counterparts, are generally air and water stable and thus easy to handle.<sup>4–11</sup> Owing to these advantageous characteristics, organoantimony derivatives have been studied as catalysts for a number of reactions that proceed by electrophilic pathways.<sup>2, 12, 13</sup> As documented in recent contributions, stibines and stiboranes featuring electron-withdrawing ligands as in the case of **A** and **B** (Figure 1) are sufficiently Lewis acidic, or sufficiently potent pnictogen bond donors, to promote a range of reactions including the transfer hydrogenation of imines using Hantzsch ester.<sup>14, 15</sup> Because Coulombic effects may enhance the affinity of antimony(V) centres for polar or charged substrates, stibonium cations such as 9-anthryltriphenylstibonium (**C**) have also been considered as antimony-based Lewis acids.<sup>16</sup> Such species, which have found applications in small anion sensing including in water,<sup>17, 18</sup> are also emerging as appealing catalytic platforms for organic reaction that involve an electrophilic activation step.<sup>19–28</sup> Efforts to increase the Lewis acidic properties of such cations have led us to consider stibonium cations such as **D** and **E** where the electron-withdrawing nature of the fluorinated aryl or halogen ligand notably increases the electron deficiency of the antimony center.<sup>28</sup> The elevated Lewis acidic properties of these cations become manifest in their ability to catalyse the dimerization of 1,1-diphenylethylene or the polymerization of THF.<sup>27, 28</sup> While these elevated Lewis acidic properties are attractive, working

with these highly electron-deficient stibonium cations is complicated by their instability toward moisture and their propensity to undergo reduction. For these reasons, we have now contemplated an alternative approach in which the Lewis acidity or pnictogen-bond donor properties of the stibonium center would be enhanced by a nearby secondary cationic moiety.

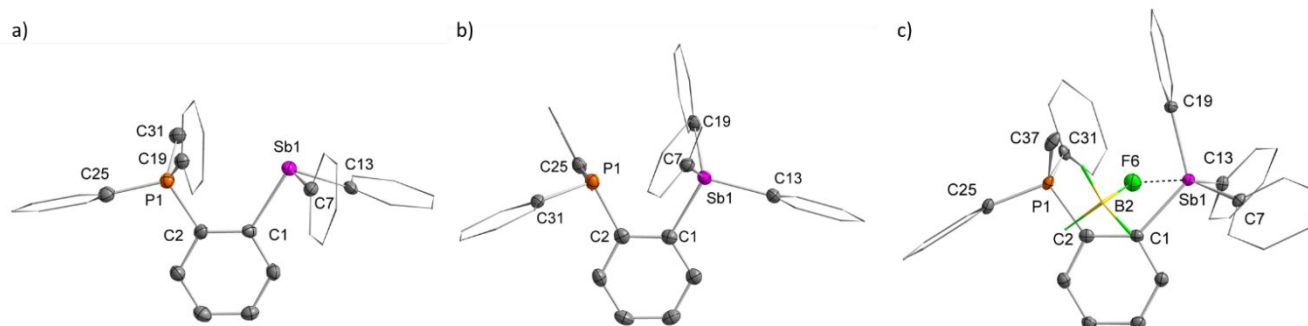


**Figure 1.** Example of stibonium cations used as Lewis acid catalysts and general structure of the dication targeted in this study.

To explore this idea, we targeted the phosphonium and stibonium cations depicted in Figure 2. These cations were synthesized as the tetrafluoroborate salts using literature protocols in the case of **[1]**<sup>+</sup>,<sup>29</sup> **[2]**<sup>+</sup>,<sup>30</sup> and **[6]**<sup>2+</sup>,<sup>26</sup> or by methylation of the known phosphinostibine  $o\text{-C}_6\text{H}_4(\text{PPH}_2)(\text{SbPh}_2)$  with MeI followed by  $\text{I}^-/\text{BF}_4^-$  anion exchange in the case of **[3]**<sup>+</sup> $[\text{BF}_4]^-$  (Scheme 1). Salt **[4]**<sup>+</sup> $[\text{BF}_4]^-$  was obtained by reaction of  $o\text{-}(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{Li}$  with  $\text{Ph}_3\text{SbBr}_2$  followed by  $\text{Br}^-/\text{BF}_4^-$  anion exchange (Scheme 1). Salt **[4]**<sup>+</sup> $[\text{BF}_4]^-$  could be converted into **[5]**<sup>2+</sup> $[\text{BF}_4]_2^-$  using trimethyloxonium tetrafluoroborate (Scheme 1). All salts obtained can be stored in air for extended periods of time. The stability of **[5]**<sup>2+</sup> is particularly surprising if one considers that  $[o\text{-C}_6\text{H}_4(\text{PPH}_2\text{Me})_2]^{2+}$  undergoes rapid

