Tunable pnictogen bonding at the service of hydroxide transport across phospholipid bilayers

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ABSTRACT: Our growing interest in the design of pnictogen-based strategies for anion transport has prompted an investigation into the properties of three simple triarylcatecholatostiboranes (**1**-**3**) of the general formula (*o*-$C_6Cl_4O_2$)$SbAr_3$ with Ar = Ph (**1**), *o*-tolyl (**2**) and *o*-xylyl (**3**) for the complexation and transport of the hydroxide anion across phospholipid bilayers. A modified hydroxypyrene trisulfonate (HPTS) assay carried out in artificial liposomes shows that **1** and **2** are potent hydroxide transporters while **3** is inactive. These results indicate that the steric hindrance imposed by the three *o*-xylyl groups prevents access by the hydroxide anion to the antimony center. Supporting this interpretation, **1** and **2** quickly react with TBAOH·30 H_2O to form the corresponding hydroxoantimonate salts [^{n}Bu$_4$N][**1**-OH] and [^{n}Bu$_4$N][**2**-OH], whereas **3** resists hydroxide coordination and remains unperturbed. Moreover, the hydroxide transport activities of **1** and **2** necessitate the presence of the +V oxidation state and coordination environment of the catecholatostiborane framework as their parent +III stibines show no hydroxide transport activity.

The transport of anions across membranes requires water-stable and appropriately lipophilic compounds capable of capturing an anion before shuttling it through the membrane.[1] Research in this field, which has implications for new treatments for diseases, has typically been dominated by hydrogen bond donors.[2] Recently, this field has witnessed the entry of main group derivatives, whose Lewis acidic properties can be leveraged for the transport of anions across phospholipid bilayers.[3] This possibility has been unambiguously established for the simple antimony(V) derivatives[4] such as the stibonium cation $[Ph_4Sb]^+$ (**A**, Figure 1) which complexes and transports halides across phospholipid bilayers.[5] Interestingly, efforts from the past few years have also shown that appropriately substituted antimony(III) derivatives such as stibine **B** function as chloride anion transporters.[3b, 6] The ability of such stibines to transport anions derives from the pnictogen bond (PnB) donicity of the antimony atom which can engage the chloride anion *via* a σ hole interaction probably dominated by electrostatic forces.[7] Given our interest in anion transporters that could respond to the changes in the redox environment of the medium,[3c, 5b, 8] we have now decided to establish whether the anion transport properties of stibines could be turned on *via* oxidation of the antimony center.

As part of our ongoing efforts toward the development of transporters for hard anions, we have chosen to test this idea with hydroxide as the anionic cargo. This choice was guided by the relevance of hydroxide transport to pH gradient modulation across biological interfaces.[9] We also note that strategies for selective hydroxide transport have implications beyond biology, with applications in new strategies for alkaline nuclear tank waste treatment.[10] However, the targeted and reversible complexation of the hydroxide anion in aqueous solutions is complicated by the high hydration energy of this anion (-430 kJ/mol)[11] and its tendency to decompose its receptors. These difficulties have been explicitly overcome only in a few documented cases,[2c, 12] adding urgency to the present work.

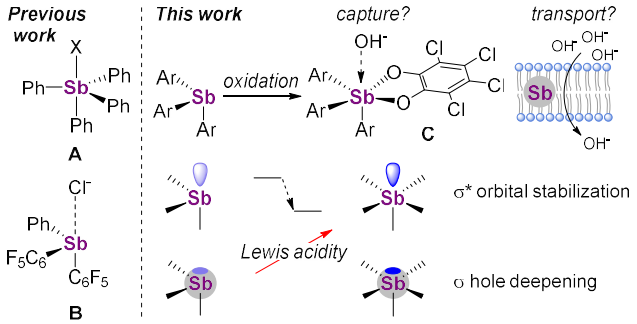

Figure 1. Important precedents and investigative framework of this study.

While σ hole interactions in triarylstibines might in principle enable hydroxide transport, we contended that the stronger PnB donor properties of antimony(V) derivatives (or stiboranes) would deliver greater activities.[13] Thus, we turned our attention to a subclass of stiboranes called catecholatostiboranes (**C**, **Figure 1**)[14] which can complex hard anions[4a] in competitive media.[15] The properties of these derivatives can be easily adjusted by the choice of catecholate ligand[15-16] and its aryl substituents,[13] providing several avenues for tuning anion complexation properties. Importantly, even with their high Lewis acidity, catecholatostiboranes are generally air and water stable,[15, 17] features that we have exploited for the biphasic capture of fluoride.[16] Although their hydroxide complexation behavior has not been structurally documented, the isolation of stiborane-water adducts,[17a, 18] reversible acid-base titration assays,[17b] and the similar complexation chemistry of fluoride and hydroxide suggest their aptitude in this regard. With these precedents as a backdrop,

we have set out to investigate the hydroxide transport properties of catecholatostiboranes and compare them to those of their trivalent precursors.

