

Steric congestion in heavy pnictines alters oxidative halogenation pathways

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ABSTRACT

Dihalotriorganopnictoranes serve as important synthetic precursors in Group 15 chemistry, but the influence of the organic substituents on the synthesis and reactivity of these compounds remains underexplored for the heavy pnictogens. We recently reported the isolation of Dipp_3Sb (Dipp = 2,6-diisopropylphenyl). The bulky Dipp substituents permit the isolation of monomeric tetrahedral stibine oxide Dipp_3SbO , yet also allow for the formation of the trigonal bipyramidal $\text{Dipp}_3\text{SbF}_2$. We now report the isolation of a sterically crowded bismuthine, Dipp_3Bi . Reaction between Dipp_3Bi and XeF_2 afforded $\text{Dipp}_3\text{BiF}_2$, which features a distorted trigonal bipyramidal geometry in the solid state. Reaction between Dipp_3Bi and PhICl_2 resulted in the generation of 1-chloro-2,6-diisopropylbenzene. Reaction between Dipp_3Sb and PhICl_2 resulted in the formation of $\text{Dipp}_3\text{SbCl}_2$, which features a square pyramidal geometry in the solid state. $\text{Mes}_3\text{SbCl}_2$, $\text{Mes}_3\text{SbBr}_2$, $\text{Mes}_3\text{BiCl}_2$, and $\text{Mes}_3\text{BiBr}_2$ (Mes = mesityl) were structurally characterized and all exhibit trigonal bipyramidal geometries in the solid state. Solution-phase spectroscopic measurements reflect the fluxionality of all of these molecules, but theoretical analyses in the gas phase suggest that the square pyramidal geometry of $\text{Dipp}_3\text{SbCl}_2$ is more thermodynamically favorable than the trigonal bipyramidal geometry, possibly due to the presence of intramolecular secondary interactions between the Dipp and Cl substituents. These results highlight the ability of Dipp substituents to alter reactivity pathways of heavy pnictines.

1. Introduction

Investigation of the Group 15 elements, the pnictogens, is in a state of rejuvenation following recent realizations of exciting reactivity that can be harnessed from carefully designed main-group compounds [1]. The variable coordination numbers and facile access to multiple oxidation states enjoyed by the pnictogens invite comparisons to transition-metal chemistry [2–6]. Of particular note are pnictogen compounds that can access variable redox states to effect catalytic chemical transformations, as well as compounds that exhibit extreme Lewis acidity that can be exploited for practical applications [7–14]. For example, catalytic hydrodefluorination of aryl C–F bonds has been achieved via an oxidative addition/reductive elimination pathway at a C_s -symmetric phosphorous triamide and an N,C,N -pincer complex of Bi(I) [15,16]. Although the catalytic redox chemistry of phosphorus is dominated by cycling between the +3 and +5 oxidation states, examples of Bi(I/III), Bi(II/III), and Bi(III/V) cycles have been reported in recent years [7,8,17,18].

Pnictogen chemistry also has a rich history in medicine. The clinically approved drug, brigatinib, features a dimethylphosphine oxide

moiety that imparts salutary pharmacokinetic properties relative to more traditionally used polar groups [19]. Arsenic trioxide is a clinically approved treatment for acute promyelocytic leukemia, and nano-material delivery platforms are in development to further expand its therapeutic potential [20]. The antimonial drugs meglumine antimoniate (Glucantime) and sodium stibogluconate (Pentostam) are used to treat the neglected tropical disease leishmaniasis; the molecular structures of these compounds are hitherto unknown but under intense investigation [21]. The role of bismuth in medicine is perhaps most widely known because of bismuth subsalicylate (Pepto-Bismol), a globally marketed gastrointestinal medication, but compounds of bismuth are also under investigation for the treatment of viral and bacterial infections [22]. Furthermore, efforts are being made toward the design of Bi^{3+} chelators that can deliver α -emitting ^{213}Bi nuclei to biological targets for cancer treatment [23,24].

Stibonium and bismuthonium species are of significant interest for their tunable Lewis acidity and have been explored for applications in ion sensing and catalysis [25–29]. An effective synthetic pathway towards σ^4, λ^5 pnictonium species involves oxidative halogenation of a σ^3, λ^3 triarylpnictine to form the σ^5, λ^5 pnictorane, followed by a

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metathesis reaction in which one pnictogen-bound halide is replaced by a weakly coordinating anion. In the resulting $\sigma^4, \lambda^5 [\text{Ar}_3\text{PnX}]^+$ species, a low-lying $\text{Pn}-\text{X} \sigma^*$ orbital is accessible from an open coordination site of the pnictogen cation [25]. An important feature for the design of these molecules is the choice of aryl substituent. If it does not provide enough steric protection, the species may undergo polymerization or other undesirable reactivity. If the aryl substituent is too large, then access to the σ^* orbital may be inhibited, attenuating substrate activation [30]. Either of the aforementioned situations may be desirable or undesirable and the pnictonium molecule must be carefully tuned to achieve the intended reactivity. A recent study employed careful ligand design to isolate a series of mono-, di-, and trinuclear fluorobismuthonium cations [28]. The authors reported that oxidative fluorination of trimesitylbismuthine (Mes_3Bi) followed by halide abstraction resulted in the formation of a mononuclear fluorobismuthonium cation. In another study, a diverse series of triarylbismuthine species were treated with iodosobenzene (PhIO) [31]. Surprisingly, treatment of Mes_3Bi with PhIO in dichloromethane (DCM) afforded the dichlorobismuthorane, $\text{Mes}_3\text{BiCl}_2$. In other cases, treatment of triarylbismuthines with PhIO afforded tetraarylbismuthonium salts, and in no cases did the authors isolate the expected bismuthine oxide. These results collectively highlight the importance of ligand design, as well as the curious reactivity of Bi(V) species.

Bulky aryl groups have been exploited with great success in the kinetic stabilization of highly reactive chemical motifs [32]. Heavy pnictogen atoms bearing bulky aryl substituents have served as important precursors in an array of fundamental and applied studies and, as noted above, oxidative halogenation is a staple reaction in pnictogen chemistry to access key intermediates in the synthesis of many interesting chemical motifs [21,25,33–37]. We recently prepared a very sterically encumbered stibine, Dipp_3Sb ($\text{Dipp} = 2,6\text{-diisopropylphenyl}$), and demonstrated that the bulky Dipp substituents resulted in notable differences in reactivity relative to the less-encumbered Mes_3Sb ($\text{Mes} = \text{mesityl}$) [38–40]. Oxidation of Dipp_3Sb with PhIO afforded Dipp_3SbO , the first example of an unperturbed monomeric stibine oxide [38]. The isolation of Dipp_3SbO allowed for experimental verification of trends in pnictoryl (Pn^+-O^-) bonding, and Dipp_3SbO was demonstrated to show a 10^6 -fold increase in Brønsted basicity over that of Dipp_3AsO [41,42]. We were curious about how the oxidative halogenation of Bi(III) would change as a function of substituent bulk and how this change would compare to that in the corresponding antimony compounds.