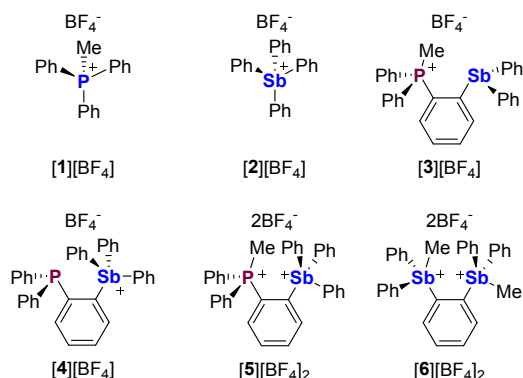
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Electronic Supplementary Information (ESI) available: Experimental details, crystallographic data of ## in cif format. NMR spectra, and additional ##. See DOI: 10.1039/x0xx00000x

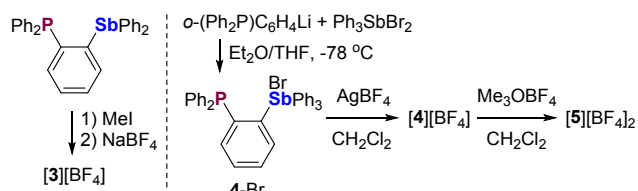


**Figure 3.** Crystal structure of a)  $[3][BF_4]$ , b)  $[4][BF_4]$  and c)  $[5][BF_4]_2$ . Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms and the free  $[BF_4]^-$  anions are omitted for clarity. Selected bond lengths (Å) and angles (deg) for  $[1][BF_4]$ : Sb1-P1 = 3.540(2), C1-Sb1-C7 = 96.1(2), C1-Sb1-C13 = 96.7(2), C7-Sb1-C13 = 98.5(2), C2-P1-C31 = 112.3(3), C2-P1-C19 = 107.6(3), C2-P1-C25 = 109.8(3), Sb1-C1-C2 = 122.7(4), P1-C2-C1 = 121.6(4); For  $[2][BF_4]$ : P1-Sb1 = 3.321(1), P1-Sb1-C13 = 161.3(1), C1-Sb1-C7 = 106.2(1), C1-Sb1-C19 = 113.3(1), C7-Sb1-C19 = 115.4(1), P1-C2-C1 = 118.3(3), Sb1-C1-C2 = 119.8(3); For  $[3][BF_4]$ : Sb1-P1 = 3.922(1), Sb1-F6 = 3.038(2), C1-Sb1-C7 = 106.4(1), C1-Sb1-C19 = 123.7(1), C7-Sb1-C13 = 108.3(1), C2-P1-C25 = 104.8(2), C2-P1-C31 = 107.6(2), C25-P1-C31 = 111.6(2).

hydrolysis in the presence of adventitious water.<sup>31</sup> No such tendency toward decomposition was observed in the case of  $[5]^{2+}$ . All new salts have been fully characterized. The phosphonium units in  $[3]^+$  and  $[5]^{2+}$  give rise to a single  $^{31}P$  NMR resonance at 23.6 ppm and 26.5 ppm, respectively. The associated  $^1H$  NMR methyl resonance appears as a doublet at 3.14 ppm ( $^2J_{H-P} = 13.0$  Hz) and 2.50 ppm ( $^2J_{H-P} = 13.3$  Hz), respectively. In the case of  $[4][BF_4]$ , the  $^{31}P$  NMR resonance at 11.4 ppm is shifted significantly downfield with respect to that of  $PPh_3$  (-6 ppm). We assign this downfield shift to the presence of a donor-acceptor interaction between the Lewis basic phosphine and the Lewis acidic antimony centre. The  $^{31}P$  NMR chemical shift of  $[4]^+$  can be compared to the value measured in  $o\text{-}C_6H_4(PPh_2)((SbPh_2)(O_2C_6Cl_4))$  (25.5 ppm) which was also shown to possess such an intramolecular P→Sb bond.<sup>13</sup>