Compounds **1**-**3** were synthesized *via* treatment of their parent stibines[19] with one equivalent of *o*-chloranil in CH_2Cl_2 **(Figure 2)**. While **1** is a known compound,[4a, 17b, 17d] the yellow-colored **2** and **3** are new and have thus been fully characterized (Figures S1-S4). The ^{1}H NMR spectra of **2** and **3** reveal four and two aromatic resonances, respectively, indicating fluxional structures with equivalent rings at room temperature. Solutions of **1** and **2** in coordinating solvents (i.e. DMSO, THF, etc.) lose their typical yellow color over time, a feature that we have previously ascribed to the coordination of a solvent molecule at the σ*(Sb-C) orbital.[17c, 20] Nevertheless, these associations are benign to the receptors, as they are stable as solutions in d_6-DMSO:D_2O (9.5:0.5 (v/v)) (Figure S9-S10).

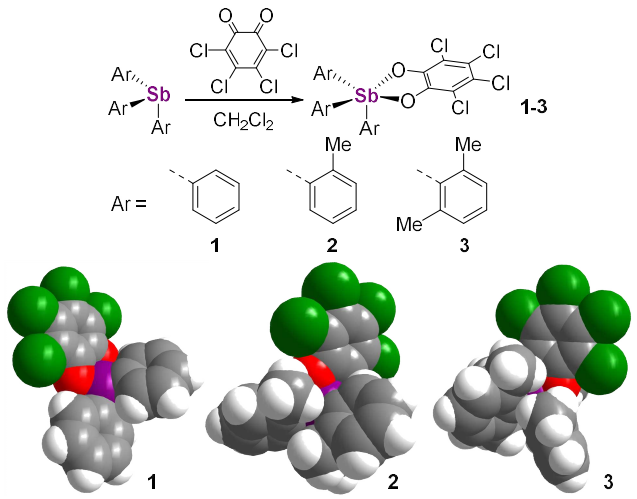

Figure 2. Left: Synthesis of stiboranes **1**-**3**. Right: Space-filling models of the solid-state structures of stiboranes **1**[17d]-**3**. For **3**, only one of the structures found in the asymmetric unit cell is shown. Color code: purple (Sb), red (O), green (Cl), grey (C), white (H).

In the solid-state, **2** adopts a geometry best described as a distorted square pyramidal, as evidenced by its crystallographically-determined geometric parameter (τ_5)[21] of 0.04, which is assigned to the one-sidedness of the *o*-tolyl substituents. Interestingly, the bulkier derivative **3** adopts a less distorted trigonal bipyramidal geometry as indicated by its τ_5 value of 0.61 which is very close to that determined for **1** (0.65).[17d] The variation seen in the τ_5 values of these simple derivatives illustrates the molecular flexibility of these pentavalent derivatives.[22] Because crystal structures only incompletely capture the possible geometries that these compounds can adopt, the value above should not be overinterpreted with regards to accessibility of the antimony center. A more pertinent parameter that captures this feature is the percent volume buried (%V_{bur}) of the antimony center of these derivatives which stand at 84.0%, 91.3% and 96.3% for **1**, **2** and **3**, respectively. Such can be seen when visualizing the crystal structures of the compounds as space-filling models (**Figure 2**), whose antimony surfaces are increasingly shielded from view with increasing substitution on their aryl rings. Accordingly, this effect accompanies an increase in the lipophilicities of the structures, as readily captured by the computed octanol/water partition coefficients (logK_{ow}) values of 7.48, 7.66, and 8.58 for **1**, **2**, and **3**, respectively.

