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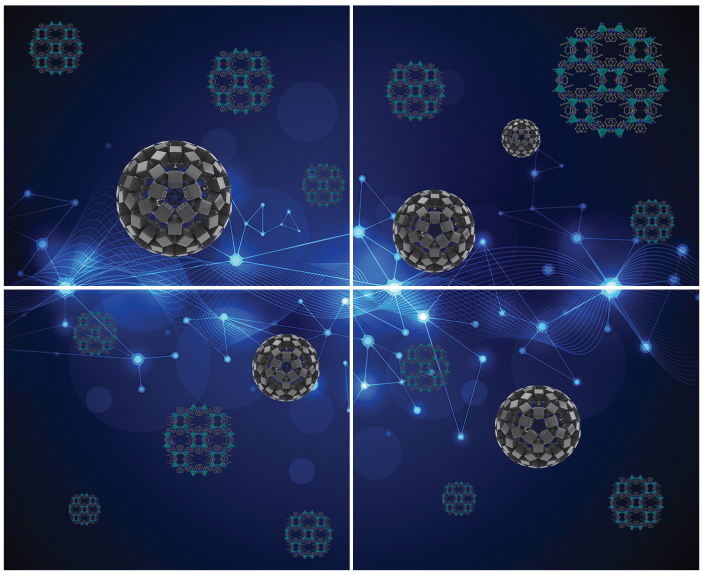

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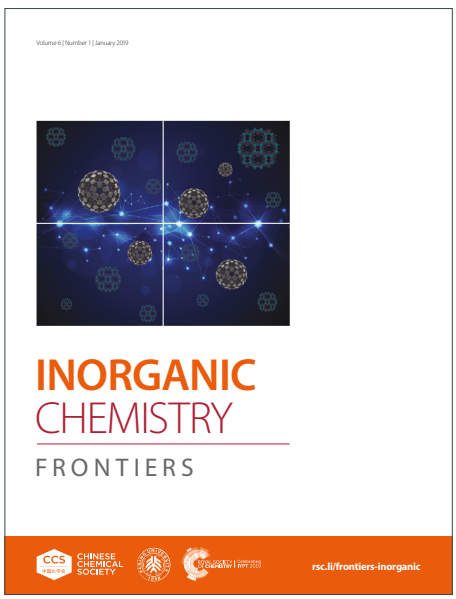

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COMMUNICATION

Acidity/hydridicity evaluation of Sb-H bonds and formation of a new Group 15 metal cluster topology

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We report the first estimates for the proton transfer ability and hydride donor ability of a fifth-row E-H bond besides Sn-H bonds. A new D_{2d}-symmetric cluster type for M_8 species (M = pnictogen) is shown, along with the first amido-stibanide. Sterically determined deprotontion and redox outcomes are demonstrated.

The chemistry of main group element-hydrogen (E-H) bonds is an important area of study due to its relevance for synthesis (e.g., reduction),[1] catalysis (e.g., hydrogenation),[2] energy storage (e.g., hydrogen surrogates),[3] and materials science (e.g., metal deposition).[4, 5] In contrast to E-H bonds involving second-, third-, and fourth-row p-block elements, the chemistry of the heavier fifth- or sixth-row elements remains underexplored due to synthetic challenges.[6, 7]

The reactivity of light E-H bonds is generally well-predicted by polarity considerations.[6, 7] For example, compounds containing B-H, Al-H, or Ga-H bonds generally behave as hydride sources and compounds containing N-H, P-H, or As-H bonds generally behave as proton sources. Only in rare cases, namely, when either very Lewis basic or very Lewis acidic co-reactants are present, or very strong π-donor groups flank protic E-H bonds, does the reactivity deviate from these trends.[8-10]