Herein, we report the synthesis and characterization of the sterically encumbered bismuthine Dipp_3Bi and describe its reactivity with the oxidative halogenation reagents XeF_2 and iodobenzene dichloride (PhICl_2). Treatment of Dipp_3Bi with XeF_2 resulted in the formation of the difluorobismuthorane $\text{Dipp}_3\text{BiF}_2$, whereas treatment of Dipp_3Bi with PhICl_2 resulted in the formation of 1-chloro-2,6-diisopropylbenzene and other decomposition products. We then compared the reactivity of Dipp_3Bi with that of a less sterically encumbered bismuthine, Mes_3Bi , as well as the antimony-containing analogues Dipp_3Sb and Mes_3Sb . Treatment of Dipp_3Sb with PhICl_2 resulted in the formation of $\text{Dipp}_3\text{SbCl}_2$, which exhibits a square pyramidal geometry in the solid state. Thermochemical calculations in the gas phase suggest that the square pyramidal geometry of $\text{Dipp}_3\text{SbCl}_2$ is more thermodynamically stable than the trigonal bipyramidal geometry. Our results collectively highlight the interesting modulation of the reactivity of heavy pnictines by the steric congestion imposed by Dipp substituents.

2. Materials and methods

2.1. General methods

Reagents and solvents were purchased from commercial vendors and used as received unless otherwise specified. Mes_3Sb , Mes_3Bi , and Dipp_3Sb were synthesized following literature protocols [28,38,43]. DCM and tetrahydrofuran (THF) were purified using an Innovative

Technology PURE-SOLV solvent purification system. All solvents were dried over 3-Å molecular sieves. NMR spectra were collected using a Bruker Avance III HD 500 spectrometer equipped with a multinuclear Smart Probe. Signals in the ^1H and ^{13}C NMR spectra are reported in ppm as chemical shifts from tetramethylsilane and were referenced using the CHCl_3 (^1H , 7.26 ppm) and CDCl_3 (^{13}C , 77.16 ppm) solvent signals. The frequencies of ^{19}F NMR signals are reported in ppm as chemical shifts from CFCl_3 (referenced to 4-fluoroaniline at -126.88 ppm). The 4-fluoroaniline reference was an 87 μM solution in CDCl_3 , collected at 298 K. Infrared (IR) spectra were collected on KBr pellets using a Thermo Nicolet Nexus 870 FT-IR spectrometer. Mass spectrometry measurements were collected using an LTQ-Orbitrap Velos Pro MS instrument. In addition to NMR analyses, the purity of novel materials was confirmed by observing agreement between experimental PXRD data of freshly prepared bulk solid and simulated powder diffraction patterns from single-crystal structures.

2.2. Synthesis of tris(2,6-diisopropylphenyl)bismuthine (Dipp_3Bi)

A dry 250 mL two-necked round bottom flask fitted with a water-jacketed Liebig condenser was charged with a stir bar and magnesium turnings (771 mg, 31.7 mmol). Under an atmosphere of N_2 , the magnesium turnings were suspended in dry THF (40 mL) and activated with 1,2-dibromoethane (690 μL , 8.0 mmol). 1-Bromo-2,6-diisopropylbenzene (4.8 mL, 23 mmol) was added dropwise and the reaction was refluxed for 3 h. After the magnesium turnings had been consumed, the colorless solution was cooled to -78°C and CuCl (2.36 g, 23.8 mmol) was added against a backflow of N_2 with an additional 15 mL of THF. The reaction mixture was allowed to warm to room temperature and stir overnight to form a pale white suspension. The resulting suspension was cooled to -78°C and a suspension of trichlorobismuthine (2.490 g, 7.900 mmol) in THF (10 mL) was then added dropwise to the reaction mixture. The reaction mixture was stirred at room temperature for 30 min before being refluxed for 19 h. The resulting dark green suspension was cooled to room temperature, opened to air, and diluted with OEt_2 (150 mL) and water (200 mL). The aqueous layer was back-extracted with OEt_2 (2×50 mL). The combined organic phases were then washed with water (2×200 mL) and with brine (250 mL). The organic layer was dried over Na_2SO_4 . The solvent was removed under reduced pressure. The resulting yellow oil was diluted with hexanes, filtered through Celite, and purified by flash chromatography (SiO_2 , 1:20 ethyl acetate: hexanes). The collected fractions were stripped of solvent to obtain a yellow oil. Yellow crystals grew from the oil and were washed with acetonitrile and collected by vacuum filtration. Yield: 0.587 g (11%). Crystals suitable for X-ray diffraction were obtained similarly. M. p. 208°C (decomp.). ESI-MS (m/z) [$\text{M}-\text{Dipp}$] $^+$ 531.246 (calc 531.246). ^1H NMR (500 MHz, CDCl_3) δ 7.28 (br s, 9H), 3.14 (br s, 6H), 1.5–0.25 (br m, 36H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 162.68, 156.68, 155.17, 128.37, 125.25, 123.65, 41.86, 37.63, 26.76, 24.93, 24.48, 23.52. In addition to NMR data, purity was confirmed by PXRD data from freshly prepared bulk solid; these powder data agreed with the simulated powder diffractogram generated from the crystal structure of Dipp_3Bi (Fig. S4).

2.3. Synthesis of difluorotris(2,6-diisopropylphenyl)bismuthorane ($\text{Dipp}_3\text{BiF}_2$)

A solution of XeF_2 (13.1 mg, 0.0774 mmol) in DCM (0.6 mL) was added dropwise to a yellow solution of Dipp_3Bi (51.5 mg, 0.0743 mmol) in DCM (0.6 mL). Bubbling occurred and the yellow color subsided. After 5 min, hexamethyldisiloxane (5 mL) was added and the solvent level was reduced to induce crystallization. Colorless crystals grew overnight. The solvent was decanted and the crystals were washed with 1 mL hexamethyldisiloxane before being dried under vacuum. Yield: 27 mg (50%). Crystals suitable for X-ray diffraction were obtained similarly. M.p. 178°C . ESI-MS (m/z) [$\text{M}-\text{F}$] $^+$ 711.377 (calc 711.377). ^1H

NMR (500 MHz, CDCl₃) δ 7.42 (s, 9H), 3.37 (br hept, J = 7.0 Hz, 6H), 1.26 (d, J = 5.9 Hz, 18H), 1.09 (d, J = 6.4 Hz, 18H). **¹³C{¹H} NMR (125 MHz, CDCl₃)** δ 167.38, 153.73, 130.72, 127.56, 36.06, 27.18, 24.51. **¹⁹F{¹H} NMR (470 MHz, CDCl₃)** δ -65.85. In addition to NMR data, purity was confirmed by PXRD data from freshly prepared bulk solid; these powder data agreed with the simulated powder diffractogram generated from the crystal structure of Dipp₃BiF₂ (Fig. S9).