Evidence for hydroxide anion complexation came following treatment of the corresponding Lewis acids with TBAOH·30 H_2O ($[TBA]^+$ = $[^nBu_4N]^+$) in CH_2Cl_2/MeOH. Beginning with **1**, the characteristic yellow color of the stiborane faded away quickly when treated with TBAOH·30 H_2O, and the corresponding hydroxoantimonate [**1**-OH]$^-$ was isolated as an $[^nBu_4N]^+$ salt (**Figure 3**). The resulting colorless solid has been characterized by multinuclear NMR as well as X-ray crystallography (Figures S5-S6). Inspection of the compound's solid-state structure confirms the presence of a hydroxide anion bound to the antimony atom, which adopts a distorted octahedral geometry like the previously characterized fluoride analogue [**1**-F]$^-$.[17b] The Sb-O1 distance in [**1**-OH]$^-$ of 2.0191(16) Å is below the sum of the covalent radii of the two elements (2.05 Å)[23] with a formal shortness ratio of 0.98,[24] confirming a strong PnB. Indeed, this bond length is on par with the Sb-O bond length found for Ph_4Sb-OH (2.048 Å)[25] as well as a methoxide-bound stiborane (2.0381(10) Å).[26]

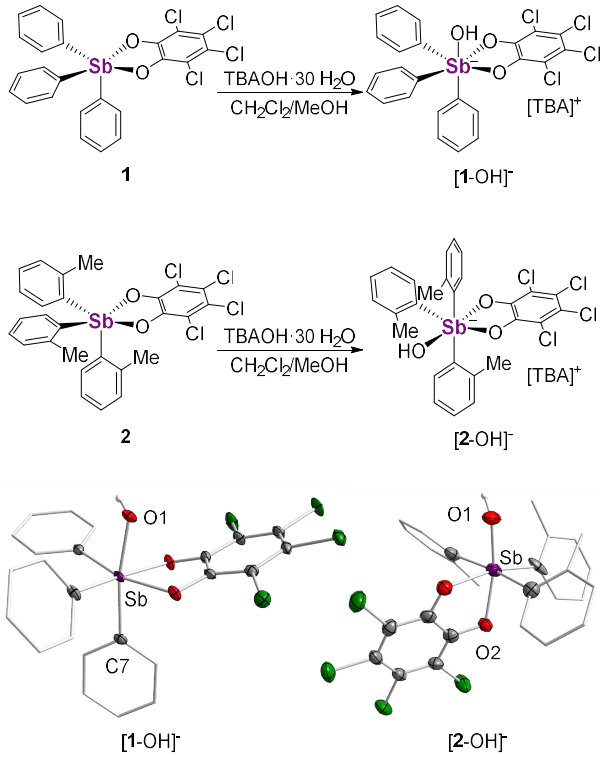

Figure 3. Top Syntheses of [**1**-OH][^{n}Bu$_4$N] and [**2**-OH][^{n}Bu$_4$N]. Bottom: solid-state structures of [**1**-OH]$^-$ and [**2**-OH]$^-$. Hydrogen atoms (excluding the hydroxide hydrogens) and $[^nBu_4N]^+$ counterions are omitted for clarity. Selected bond lengths (Å) and angles (°) for [**1**-OH]$^-$: Sb-O_1 = 2.0191(16), O_1-Sb-C_7 = 169.96(8). Selected bond lengths (Å) and angles (°) for [**2**-OH]$^-$: Sb-O_1 = 2.006(4), O_1-Sb-O_2 = 165.29(15).

Despite its crowded surface, **2** readily reacts with

TBAOH·30 H_2O, furnishing crystals of [**2**-OH][^{n}Bu$_4$N] that reveal the docking of hydroxide to the antimony atom (**Figure 3**). While it also adopts a distorted octahedral geometry, [**2**-OH]$^-$ positions its bound hydroxide *trans* to its oxygen ligand at a Sb-O_1 distance of 2.006(4) Å. Such a configuration, which has some precedence with other bulky stiborane Lewis adducts,[17c] further speaks to the flexibility of Sb(V) species.[22b] No hydroxide-bound adduct of **3** could be obtained and no reaction was seen following the addition of excess TBAOH·30 H_2O to the stiborane in $CDCl_3$:d_6-DMSO (1:1 (v/v)) by ^{1}H NMR (Figure S11), suggesting that the steric bulk around the antimony atom prohibits contact with the anion.[27]

Visualization of the electrostatic potential maps of the hydroxide-accepting structures of **1** and **2** were then generated by removing the bound hydroxide from [**1**-OH]$^-$ and [**2**-OH]$^-$, respectively. This approach allows us to identify the antimony-centered σ holes associated to $V_{S,max}$ values of 46.8 kcal·mol^{-1} and 57.6 kcal·mol^{-1}, respectively at the sites of hydroxide anion complexation (**Figure 4**). The depths of these σ holes are commensurate with the electron-withdrawing abilities of the element *trans* to the electropositive surface,[28] with the more polar Sb-O bond of **2** giving rise to a deeper σ hole than the Sb-C bond of **1**. A similar analysis of the parents Ph_3Sb and (o-tol)$_3$Sb could not locate antimony-centered $V_{S,max}$ values, reflecting the deepening of the associated σ hole provided by oxidation to the +V state.[13] Oxidation also lowers the antimony-centered acceptor LUMO energy which were computed at the relaxed geometries (-1.70 eV for **1**[29] and -1.59 eV for **2** vs. -0.59 eV for Ph_3Sb and -0.50 eV for (o-tol)$_3$Sb).