For heavier elements, simple bond polarity arguments are not always good predictors of reactivity as radical processes like bond homolysis can also be accessible for their long and weak E-H bonds.[6, 7] This feature underpins the widespread use of light or radical-activated organotin hydrides such as $^{n}Bu_3SnH$ in organic synthesis.[11] Thus, the ability to access diverse fission pathways offers a rich bouquet of chemical reactivity for heavy main group E-H species with demonstrated practical applications. A deeper understanding of fundamental parameters for heavy E-H bonds is needed to enable the rational development of their multifaceted chemistry, but such data remain elusive. For example, widely employed acidity and hydridicity references lack values for fifth- and sixth-row main group elements (with the exception of tin), and, to the best of our knowledge, such values have not been experimentally reported for antimony or bismuth.[1, 12, 13] Nevertheless, species with reactive Sb-H bonds are implicated in fascinating stoichiometric and catalytic processes,[14-19] motivating the pursuit of fundamental data about this functional group and a deeper understanding of its reaction modes.

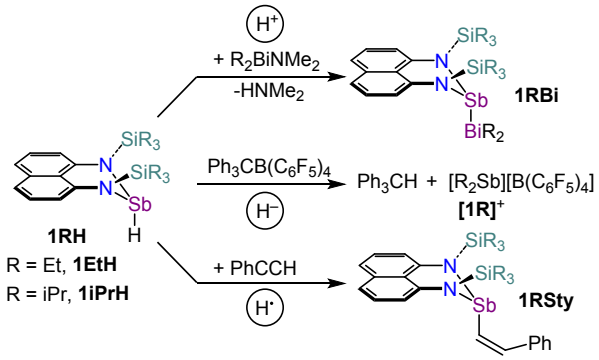

Figure 1. Observed modes of reactivity for derivatives of **1RH**.

We have been studying the chemistry of Sb-H bonds in derivatives of **1RH**, starting with the discovery of hydrostibination in 2019.[20] Our original report showed that **1EtH** is a source of hydride, rapidly yielding Ph_3CH in reactions with the Ph_3C^+ cation (with presumed formation of unisolable [**1R**]$^+$). Subsequently, we found that **1EtH** is also a source of protons towards M-N or M-C bonds, giving the first examples of bismuthanylstibanes **1RBi** and Sb-Fe bimetallics.[21, 22] Finally, we found evidence of Sb-H homolysis and a radical mechanism in the reaction of **1RH** with phenylacetylene to give styrene **1RSty**.[23] Thus, derivatives of **1RH** show diverse reactivity modes within a single molecular platform. Recognizing this feature and the abovementioned scarcity of reactivity data for heavy E-H bonds,[24, 25] here we provide the first estimates of proton and hydride transfer ability for **1RH** (R = Et, iPr) by bracketing experiments and product isolation studies. We also reveal a

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new main group cluster topology. Our results deepen the fundamental understanding of Sb-H bonds and metallocluster formation to guide further developments in antimony chemistry, while providing insights that may also translate to other heavy main group E-H bonds.

As compounds **1EtH** and **1iPrH** are both highly air and moisture sensitive, standard titration experiments using protic solvents are unsuitable for establishing their proton transfer ability. Moreover, as we show later, the anions formed by deprotonation only have a fleeting existence, precluding the establishment of a true equilibrium between the derivatives of **1RH**, H^+, and [**1R**]$^-$. Given these limitations, we adopted a bracketing approach involving the combination of **1RH** with organic bases whose pKa values are known in THF to look for evidence of proton transfer. The pKa of the most basic species that fails to react with **1RH** forms one limit of the pKa bracket, while the pKa of the least basic species that deprotonates **1RH** forms the other limit. An additional limitation arises from the possibility of base coordination to the metal rather than deprotonation as we have previously shown the derivatives of **1RH** exhibit antimony-centred Lewis acidity and coordination.[20, 23] To thwart such coordination and promote reactivity at the Sb-H bond, only bases of moderate to high steric bulk that were soluble in non-protic solvents were suitable.