2.4. Synthesis of dichlorotris(2,6-diisopropylphenyl)stiborane (Dipp₃SbCl₂)

A solution of Dipp₃Sb (49 mg, 0.081 mmol) in DCM (0.6 mL) was added dropwise to a solution of PhICl₂ (24 mg, 0.088 mmol) in DCM (0.6 mL). The yellow iodobenzene dichloride solution immediately became colorless and the solution was passed through Celite with an additional 1 mL of DCM for quantitative transfer. Pentane (10 mL) was added and the solvent was stripped to yield a colorless crystalline solid. The product was washed with pentane (2 x 1 mL) and dried under vacuum. Crystals suitable for X-ray diffraction were grown by slow evaporation of a mixture of DCM/pentane. Yield: 30 mg, 58%. M.p. 167 °C. **ESI-MS (m/z)** [$M-Cl_2+OH$]⁺ 621.305 (calc 621.305) (HR-MS experiment only detected hydrolysis product Dipp₃SbOH⁺ highlighting the instability of this species). **¹H NMR (500 MHz, CDCl₃)** δ 7.38 (s, 3H), 7.28 (d, J = 5.7 Hz, 6H), 3.58 (br s, 6H), 1.24 (d, J = 5.6 Hz, 18H), 0.99 (d, J = 6.1 Hz, 18H). **¹³C{¹H} NMR (125 MHz, CDCl₃)** δ 152.06, 130.92, 126.62, 36.47, 26.68, 24.17. In addition to NMR data, purity was confirmed by PXRD data from freshly prepared bulk solid; these powder data agreed with the simulated powder diffractogram generated from the crystal structure of Dipp₃SbCl₂ (Fig. S13).

2.5. Reaction between Dipp₃Bi and iodobenzene dichloride (PhICl₂)

Dipp₃Bi (8.2 mg, 0.011 mmol) and PhICl₂ (3.4 mg, 0.012 mmol) were dissolved in CDCl₃ (0.6 mL) to form a yellow solution. A colorless solid precipitated rapidly. After 2 h, ¹H and ¹³C{¹H} NMR analyses revealed the generation of 1-chloro-2,6-diisopropylbenzene [44], along with other unknown decomposition products (Figs. S14, S15).

2.6. Crystal growth of dichlorotrimesitylbismuthorane cyclohexane solvate [Mes₃BiCl₂·(C₆H₁₂)]

Mes₃BiCl₂ was synthesized according to a modified literature protocol [45]. Briefly, Mes₃Bi (55 mg, 0.079 mmol) and PhICl₂ (24 mg, 0.087 mmol) were dissolved in DCM (3 mL) to form a colorless solution. After 5 min, cyclohexane (20 mL) was added, and the reaction mixture was filtered through a Celite pad. The solvent level was reduced under reduced pressure to induce crystallization of pale-yellow crystals that were suitable for X-ray diffraction. NMR analysis of the crystals match literature reported values for Mes₃BiCl₂ [46]. **¹H NMR (500 MHz, CDCl₃)** δ 7.15 (s, 6H), 2.73 (s, 18H), 2.32 (s, 9H). **¹³C{¹H} NMR (125 MHz, CDCl₃)** δ 168.17, 141.98, 141.08, 132.24, 25.61, 20.94.

2.7. Crystal growth of dibromotrimesitylbismuthorane chloroform solvate [Mes₃BiBr₂·(CHCl₃)]

Mes₃BiBr₂ was synthesized according to a modified literature protocol [45]. Mes₃Bi (50 mg, 0.088 mmol) was dissolved in CHCl₃ (0.6 mL) and added to liquid Br₂ (15 mg, 0.095 mmol), resulting in a yellow solution. Vapor diffusion of pentane into the reaction mixture resulted in the precipitation of yellow crystals suitable for X-ray diffraction. Mes₃BiBr₂ has been reported and described as thermally unstable when dried, preventing many characterization techniques. **¹H NMR (500 MHz, CDCl₃)** δ 7.13 (s, 6H), 2.75 (s, 18H), 2.33 (s, 9H).

2.8. Crystal growth of dichlorotrimesitylstiborane (Mes₃SbCl₂)

A solution of Mes₃Sb (198 mg, 0.413 mmol) in DCM (2 mL) was added dropwise to a yellow solution of PhICl₂ (114 mg, 0.414 mmol) in DCM (1 mL). The colorless reaction mixture was passed through a Celite pad. The solvent was stripped to form a colorless solid. Recrystallization from hot hexanes afforded crystals suitable for X-ray diffraction. NMR analysis of the crystals match literature reported values for Mes₃SbCl₂ [43]. **¹H NMR (500 MHz, CDCl₃)** δ 7.00 (s, 6H), 2.66 (s, 18H), 2.31 (s, 9H). **¹³C{¹H} NMR (125 MHz, CDCl₃)** δ 145.50, 142.34, 140.87, 131.09, 25.51, 21.01.

2.9. Crystal growth of dibromotrimesitylstiborane (Mes₃SbBr₂)

A solution of Mes₃Sb (192 mg, 0.400 mmol) in DCM (2 mL) was added dropwise to a solution of Br₂ (64.1 mg, 0.406 mmol) in DCM (1 mL). The yellow reaction mixture was stirred for 5 min before hexanes were added resulting in white precipitate that was collected via vacuum filtration. Recrystallization from hot hexanes afforded crystals suitable for X-ray diffraction. NMR analysis of the crystals match literature reported values for Mes₃SbBr₂ [43]. **¹H NMR (500 MHz, CDCl₃)** δ 6.98 (s, 6H), 2.70 (s, 18H), 2.32 (s, 9H). **¹³C{¹H} NMR (125 MHz, CDCl₃)** δ 145.65, 142.12, 140.87, 131.16, 26.20, 20.97.