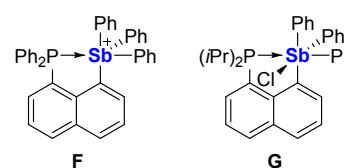


**Figure 2.** Cationic phosphorus and antimony Lewis acids investigated herein.



**Scheme 1.** Synthesis of  $[3][BF_4]$  (left),  $[4][BF_4]$  (right) and  $[5][BF_4]_2$  (right).

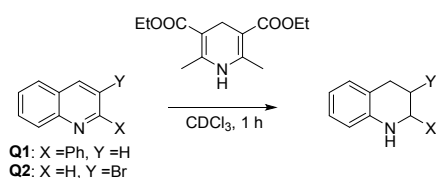
The crystal structures of  $[3][BF_4]$ ,  $[4][BF_4]$ , and  $[5][BF_4]_2$  have been determined (Figure 3). The first notable feature of these structures concerns the short contacts that may exist between the anion and the group 15 atoms. While both  $[3][BF_4]$  and  $[4][BF_4]$  are free of such short contacts, one of the two anions in  $[5][BF_4]_2$  forms a Sb-F interaction of 3.038(2) Å. The presence of this short interaction reflects the enhanced Lewis acidic or pnictogen bond donor character of the antimony atom in this dicationic derivative. A second noteworthy point relates to the P-Sb separation of 3.321(1) Å in the structure of  $[4][BF_4]$ . Although this distance is longer than that in  $o\text{-}C_6H_4(PPh_2)((SbPh_2)(O_2C_6Cl_4))$  (3.0268(12) Å), the P1-C2-C1 angle (118.3(3)°) is smaller than 120°, indicating attraction of the two group 15 centres. We interpret this small distortion as manifesting the presence of a weak intramolecular P→Sb interaction (see SI). This weak P-Sb interaction is reminiscent of that present in naphthalene based-systems<sup>32</sup> such as **F**<sup>23</sup> and **G**<sup>33</sup>. Given the constraints imposed by the naphthalene backbone, these dative interactions are shorter and thus likely stronger.



In the next phase of this study, we decided to test the cations represented in Figure 2 as catalysts for the transfer hydrogenation reaction known to occur between Hantzsch ester and quinolines.<sup>34</sup> The first set of reactions was carried out in  $CDCl_3$  with a 5 mol% catalyst loading using 2-phenylquinoline as a substrate. We found that the monophosphonium cations  $[1][BF_4]$  and  $[3][BF_4]$  were essentially inactive (entries 1 and 3). Conversely, the reaction proceeded smoothly in the presence of the monostibonium salts  $[2][BF_4]$  and  $[4][BF_4]$ , reaching 26% and 24% conversion, respectively, after 1 hour (entries 2 and 4). The comparable activity of these two cations shows that the weak P → Sb in

[4]<sup>+</sup> has no significant influence on the reactivity of the stibonium cation. The results obtained with these four monocations show that the antimony species are significantly more active, in line with their documented intrinsic higher Lewis acidity.<sup>16, 35, 36</sup> With the view of verifying that the Lewis acidity of the stibonium cation would be enhanced by a nearby secondary cationic moiety, we became eager to evaluate [5][BF<sub>4</sub>]<sub>2</sub> (entry 5) which indeed afforded a significantly higher conversion (61% yield) than those obtained with the monostibonium salts [2][BF<sub>4</sub>] and [4][BF<sub>4</sub>]. The use of the bistibonium salt [6][BF<sub>4</sub>]<sub>2</sub> afforded a further enhancement in activity, with a conversion of 90% after 1 hour (entry 6). The greater activity of [6]<sup>2+</sup> is assigned to the presence of two adjacent Lewis acidic antimony centres which can cooperatively activate the substrate. The previous characterization of [6-η<sub>2</sub>-DMF]<sup>2+</sup>, an adduct in which the DMF carbonyl oxygen atom interacts with the two antimony atoms, illustrate this possibility.<sup>26</sup> We have also tested **B** as a catalyst (entry 7) and found that it afforded only a ~5% yield after 1 hour, which is just slightly higher than for the uncatalyzed reaction (entry 8). This low yield underscores the role played by the cationic nature of the Lewis acid in these reactions. We have also studied these group 15 catalysts in the hydrogenation of 3-bromoquinoline, a more reactive substrate. The results (entries 9-16), although less contrasted than those obtained with 2-phenylquinoline, support the above conclusions that dicationic systems are the most active and that stibonium cations supersede their phosphonium counterparts.