Through pairwise reactions between equimolar amounts of **1EtH** and >20 bases, we successively narrowed the limits of the pKa range spanned by the limiting bases. This process culminated with the finding that piperidine (pKa of conjugated acid in THF = 14.3)[26] failed to deprotonate **1EtH** while 1,1,3,3-tetramethylguanidine (TMG, pKa of conjugated acid in THF = 15.5)[26] succeeded, bracketing the proton transfer ability of **1EtH** to within the 14.3-15.5 pKa range in THF (Figure S1-5). No other suitable base could be found within this range to further narrow the pKa bracket. The analogous sequence of experiments with **1iPrH** indicated a proton transfer ability value in the 20.2-21.0 pKa range, with the phosphazene base ^{t}butylimino-tri(pyrrolidino)phosphorane (BTTP, pKa of conjugate acid in THF = 20.2)[26] being unable to significantly deprotonate this compound, while 7-methyl-1,5,7-trizabicyclodecene (TBD, pKa of conjugate acid in THF = 21.0)[26] was successful (Figure S6-9). To the best of our knowledge, despite being ranges rather than absolute values, these represent the first *experimental* acidity measurements for any fifth- or sixth-row main group E-H bond, besides Sn-H bonds.

The significant reduction in acidity going from **1EtH** to **1iPrH** was surprising, given that the Sb-H group is well-separated from the substitutional changes occurring in the silyl groups. We hypothesized that this may have a kinetic origin, namely, that the bulky triisopropylsilyl groups prevent approach of the base to the Sb-H bond, thereby suppressing deprotonation that may otherwise readily occur in a less hindered case. To evaluate this possibility, we calculated the energies for transferring a proton from each compound to the di-isopropylamide anion using density functional theory and a polarization continuum model for THF. The ΔG for this reaction (-34.07 kcal/mol) captures the relative acidity of **1EtH** and iPr_2NH, indicating that the latter is 24.99 pKa units less acidic than the former. Based on the experimentally known pKa of iPr_2NH (35.7 in THF), a DFT-calculated value of 10.71 is obtained for **1EtH**.[27] The analogous calculation for **1iPrH** yielded a calculated pKa of 9.06. These calculated values, which reflect *thermodynamic*, not kinetic, outcomes by ignoring counterion, solvation, and steric effects, are quite close to one another (within 2 pKa units). By comparison, the experimental brackets for the two compounds are separated by almost 6 pKa units, supporting our hypothesis of kinetic inhibition for **1iPrH**.

Next, we sought to isolate the stibanide anions resulting from deprotonation of **1RH**. Breunig has previously characterized derivatives of $R_2SbLi(THF)_3$ (R = Ph, Mes; Mes = 2,4,6-trimethylphenyl) by deprotonation of the corresponding R_2SbH precursor with nBuLi in THF.[28] Power also generated the Ph_2Sb^- anion in a crown ether solvated lithium salt via deprotonation of Ph_2SbH with nBuLi.[29] More recently, von Hänisch isolated alkali metal salts of the parent stibanide, $[SbH_2]^-$, via reaction between SbH_3 and nBuLi or MO^{t}Bu salts (M = Na, K, Rb, Cs).[30] In contrast to such compounds, derivatives of **1RH** feature π-electron-rich amido groups and stibanides featuring such groups remain unknown, further motivating our attempts to isolate them.

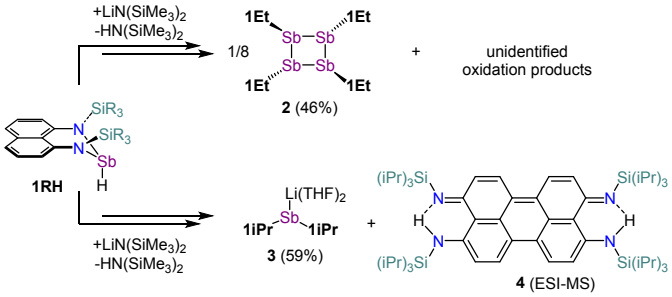

Figure 2. Formation of compounds **2** and **3** and oxidation product **4** detected by ESI-MS.