2.10. X-ray crystallography

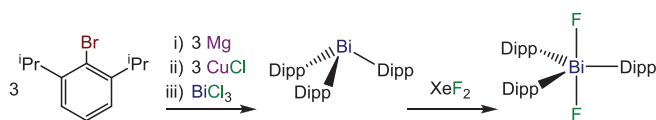
Crystals of Dipp₃Bi, Dipp₃BiF₂, Mes₃BiCl₂·C₆H₁₂, Mes₃BiBr₂·CHCl₃, Mes₃SbCl₂, Mes₃SbBr₂, and Dipp₃SbCl₂ were grown as described above, selected under a microscope, loaded onto a MiTeGen polyimide sample loop using Paratone-N, and mounted onto a Rigaku XtaLAB Synergy-S single-crystal diffractometer. Each crystal was cooled to 100 K under a stream of nitrogen. Diffraction of Cu K α radiation from a PhotonJet-S microfocus source was detected using a HyPix6000HE hybrid photon counting detector. Screening, indexing, data collection, and data processing were performed with CrysAlisPro [47]. The structures were solved using SHELXT and refined using SHELXL following established strategies [48–50]. All non-H atoms were refined anisotropically. C-bound H atoms were placed at calculated positions and refined with a riding model and coupled isotropic displacement parameters (1.2 $\times$ U_{eq} for non-methyl C–H atoms and 1.5 $\times$ U_{eq} for methyl groups).

2.11. Powder X-ray diffraction (PXRD)

Bulk samples of Dipp₃Bi, Dipp₃BiF₂, and Dipp₃SbCl₂ were ground using an agate mortar and pestle. The fine white powders were each loaded onto a MiTeGen polyimide sample loop using Paratone-N and mounted onto a Rigaku XtaLAB Synergy-S single-crystal diffractometer. The powder was cooled to 100 K under a stream of nitrogen. The diffraction of Cu K α radiation was collected while the sample underwent a Gandolfi scan. Data collection and processing were performed using CrysAlisPro. Simulated PXRD diffractograms were generated from the crystal structures of Dipp₃Bi, Dipp₃BiF₂, and Dipp₃SbCl₂ using Mercury and compared to the experimentally determined diffractograms.

2.12. Computational experiments

All geometry optimizations and frequency calculations were performed using ORCA 5.0.1 [51]. Geometry optimizations were performed on Dipp₃BiF₂, Dipp₃SbF₂, and Dipp₃SbCl₂ starting from crystallographic coordinates employing the BP86 pure functional and def2-SVP basis set, with the RI approximation and def2/J auxiliary basis set [52]. The optimized coordinates were then used as a starting point for a subsequent geometry optimization using the PBE0 hybrid functional and def2-TZVPP basis set, with the RIJCOSX approximation and def2/J auxiliary basis set [53–57]. Frequency calculations were then performed at the same level of theory in the gas phase. We then optimized



Scheme 1. Synthesis of Dipp₃Bi and oxidative fluorination to form Dipp₃BiF₂.

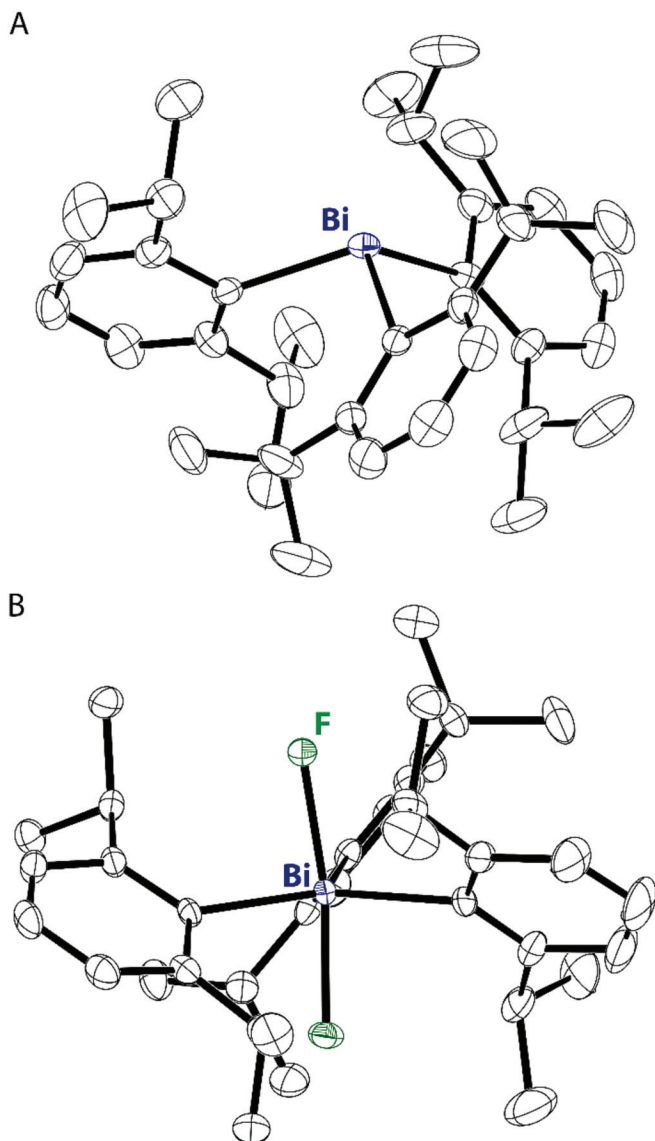


Fig. 1. Thermal ellipsoid plots (50% probability) of (A) Dipp₃Bi and (B) Dipp₃BiF₂. Color code: Bi navy, F light-green, and C black. Hydrogen atoms are omitted for clarity and only one of the crystallographically inequivalent molecules of Dipp₃BiF₂ is depicted. ((Colour online.))

structures of Dipp₃BiF₂(linear) and Dipp₃SbCl₂(linear) starting from the coordinates of Dipp₃SbF₂, where the antimony or fluorine atoms were replaced by bismuth or chlorine, respectively, in order to find a minimum on the potential energy surface where the X–Pn–X bond angle approximates 180°. EDA was performed using Gaussian 09 [58]. Single point energy calculations (PBE0/QZVP) were performed on the 2Cl and Dipp₃Sb fragments using coordinates from the optimized trigonal bipyramidal and square pyramidal structures. ΔE_{tot} was obtained by subtracting the energies of the 2Cl and Dipp₃Sb fragments from that of the Dipp₃SbCl₂ molecule. MultiWFN (Version 3.7) was used to generate an input file for Dipp₃SbCl₂ with an initial guess for the combined 2Cl

and Dipp₃Sb fragments with no orbital interaction [59]. The energy of the initial guess wavefunction was subtracted from the final converged energy to obtain ΔE_{orb} . For the NCI analysis, single point energy calculations were performed using ORCA 5.0.1 on the optimized coordinates using the PBE0 hybrid functional and old-DKH-TZVPP all-electron, relativistically contracted basis set following the Douglass-Kroll-Hess formalism, with the RIJCOSX approximation and SARC/J auxiliary basis set [60–63]. Non-covalent interactions were calculated using MultiWFN and the results were visualized in VMD [64].