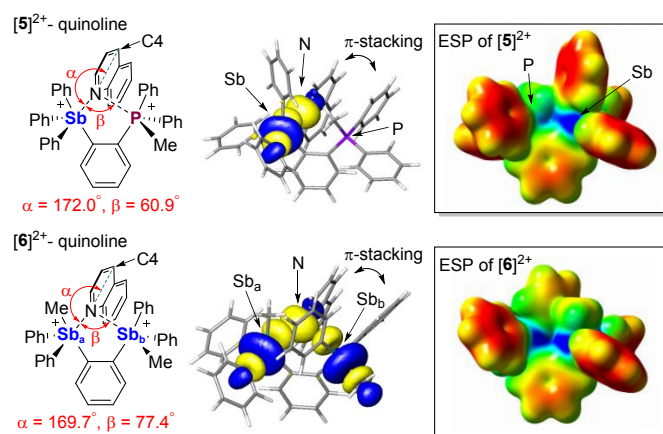
**Table 1.** Transfer hydrogenation of quinolines.



Entry	Cat.	Substrate	Time	Yield
1	[1][BF <sub>4</sub> ]	Q1	1 h	<1%
2	[2][BF <sub>4</sub> ]	Q1	1 h	26%
3	[3][BF <sub>4</sub> ]	Q1	1 h	< 1%
4	[4][BF <sub>4</sub> ]	Q1	1 h	24%
5	[5][BF <sub>4</sub> ] <sub>2</sub>	Q1	1 h	61%
6	[6][BF <sub>4</sub> ] <sub>2</sub>	Q1	1 h	90%
7*	<b>B</b>	Q1	1 h	5%
8	-	Q1	1 h	3%
9	[1][BF <sub>4</sub> ]	Q2	10 min	23%
10	[2][BF <sub>4</sub> ]	Q2	10 min	60%
11	[3][BF <sub>4</sub> ]	Q2	10 min	< 1%
12	[4][BF <sub>4</sub> ]	Q2	10 min	51%
13	[5][BF <sub>4</sub> ] <sub>2</sub>	Q2	10 min	76%
14	[6][BF <sub>4</sub> ] <sub>2</sub>	Q2	10 min	86%
15	<b>B</b>	Q2	10 min	30%
16	-	Q2	10 min	< 1%

Lastly, DFT calculations were used to simulate the double activation of the substrate by the dicationic systems, a step