Combining **1EtH** with LiHMDS resulted in an immediate colour change to dark red/orange and formation of hexamethyldisilazane, as per ^{1}H NMR spectroscopy. The prominent ^{1}H NMR resonance of the Sb-H group at ca. 10 ppm also disappeared, as did the associated Sb-H stretch at 1883 cm^{-1} in the IR spectrum (Figure S20). Storage of the solution at -30 °C yielded red crystals identified by a diffraction experiment as compound **2**, which has the overall formula $(LSb-Sb)_4$, where L is the triethylsilyl naphthalenediamine ligand. This outcome confirms the deprotonation but indicates that the subsequent anion is unstable towards redox rearrangement and ligand loss, instead yielding polystibanes. Such redox chemistry has previously only been observed in reactions of antimony centres containing a single organic group [e.g. $RSbCl_2$ or *cyclo*-$(RSb)_n$] and reducing agents such as alkali metals.[28, 31] Cluster formation has, however, *not* been observed following deprotonation of Ar_2SbH or SbH_3,[30] highlighting the distinct reactivity of amido-substituted secondary stibanes. It is likely that the increased

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lability of the very polar Sb-N bonds compared to Sb-C or Sb-H bonds permits reaction trajectories involving the loss of even chelating amido ligands. The electron-rich nature of the naphthalenediamine ligand also makes it more susceptible to oxidation.[32-34]

The structure of compound **2** is remarkable for two reasons. First, the open D_{2d}-symmetric metal core (Figure 3b) is unprecedented for pnictogens. Reported molecular Sb_8 compounds form S_8-like eight-membered rings,[35] realgar-like closed polycycles,[36] or interconnected 2 x Sb_4 rings.[37] Second, the planarity of the Sb_4 core (D_{4h}) is unexpected in the absence of any obvious multiple bonding. Indeed, four-membered pnictogen rings form folded structures (Figure 3c), whereas the Sb_4 core of **2** is more reminiscent of σ-aromatic $[M_4]^{4+}$ rings.[38]