3. Results and discussion

3.1. Synthesis and fluorination of Dipp₃Bi

We have previously synthesized Dipp₃Pn (Pn = P, As, Sb) by adapting a protocol whereby 1-bromo-2,6-diisopropylbenzene is converted to an organocopper(I) reagent before the aryl group is installed on the pnictogen center (Scheme 1) [38,65]. Refluxing a mixture of BiCl₃ and the organocopper(I) reagent in THF resulted in the formation of a dark green suspension. Purification by liquid–liquid extraction and flash chromatography (SiO₂/hexanes) yielded a yellow oil, from which yellow crystals of Dipp₃Bi formed in 11% yield. The crystals were collected and washed with MeCN. ¹H and ¹³C NMR spectroscopic analyses of the crystalline product revealed very broadened signals, consistent with a single Dipp environment and partially restricted rotation about the C_{ipso}–Bi bond (Figs. S1, S2). The breadth of the resonances is also consistent with the reported ¹H NMR spectrum of Tipp₃Bi (Tipp = 2,4,6-triisopropylphenyl) [65]. Interestingly, the NMR spectra of other Dipp₃Pn (Pn = P, As, Sb) compounds show sharp, decoalesced signals indicating that rotation about the C_{ipso}–Pn bond is slow on the NMR time scale. We suggest that the lengthening of the Pn–C_{ipso} bond in the case of Bi reduces the energetic barrier of rotation, such that the signals have coalesced (¹H) or broadened (¹³C) at room temperature. A single-crystal X-ray diffraction experiment (Fig. 1A) revealed that Dipp₃Bi had crystallized in space group $I\bar{4}3d$. In the crystal, the molecules reside on crystallographic 3-fold rotation axes, allowing them to assume their full C₃ point-group symmetry. The crystallographically equivalent Bi–C bond lengths are 2.302(5) Å and the C–Bi–C bond angles are 106.16(12)°. The crystal structure of Dipp₃Bi is isomorphous with the previously reported crystal structure of Dipp₃Sb [38].

Difluorobismuthoranes have been well characterized and used as synthetic precursors, so we sought to similarly fluorinate Dipp₃Bi [28]. We previously reported the isolation of Dipp₃SbF₂, suggesting that the

Table 1
Selected crystallographic metrics.^[a]

Compound	X–Pn–X bond angle (°)	Pn–X bond length (Å)	τ parameter
Dipp ₃ BiF ₂	169.68(6)/169.82(6)	2.1265(14)/2.1265(14), 2.1132(14)/2.1099(14)	0.716(2)/0.723(2)
Dipp ₃ SbF ₂ ^[b]	180.00(7)	1.971(3), 1.967(3)	1.00(2)
Dipp ₃ SbCl ₂	154.89(2)	2.4864(4)	0.087(2)
Mes ₃ BiF ₂ ^[c]	179.00(4)	2.1222(10), 2.1223(10)	0.954(1)
Mes ₃ SbF ₂ ^[d]	179.53(5)	1.9821(10)	0.972(1)
Mes ₃ BiCl ₂	180	2.645(6), 2.582(6)	1.00(2)
Mes ₃ SbCl ₂	177.29(2)/178.55(3)	2.4976(7)/2.4810(8), 2.4790(7)/2.4748(8)	0.920(2)/0.929(2)
Mes ₃ BiBr ₂	178.326(13)	2.8109(4), 2.7643(4)	0.913(3)
Mes ₃ SbBr ₂	173.724(9)/177.953(9)	2.6730(3)/2.6829(3), 2.6694(3)/2.6427(3)	0.839(2)/0.943(2)

[a] Values for crystallographically independent molecules are separated by slashes. [b] Crystallographic data of Dipp₃SbF₂ were obtained from a prior report [38]. [c] Crystallographic data of Mes₃BiF₂ were obtained from a prior report [28]. [d] Crystallographic data of Mes₃SbF₂ were obtained from a prior report [25].

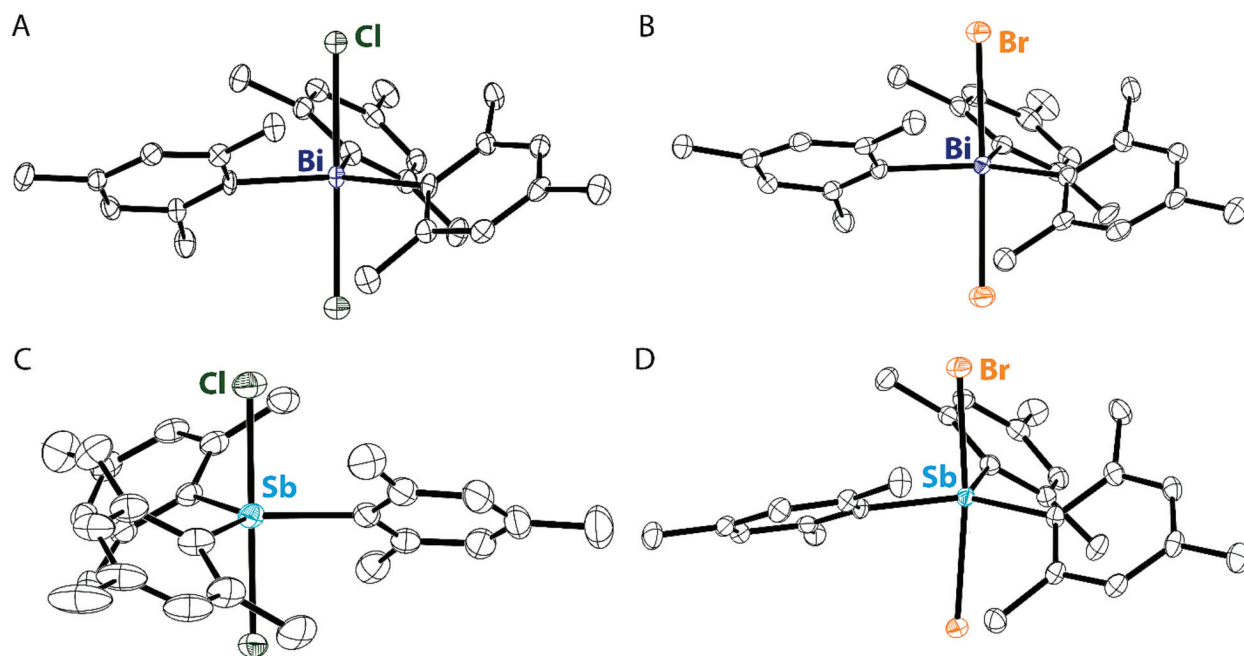


Fig. 2. Thermal ellipsoid plots (50% probability) of (A) $\text{Mes}_3\text{BiCl}_2$, (B) $\text{Mes}_3\text{BiBr}_2$, (C) $\text{Mes}_3\text{SbCl}_2$, and (D) $\text{Mes}_3\text{SbBr}_2$. Color code: Bi navy, Sb teal, Cl dark-green, Br orange, and C black. Hydrogen atoms are omitted for clarity. For C and D, only one of the crystallographically independent molecules is depicted. ((Colour online.))