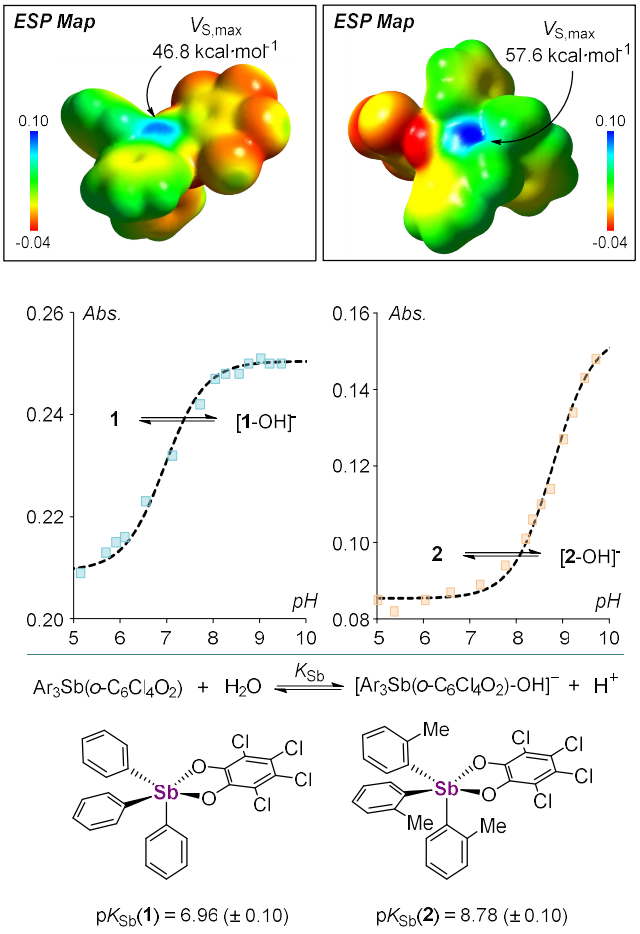

Figure 4. Top: Electrostatic potential maps of the hydroxide-accepting geometries of **1** and **2** (isovalue: 0.0015 a.u, gradient scale values given in a.u.). Bottom: Spectrophotometric titration data collected for **1** and **2** in H_2O:THF (9.5:0.5 (v/v), 0.01 M ethanolamine, 0.045 M Triton X-100). Bottom: Summary of pK_{Sb} values for compounds **1** and **2**.

Prior to testing these compounds for anion transport, it became imperative to confirm their ability to engage hydroxide anions in aqueous media. We thus sought to measure their pK_{Sb} values – that is, the pH values at which the stiboranes are bound by hydroxide – by acid-base titration monitored by UV-vis spectroscopy, as we had previously reported for **1**.[17b] We repeated this experiment using a slightly different medium leading to pK_{Sb} values of 6.96 (± 0.10) and 8.78 (± 0.10) for **1** and **2**, respectively (**Figure 4**). The higher value measured for **2** reflects how the *ortho*-methyl substituents lower the Lewis acidity of the antimony center. This passivating substituent effect becomes extreme in the case of **3** as indicated by the lack of spectral changes in the pH 5-10 window chosen for this study. While we propose that formation of [**1**-OH]$^-$ and [**2**-OH]$^-$ results from the direct complexation of a hydroxide anion, we cannot rule out the incipient involvement of a water adduct that would undergo subsequent deprotonation.

With these results in hand, we then set about testing these compounds with prepared 1-palmitoyl-2-oleoyl-glycero-3-phosphocholine (POPC) large unilamellar vesicles (LUVs) loaded with hydroxypyrene trisulfonate

(HPTS), a fluorescent pH indicator.[30] These LUVs were subjected to a KOH pulse to produce a pH gradient, followed by an injection of the potassium-cation selective transporter valinomycin.[2c] Hydroxide transport from the external medium to the vesicle interior was then initiated by the addition of the antimony derivative, and HPTS fluorescence was monitored (see Section 4.2 in the Supporting Information for more details). To begin, injection of a THF blank revealed no significant hydroxide transport. However, addition **1** and **2** as THF solutions elicited rapid and potent dissipation of the pH gradient (**Figure 5**).