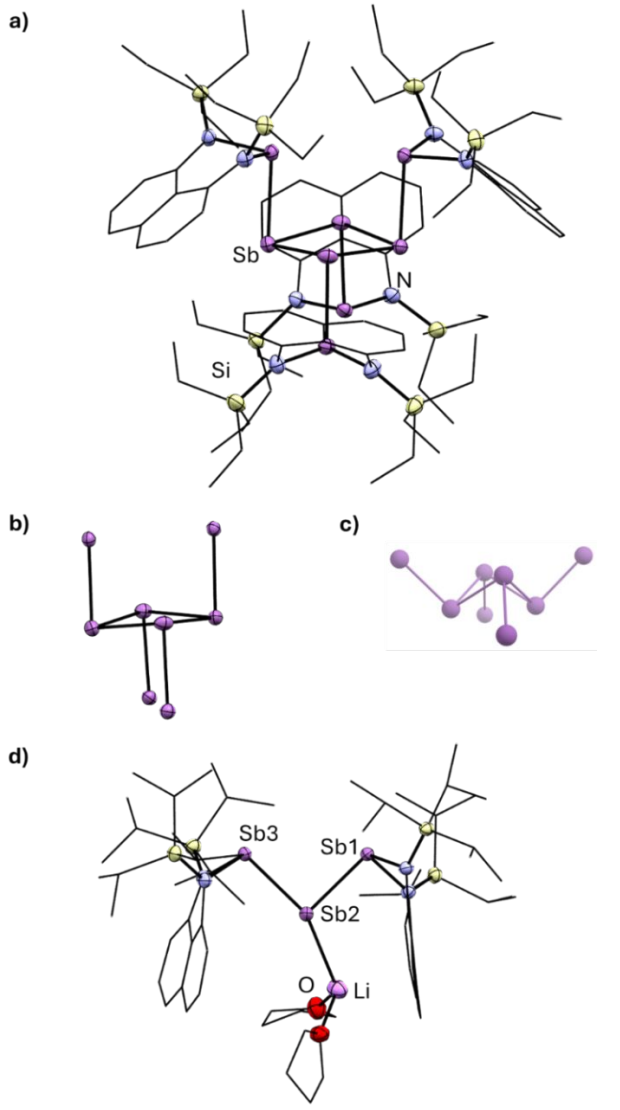

Figure 3. a) Structure of **2** in the solid state as determined by single crystal diffraction. Hydrogen atoms have been omitted, and ellipsoids are drawn at 50% probability. b) The Sb_8 core of compound **2** with amido ligands omitted for clarity. c) The folded structure of the Sb_8 core, as found in the calculated structure of N-Me substituted derivative **2'**. d) Structure of **3** in the solid state as determined by single crystal diffraction. Hydrogen atoms have been omitted, and ellipsoids are drawn at 50% probability. Lithium aryl interactions are omitted but are comprised by an η^4 interaction with the naphthalene ring.

Multiple bonding can be ruled out as the cause of planarity since the Sb-Sb bond distances within the Sb_4 core [2.8452(4)-2.8683(4) Å] are comparable to those between the core and peripheral Sb atoms [2.8264(4)-2.8342(4) Å]. Lattice packing effects can also be discounted since the DFT-calculated structure of an isolated molecule closely resembles the one that is experimentally observed. And although we have previously shown that silylnaphthalene diamine ligands are exceptional dispersion donors,[39] this feature appears to have only a minor effect in terms of promoting planarity – DFT calculations including or omitting dispersion corrections gave very similar geometries, matching the experimental structure (Figure S23). Instead, it appears that the high steric repulsion between the silyl groups forces the ring to be flat such that the distance between the ligands is maximized. Consistently, the only other molecule showing such an open D_{2d} M_8 arrangement (M = main group metal) is $[(Me_3Si)_3Ge\text{-}Ge]_4$, which features the very large $(Me_3Si)_3Ge$ group.[40] Further supporting this steric repulsion argument, the DFT-optimized geometry of a hypothetical, sterically *unhindered*, N-Me substituted derivative showed a heavily puckered ring (metal portion shown in Figure 3c, see Figure S22) that reflects the expected shape for such a species.

The analogous anion isolation experiment of **1iPrH** with LiHMDS also showed complete loss of the Sb-H functional group by NMR and IR spectroscopy. However, recrystallization of the reaction mixture in this case gave a lithium tristibanide salt **3** as a THF solvate (Figure 3d). Tristibanides have previously been prepared by reduction of cyclotetrastibanes or triarylstibanes with alkali metals.[29, 41] Formation of an Sb_3 rather than Sb_8 unit from **1iPrH** is likely due to the high steric bulk of the triisopropylsilyl groups, which prevents the more extensive aggregation needed to make the Sb_8 cluster found in **2**. In this context, compound **3** can be considered a kinetic snapshot of a stabilized intermediate en route to larger clusters. The Sb-Sb bond distances in the tristibanide **3** [2.7704(9) and 2.7546(8) Å] are on average 0.07 Å shorter than the corresponding values in the neutral polystibane **2**, while the average Sb-N distance in **3** (2.083Å) is slightly longer than in **2** (2.042 Å). We ascribe these differences to hyperconjugation between the lone pairs at Sb2 and the Sb1-N σ* acceptor orbitals, which would increase Sb2-Sb1 covalency at the expense of Sb1/3-N bonding.