steric environment imposed by the Dipp groups would not preclude the formation of the difluorobismuthorane [38]. Dropwise addition of a yellow DCM solution of Dipp_3Bi to a DCM solution of XeF_2 resulted in immediate effervescence and discharge of color from the solution. Addition of hexamethyldisiloxane to the reaction mixture followed by slow evaporation of the DCM afforded colorless crystals of $\text{Dipp}_3\text{BiF}_2$ in a 50% yield. ^1H and ^{13}C NMR spectroscopic analyses of the product were consistent with the D_3 symmetry expected for a *trans*-dihalotriarylpnictorane (Figs. S5, S6). ^{19}F NMR spectroscopy revealed a single signal at -65.85 ppm, significantly upfield of the fluorine resonances of both Mes_3BiF_2 (-100.41 ppm) and $\text{Dipp}_3\text{SbF}_2$ (-74.35 ppm) [28].

$\text{Dipp}_3\text{BiF}_2$ crystallized in space group $P\bar{1}$ with $Z' = 2$ (Fig. 1B). Interestingly, the crystal structure of $\text{Dipp}_3\text{BiF}_2$ features a bent F–Bi–F bond angle of $169.68(6)^\circ/169.82(6)^\circ$ (values are provided for both of the crystallographically independent molecules in the asymmetric unit), whereas Ph_3BiF_2 and Mes_3BiF_2 crystallize with almost perfectly linear F–Bi–F bond angles [28]. The τ parameter $0.716(2)/0.723(2)$ captures the distorted trigonal bipyramidal geometry of $\text{Dipp}_3\text{BiF}_2$ (Table 1). The Bi–F bond lengths of $\text{Dipp}_3\text{BiF}_2$ are $2.1265(14)/2.1265(14)$ and $2.1132(14)/2.1099(14)$ Å. Mes_3BiF_2 features similar Bi–F bond lengths but a markedly less distorted trigonal bipyramidal geometry with a τ parameter of $0.954(1)$.

3.2. Crystallographic characterization of dihalotrimesitylpnictoranes

In addition to the Mes_3BiF_2 described above, Mes_3Bi has been previously reported to undergo oxidation to form $\text{Mes}_3\text{BiCl}_2$ or $\text{Mes}_3\text{BiBr}_2$, but a lack of crystallographic data prevented us from gaining comparative insight into the structures of the dihalotriarylbismuthoranes. Modifying literature procedures, we reprepared $\text{Mes}_3\text{BiCl}_2$ and $\text{Mes}_3\text{BiBr}_2$ and determined their crystal structures using single-crystal X-ray diffraction methods (Fig. 2A, B) [45]. For comparison, we also structurally characterized $\text{Mes}_3\text{SbCl}_2$ and $\text{Mes}_3\text{SbBr}_2$ (Fig. 2C, D) [25,43].

$\text{Mes}_3\text{BiCl}_2$ crystallized as a cyclohexane solvate from a mixture of DCM and cyclohexane in space group $P31c$ on a 3-fold rotation axis, crystallographically imposing linearity on the Cl–Bi–Cl angle. The Bi–Cl bond lengths are $2.645(6)$ and $2.582(6)$ Å. $\text{Mes}_3\text{BiBr}_2$ crystallized as the yellow chloroform solvate from a mixture of chloroform and pentane in

space group $P2_1/n$. In our experience, $\text{Mes}_3\text{BiBr}_2$ decomposes readily when removed from solvent, as has been noted previously [45]. The Br–Bi–Br bond angle is close to linear at $178.326(13)^\circ$ and the Bi–Br bond lengths are $2.8109(4)$ and $2.7643(4)$ Å.

The antimony compounds $\text{Mes}_3\text{SbCl}_2$ and $\text{Mes}_3\text{SbBr}_2$ were each crystallized from hot hexanes, and both formed crystals in space group $P\bar{1}$ with two molecules in the asymmetric unit. $\text{Mes}_3\text{SbCl}_2$ features an almost linear Cl–Sb–Cl bond angle of $177.29(2)/178.55(3)^\circ$ and the Sb–Cl bond lengths are $2.4976(7)/2.4810(8)$ and $2.4790(7)/2.4748(8)$ Å. Although the difference is subtle, $\text{Mes}_3\text{SbBr}_2$ features a more bent X–Sb–X bond angle of $173.724(9)/177.953(9)^\circ$ with Sb–Br bond lengths of $2.6730(3)/2.6829(3)$ and $2.6694(3)/2.6427(3)$ Å. We propose that the bromide substituents are sufficiently large to cause a significant steric repulsion with the Mes groups, such that the Br–Sb–Br bond angle distorts further from linearity. The structures of $\text{Mes}_3\text{SbCl}_2$ and $\text{Mes}_3\text{SbBr}_2$ are depicted in space-filling diagrams to highlight the difference in the size and steric environment of the halogen atoms (Fig. S24).

3.3. Oxidative chlorination of Dipp_3Bi and Dipp_3Sb

With the structural data from the dihalotrimesitylstiboranes and dihalotrimesitylbismuthoranes in hand, we next attempted to oxidatively chlorinate Dipp_3Bi with PhICl_2 (Scheme 1). Dissolution of Dipp_3Bi and PhICl_2 in CDCl_3 under dry, air-free conditions resulted in the formation of a yellow solution. A colorless amorphous solid rapidly precipitated from the reaction mixture. We propose that the precipitate is composed of polymeric Bi-containing species [30,31]. ^1H and ^{13}C NMR spectra of the supernatant reveal the generation of 1-chloro-2,6-diisopropylbenzene (Figs. S14, S15), which we suggest forms through a reductive elimination mechanism. We tentatively suggest that DippCl is generated by reductive elimination from a transient Bi(V) species, but we acknowledge that it could also arise from ligand exchange between Dipp_3Bi and PhICl_2 and subsequent reductive elimination from the resulting I(III) species. We note the presence of other unidentified decomposition products in the supernatant (Figs. S14, S15). Bi(V) complexes frequently reduce to Bi(III) because of the stability of the latter, and electronegative substituents are often needed to stabilize Bi(V) compounds. The isolation of $\text{Mes}_3\text{BiCl}_2$