that would precede transfer of a hydride from the Hantzsch ester.<sup>37</sup> We first investigated [5]<sup>2+</sup> using quinoline as a model substrate. The lowest energy structure shows coordination of the quinoline molecule to the antimony centre via a Sb-N contact of 3.11 Å. The value of the  $\alpha$  angle (172.0°) defined in Figure 5 indicates that the antimony atom is positioned along a direction aligned with the nitrogen lone pair. As confirmed by Natural Bond Orbital calculations, the two atoms are connected by a donor-acceptor interaction of  $lp(N) \rightarrow \sigma^*(Sb-C)$  character. As suggested by application of the NBO deletion protocol, these interactions stabilize the complex by  $E_{del} = 12.6$  kcal/mol. No short contacts are observed between the quinoline nitrogen and the potentially acidic phosphorus atom.<sup>38, 39</sup> However, the quinoline appears to be engaged in a  $\pi$ -stacking interaction with a phosphorus-bound phenyl ring (Figure 4). This interaction may help orient the substrate within the bifunctional pocket of [5]<sup>2+</sup>, thereby assisting coordination of the nitrogen atom to the Lewis acidic antimony center. In [6]<sup>2+</sup> - quinoline, the quinoline is preferentially bound to one of the antimony atoms (Sb<sub>a</sub>) with which it forms an Sb<sub>a</sub>-N contact of 3.16 Å, close the corresponding distance in [5]<sup>2+</sup> - quinoline. The value of the  $\alpha$  angle (169.7°) is also close to that in [5]<sup>2+</sup> - quinoline. As indicated by the Sb<sub>a</sub>-N-Sb<sub>b</sub> angle of 77.4° (defined as  $\beta$  in Figure 4), the second antimony atom Sb<sub>b</sub> is positioned along a direction approximately perpendicular to the Sb<sub>a</sub>-N vector, leading to a longer Sb<sub>b</sub>-N distance of 3.58 Å. These Sb-N distances are both within the sum of van der Waals radii of the two elements ( $\Sigma_{vdWR}(Sb,N) = 4.13$  Å),<sup>40</sup> suggesting donor-acceptor bonding. Congruent with this view, an NBO analysis indicates that the quinoline molecule interacts with the two antimony centres via  $lp(N) \rightarrow \sigma^*(Sb-C)$  interactions which contribute  $E_{del} = 10.9$  kcal/mol to the stability of the complex. We also note that, as in [5]<sup>2+</sup> - quinoline, the quinoline is engaged in a  $\pi$ -stacking interaction with a phenyl ring bound to Sb<sub>b</sub>. Last, we note that the electrostatic potential surface of [5]<sup>2+</sup> and [6]<sup>2+</sup> shows a distinct, yet buried positive area that corresponds to the intersecting  $\sigma$ -holes of the pnictogen atoms (Figure 4). These features indicate that these adducts are also stabilized by an ionic contribution. We propose that the cooperativity of the two Lewis acidic pnictogen units is at the origin of the superior catalytic activity of [5]<sup>2+</sup> and [6]<sup>2+</sup>. Similar effects have been invoked in the case of benzodiselenazoles which also act as catalysts for the transfer hydrogenation of quinolines.<sup>34, 37</sup>



**Figure 4.** Optimized structure of  $[5]^{2+}$ -quinoline and  $[6]^{2+}$ -quinoline. NBOs of the nitrogen lone pair (lp(N)) and the major accepting antibonding orbital ( $\sigma^*(\text{Sb}-\text{C})$ ) are also shown (isovalue = 0.05). The inset shows that ESP of  $[5]^{2+}$  and  $[6]^{2+}$  (isosurface: 0.005 au; red: 0.18 au, blue: 0.32 au).

In conclusion, we have synthesized and studied a series of bifunctional *ortho*-phenylene phosphorus and antimony derivatives in which one if not both of the group 15 centres exist as pnictogenium cations. Using the transfer hydrogenation of quinolines with Hantzsch ester as a benchmark, we find that the dicationic derivatives  $[5][\text{BF}_4]_2$  and  $[6][\text{BF}_4]_2$  are the most active. This reactivity illustrates the benefits that result from the introduction of a second cationic functionality in these derivatives. The higher catalytic activity displayed by the bis-stibonium dication  $[6]^{2+}$  may be assigned to the juxtapositions of two Lewis acidic antimony(V) units that may cooperatively activate the substrate. Last but not least, the results obtained in this study show that simple stibonium cations such as  $[2]^+$  ( $[\text{SbPh}_4]^+$ ) are significantly more active than neutral electron-deficient stiboranes such as **B**.

## Conflicts of interest

There are no conflicts to declare.

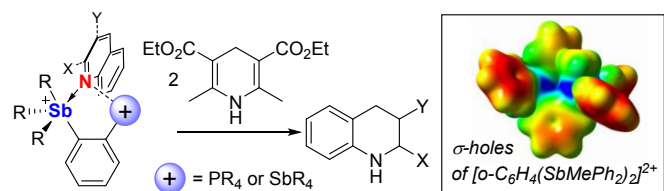
## Acknowledgements

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Bifunctional group 15 dications are effective transfer hydrogenation catalysts, the activity of which culminates in the case of the bis-sibonium dication  $[\text{o-C}_6\text{H}_4(\text{SbMePh}_2)_2]^{2+}$ .