To determine the fate of the lost ligand equivalents in formation of **2** and **3**, we conducted mass spectrometric analyses of reaction mixtures from which these clusters were obtained (Figure S24-30). The spectra for the reaction involving **1iPrH** showed formation of tetraaminoperylene **4** (Figure S28), which is the expected oxidation product in line with Gade's previous report that 1,8-bis(silylamino)naphthalene complexes of thallium (a fifth-row metal like antimony) undergo loss of reduced thallium metal with concomitant formation of tetraaminoperylenes.[32]

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To estimate the hydride ion affinity of [**1R**]$^+$, a similar bracketing methodology was applied. After testing >20 boron, carbon, and silicon-based Lewis acids, we observed that i) boron Lewis acids were unsuitable due to formation of multiple B-C/Sb-H metathesis products, and ii) both stibanes readily transferred a hydride to the $[Ph_3C]^+$ cation (calculated hydride ion affinity = 471.5 kJ/mol in dichlorobenzene).[42] The latter reactions result in the clean disappearance of the Sb-H resonance and appearance of the C-H resonance of triphenylmethane. Moreover, we found that neither stibane transferred a hydride to the $[Et_3Si]^+$ cation (calculated hydride ion affinity = 463.6 kJ/mol in dichlorobenzene).[42] This allows us to bracket the hydride ion affinity of [**1R**]$^+$ as being in the 463.6-471.5 kJ/mol range, which almost perfectly encapsulates the DFT-calculated HIA values of 461 kJ/mol for **1EtH** and 460 kJ/mol for **1iPrH**, indicating minimal steric modulation. Diarylstibenium cations have previously been prepared by hydride abstraction from secondary stibanes.[43, 44] N-heterocyclic stibenium ions, including those featuring a naphthalenediamine core, have been structurally authenticated previously.[45-48] However, several attempts showed that isolation of these highly reactive cations with N-silyl ligands was not possible in our hands. Once generated, they decomposed with half-lives on the order of hours in solvent, precluding access to pure samples. Crystallization attempts gave oils that continued to degrade even under inert atmosphere. Nevertheless, in line with the bracketing above, we confirmed that addition of Et_3SiH to the putative [**1R**]$^+$ product in the reaction between **1RH** and $[Ph_3C]^+$ immediately regenerated the resonances for **1RH** (Figure S10-13), supporting the intermediacy of a stibenium ion abstracting hydride from Et_3SiH.

In summary, we have determined the first estimates for the proton transfer ability and hydride donor ability of two stibanes, providing rare fundamental data about fifth-row E-H bonds. The proton transfer ability estimates reflect *effective* acidity rather than absolute acidity because true equilibrium between **1RH** and **[1R]**$^-$ is prevented by the onward redox reactivity of the stibanides to give clusters and chains. Nevertheless, observations employing a broad range of bases reproducibly and unambiguously indicate that diamidostibanes are comparable in acidity to protonated guanidines (pKa ~15), except when sterically very hindered. The latter point is made by **1iPrH**, which shows comparably low acidity to protonated phosphazene superbases (pKa ~20). As part of attempts to isolate stable stibanides, we additionally isolated the first D_{2d}-symmetric M_8 cluster for the pnictogens, evidencing a topology that has only been observed in the case of one germanium species.[40] The first amido-substituted tristibanide was also isolated. The isolation of these clusters evidences divergent behaviour towards bases as a function of substituent at Sb (aryl vs amido), and steric bulk ($NSiEt_3$ vs $NSi(^iPr)_3$). On the other end of the spectrum, bracketing experiments indicate that the stibanes are slightly weaker hydride donors (HIA ~460 kJ/mol) than trialkylsilanes like Et_3SiH. Here, the stibenium products could not be isolated due to instability, but strong evidence of their formation and persistence was observed by reverse titration with Et_3SiH. Collectively, these results provide insights into Sb-H bonds, which may have implications for future applications in areas such as catalysis, main group nanocluster formation, and metal deposition.

Conflicts of interest

There are no conflicts to declare.

Data availability

Crystallographic data for compounds **2** and **3** has been deposited at the Cambridge Structural Database under accession numbers 2495433-2495434.

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The data supporting this article have been included as part of the Supplementary Information.

Crystallographic data for compounds **2** and **3** has been deposited at the Cambridge Structural Database under accession numbers 2495433-2495434.

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