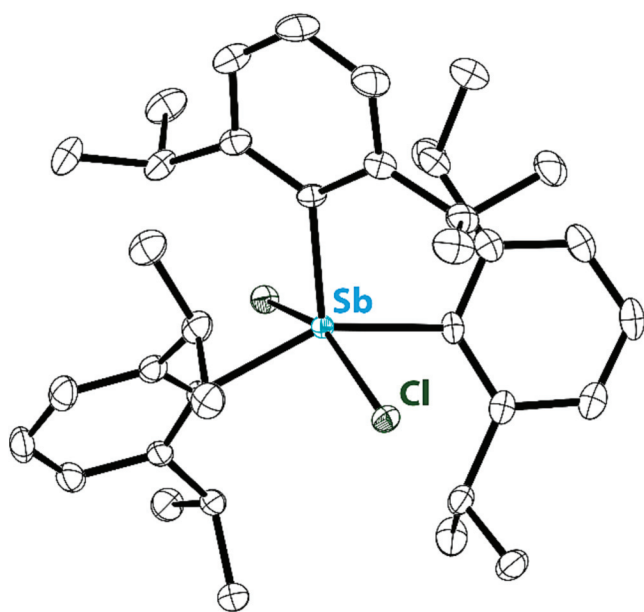
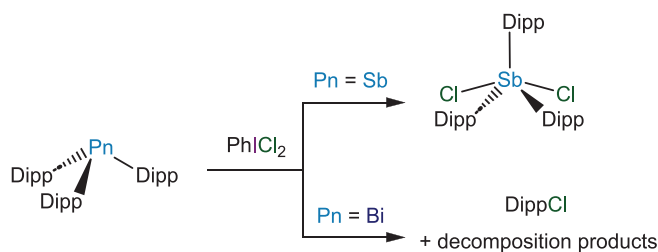


Fig. 3. Thermal ellipsoid plot (50% probability) of $\text{Dipp}_3\text{SbCl}_2$. Color code: Sb teal, Cl dark-green, and C black. Hydrogen atoms are omitted for clarity. ((Colour online.))



Scheme 2. Oxidative chlorination of Dipp_3Sb and Dipp_3Bi with PhICl_2 .

indicates that axial chloride substituents are sufficiently electronegative to stabilize a dichlorotriarylbismuthorane. Our findings suggest that it is the increased steric pressure imposed by the Dipp substituents that destabilizes the 5-coordinate $\text{Dipp}_3\text{BiCl}_2$ in favor of decomposition through a reductive elimination process. Other examples of reductive elimination from Bi(V) species have been reported [8]. The formation of the organic reductive elimination product indicates that the oxidation did indeed occur. It is possible that low-temperature experiments could permit the isolation of the bismuthorane but we have not yet had success in this regard. Because Sb(V) species are less prone to reductive elimination than Bi(V) species [7], we investigated the oxidation of Dipp_3Sb with PhICl_2 . Addition of a colorless DCM solution of Dipp_3Sb to a yellow DCM solution of PhICl_2 resulted in the immediate loss of color. Addition of pentane to the reaction mixture, followed by slow evaporation of the DCM resulted in the formation of colorless crystals of $\text{Dipp}_3\text{SbCl}_2$ in 50% yield. The ^1H and ^{13}C NMR spectra of the product are consistent with other symmetric dihalotriarylpnictoranes, and an X-ray diffraction experiment unambiguously confirmed the identity of the species (Fig. 3, Scheme 2).

$\text{Dipp}_3\text{SbCl}_2$ crystallizes in space group $C2/c$ on a 2-fold rotation axis. Unlike $\text{Mes}_3\text{SbCl}_2$, which features a Cl-Sb-Cl bond angle of $177.29(2)^\circ$, $\text{Dipp}_3\text{SbCl}_2$ features a Cl-Sb-Cl bond angle of $154.89(2)^\circ$ in the solid-state. $\text{Dipp}_3\text{SbCl}_2$ features a remarkably low τ parameter of 0.087(2), indicating that this species can be appropriately characterized as square pyramidal. The crystallographic 2-fold rotation axis bisects the apical Dipp group. To the best of our knowledge, there are no other examples of dihalotriarylpnictoranes that have crystallized with a square pyramidal geometry. In all other cases, such as $\text{Dipp}_3\text{SbF}_2$, the apicophilic halide

ions reside in the axial positions of a trigonal bipyramid and the bulky aryl substituents occupy the equatorial positions. We suggest that the square pyramidal geometry of $\text{Dipp}_3\text{SbCl}_2$, as compared to e.g., $\text{Dipp}_3\text{SbF}_2$, arises from a combination of the extreme steric crowding of the Dipp groups, the larger size of the chloride ligands (as compared to fluoride), and the lower apicophilicity of chloride than fluoride. The decreased steric pressure exerted by mesityl substituents accounts for the trigonal bipyramidal structures of $\text{Mes}_3\text{SbCl}_2$ and $\text{Mes}_3\text{SbBr}_2$.

3.4. Theoretical investigation of dihalopnictoranes

A natural question that arises during the analysis described above is whether the square pyramidal geometry assumed by $\text{Dipp}_3\text{SbCl}_2$ in the crystal structure is simply a product of crystal packing forces. A gas-phase geometry optimization (PBE0/def2-TZVPP) of $\text{Dipp}_3\text{SbCl}_2$ starting from the crystallographic coordinates converged upon a square pyramidal geometry ($\tau = 0.10$), very similar to that in the crystal structure. This result confirms that the square pyramidal geometry is a local minimum on the potential energy surface (PES) of the compound, but not that it is the most stable geometry. A separate geometry optimization starting from a linear input structure confirmed that the linear structure (Cl-Sb-Cl angle of 179.62°) is also a local minimum on the PES. A thermochemical analysis indicated that square pyramidal was the more thermodynamically favored geometry; the square pyramidal geometry features a ΔH that is 9.3 kcal/mol lower than that of the trigonal bipyramidal geometry (Table S3).

As described above, we had also noted that in the crystal structure of $\text{Dipp}_3\text{BiF}_2$, the crystallographically independent molecules exhibited slightly bent F-Bi-F angles of $169.68(6)^\circ$ and $169.82(6)^\circ$. Geometry optimization starting from the crystallographic coordinates confirmed the distorted trigonal bipyramidal structure, albeit with an even more linear F-Bi-F bond angle of 173.04° . As with $\text{Dipp}_3\text{SbCl}_2$, we also optimized the structure of $\text{Dipp}_3\text{BiF}_2$ starting from a linear input geometry, which converged upon a structure with a linear F-Bi-F angle of 180.00° . Thermochemical analysis of $\text{Dipp}_3\text{BiF}_2$ determined the linear geometry to be slightly more thermodynamically stable, with a ΔH that is 1.1 kcal/mol more stable than that of the distorted geometry (Table S3). The small difference in energies is consistent with the small difference in geometry, but nevertheless highlight the shallow nature of the PES.