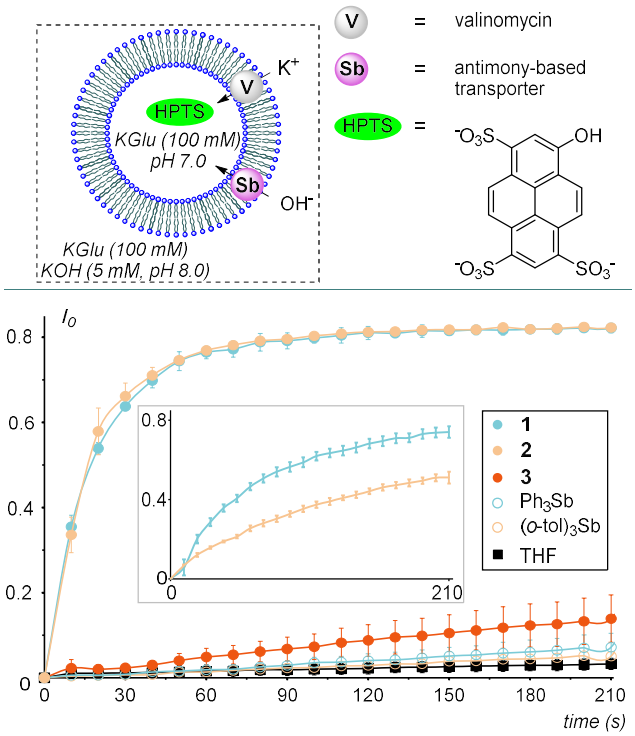

Figure 5. Top: Experimental design featuring the hydroxide transport by the various antimony compounds in the presence of valinomycin (0.005 mol% with respect to lipid concentration). Bottom: Valinomycin-coupled hydroxide influx into POPC vesicles triggered by addition of a THF solution of stiboranes **1-3**, Ph_3Sb, or $(o\text{-tol})_3Sb$ (2 mol% with respect to lipid concentration) as monitored by HPTS fluorescence. POPC concentration: 0.1 mM. Error bars represent the standard deviations of three experiments. Inset shows the superior hydroxide transport activity of **1** compared to **2** at 0.05 mol%, near the EC_{50} value of **2**.

Further analysis reveals that **1** outperforms **2** in this regard as indicated by the EC_{50} values at 210 s of 6.9 10^{-3} mol% for **1** and 37 10^{-3} mol% for **2** (Figures S15-S16). We ascribe this differential activity to the muted Lewis acidity of **2** compared to **1** due to the steric and electronic effects of the appended *ortho*-methyl groups. This is further supported by the lack of activity of **3** whose Lewis acidic surface is inaccessible to the target anion. Further mechanistic insight can be gleaned from the derived Hill coefficients of each active stiborane being n~ 1, indicating the transport of one hydroxide anion per one receptor. Satisfyingly, administering **2** to POPC LUVs loaded with carboxyfluorescein revealed no leakage, indicating that its activity likely does not result from destabilization of the vesicle membrane (Figure S17). We then became curious whether their corresponding stibines were capable of hydroxide transport as well. Indeed, neither Ph_3Sb nor $(o\text{-tol})_3Sb$ were active as hydroxide transporters 2 mol% with respect to lipid concentration, suggesting that the strong Sb(V)-centered PnB is necessary for hydroxide transport.

These results serve to introduce new members of a growing class of hydroxide transporters based on strong, but reversible antimony-centered PnBs of neutral catecholatostiboranes. These compounds can be leveraged to adjust transmembrane pH gradients *via* the transmembrane transport of hydroxide. This activity is controllable on two fronts. First, the superior PnB donor properties of the +V oxidation state provide catecholatostiboranes the ability to shuttle hard anions across phospholipid membranes compared to their lower valent counterparts. Second, the hydroxide transport activity of these stiboranes can be tuned by prohibiting or enabling access to the antimony(V) surface. Investigation into the transport of other anions by this class of transporters in our laboratory is underway.

ASSOCIATED CONTENT

Experimental and computational details. Crystallographic data in cif format. Optimized structures in xyz format. These materials are available free of charge *via* the Internet at http://pubs.acs.org.

Accession Codes

CCDC 2323724-2323727 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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