To probe the underlying reasons for the enhanced thermodynamic stability of $\text{Dipp}_3\text{SbCl}_2$ in the square pyramidal geometry relative to the trigonal bipyramidal geometry, we performed an energy decomposition analysis (EDA) of each geometry (PBE0/QZVP). The square pyramidal geometry could be stabilized by alleviation of steric repulsion or by the formation of more favorable bonding interactions relative to the trigonal bipyramidal state. We found that the ratio of $\Delta E_{\text{orb}}/\Delta E_{\text{total}}$ was slightly greater in the square pyramidal geometry suggesting that the driving force could be the formation of more favorable bonding interactions, rather than attenuation of steric repulsion (Table S4).

We have previously shown that Dipp substituents engage in stabilizing intramolecular hydrogen bonding interactions in pnictine oxide and hydroxypnictonium species [38,41]. The EDA results above suggested that the geometries of $\text{Dipp}_3\text{SbCl}_2$ and $\text{Dipp}_3\text{BiF}_2$ that deviate from trigonal bipyramidal might also be stabilized by such intramolecular secondary interactions. We checked for their presence between the halides and the Dipp substituents using non-covalent interaction (NCI) analysis [66]. NCI analysis identifies regions of space between atoms where singularities in the reduced gradient of the electron density are present. The results of the analysis are typically depicted using isosurface plots. The isosurfaces are color-mapped with the function $\text{sign}(\lambda_2)\rho$, where λ_2 is the second largest eigenvalue of the Hessian matrix, or Laplacian, and ρ is the electron density. Regions where $\text{sign}(\lambda_2)\rho$ is close to 0 or negative represent attractive forces of strength comparable to hydrogen bonding interactions. Our NCI analysis of $\text{Dipp}_3\text{SbCl}_2$ reveals the presence of attractive interactions between the

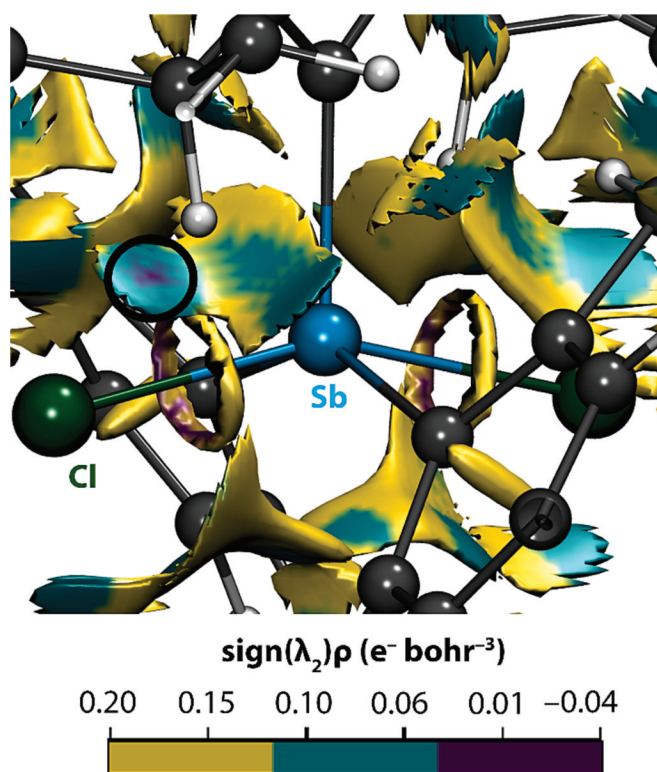


Fig. 4. NCI analysis of $\text{Dipp}_3\text{SbCl}_2$ depicting reduced gradient surfaces (iso-value = 0.45 a.u.) with the function $\text{sign}(\lambda_2)\rho$ (where λ_2 is the second-largest eigenvalue of the Laplacian) color-mapped on the surface. Purple is indicative of H-bonding interactions, aqua is indicative of van der Waals interactions, and yellow is indicative of steric repulsions. H-bonding interactions are highlighted with a black circle for clarity. Color code: Sb teal, Cl dark green, C black, H grey. ((Colour online.))

benzylic protons of the apical Dipp substituent and the chloride substituents (Fig. 4). We performed a similar analysis on $\text{Dipp}_3\text{BiF}_2$ and found similar, albeit significantly weaker, attractive interactions between Dipp and fluoride substituents (Fig. S23). NCI analysis of $\text{Dipp}_3\text{SbF}_2$ and the trigonal bipyramidal geometries of $\text{Dipp}_3\text{SbCl}_2$ and $\text{Dipp}_3\text{BiF}_2$ were also performed. In these cases, the NCI analysis indicates the presence of van der Waals interactions between the Dipp and halide substituents rather than stronger H-bonding interactions.

4. Conclusion

We have isolated and characterized a very sterically encumbered bismuthine, Dipp_3Bi . Dipp_3Bi was subject to oxidative halogenation reactions and was found to have reactivity remarkably different from that of Mes_3Bi and Dipp_3Sb . The reaction between Dipp_3Bi and XeF_2 afforded a difluorobismuthorane with a bent F–Bi–F bond angle. The reaction between Dipp_3Bi and PhICl_2 resulted in decomposition and the generation of products including 1-chloro-2,6-diisopropylbenzene. The reaction between Dipp_3Sb and PhICl_2 resulted in the formation of $\text{Dipp}_3\text{SbCl}_2$, which features a highly unusual distorted square pyramidal geometry in the solid state. Theoretical data suggest that the square pyramidal geometry of $\text{Dipp}_3\text{SbCl}_2$ is more thermodynamically stable than trigonal bipyramidal geometry. Ultimately, our results demonstrate the ability of bulky aryl substituents to modulate the reactivity of heavy pnictines.

CRediT authorship contribution statement

John S. Wenger: Conceptualization, Methodology, Resources, Investigation, Validation, Writing – original draft, Writing – review &

editing, Visualization. **Addis Getahun:** Conceptualization, Methodology, Resources, Investigation, Validation, Writing – original draft, Writing – review & editing, Visualization. **Timothy C. Johnstone:** Conceptualization, Methodology, Resources, Investigation, Validation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Timothy C. Johnstone reports financial support was provided by National Science Foundation. Timothy C. Johnstone reports financial support was provided by American Chemical Society. Timothy C. Johnstone reports financial support was provided by Arnold and Mabel Beckman Foundation.

Data availability

Data will be made available on request.

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Appendix A. . Supplementary data

CCDC 2297429–2297430 contain the supplementary crystallographic data for $\text{Mes}_3\text{SbCl}_2$, $\text{Mes}_3\text{SbBr}_2$, Dipp_3Bi , $\text{Mes}_3\text{BiBr}_2 \cdot \text{CHCl}_3$, $\text{Dipp}_3\text{BiF}_2$, $\text{Mes}_3\text{BiCl}_2 \cdot \text{C}_6\text{H}_{12}$, and $\text{Dipp}_3\text{SbCl}_2$. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Appendix B. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2023.116730>.

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