

# Cyanide and Azide Anion Complexation by a Bidentate Stibonium-Borane Lewis Acid

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 80<sup>th</sup> birthday*

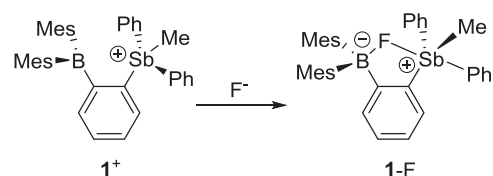
Our ongoing interest in the chemistry of polyfunctional Lewis acids has led us to investigate the reaction of the stibonium-borane [*o*-(Ph<sub>2</sub>MeSb)(Mes<sub>2</sub>B)C<sub>6</sub>H<sub>4</sub>]<sup>+</sup> (**1**<sup>+</sup>) with cyanide and azide, two toxic anions. Both anions react with **1**<sup>+</sup> to afford the corresponding neutral complexes **1**-CN and **1**-N<sub>3</sub>. Structural and computational studies show that the coordinated anion interacts with both the boron and antimony atoms of the bidentate Lewis acid. While the azide complex features a typical  $\kappa^2N^1 : N^1$  bridging azide ligand, the cyanide complex possesses a cyanoborate moiety whose cyanide interacts side-on with the stibonium center. The Lewis acid–anion interactions observed in these complexes have also been studied computationally using the Natural Bond Orbital method.

**Key words:** Lewis Acid, Boron, Antimony, Azide, Cyanide

## Introduction

The complexation of anions by organo-element Lewis acids is an area of active research with applications in anion sensing [1–19], small molecule activation [20–24] and organometallic catalysis [25–27]. One strategy used to increase the anion affinity of such systems is based on the incorporation of two Lewis acids in a bidentate motif that support anion chelation [6, 9, 11, 14, 28–47]. Examples of such systems include bidentate diboranes which have proven especially useful for the complexation of small anions including hydride [48, 49] and fluoride [11, 50–52]. As part of our contribution to this field of research [9], we have also investigated heteronuclear bidentate Lewis acids containing a boron atom and another Lewis acidic main group element such as phosphorus (**A**<sup>+</sup>, Fig. 1) [39], sulfur (**B**<sup>+</sup>, Fig. 1) [41], antimony (**1**<sup>+</sup>, Scheme 1) [45], tellurium (**C**<sup>+</sup>, Fig. 1) [46] or mercury (**D**, Fig. 1) [53, 54].

Fluoride anion complexation studies have shown that the stibonium-borane derivative **1**<sup>+</sup> is the most powerful Lewis acid of this group (Scheme 1) [45], a finding that illustrates the elevated fluoride affinity of antimony(V) species [55–62]. We have now decided to study the reaction of this derivative with cyanide and



Scheme 1.

azide. In this paper, we report the results of this study and show that the boron and antimony atoms of **1**<sup>+</sup> act in concert to support the coordination of these potentially toxic anions.

## Results and Discussion

Addition of 1 equiv. of TBACN or TBAN<sub>3</sub> (TBA = tetra(*n*-butyl)ammonium) to solutions of [**1**]OTf in dry CDCl<sub>3</sub> resulted in quantitative conversion to the adducts **1**-CN and **1**-N<sub>3</sub>, respectively, as confirmed by multinuclear NMR spectroscopy (Scheme 2). The aliphatic region of the <sup>1</sup>H NMR spectrum of **1**-CN taken at room temperature displayed three distinct resonances in a 3 : 3 : 6 ratio, corresponding to the mesityl *ortho*-CH<sub>3</sub> groups. A similar pattern is observed for the aromatic mesityl

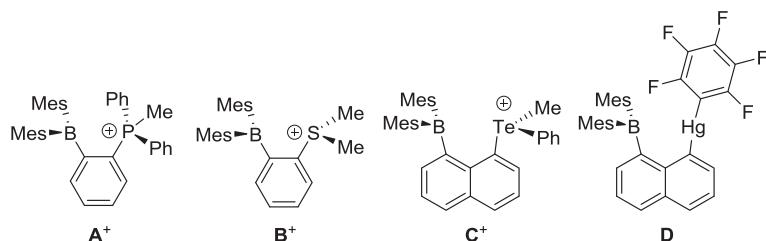
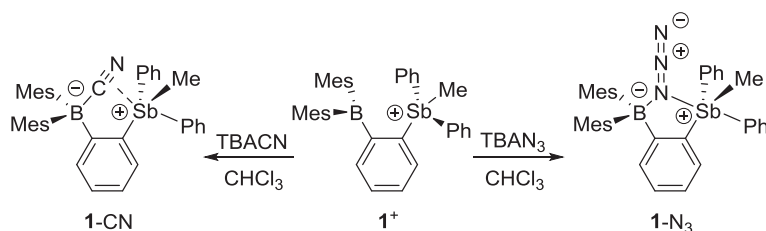


Fig. 1.



Scheme 2.

C–H signals, which appear in the 6.6–6.8 ppm range as broad signals in a 1 : 1 : 2 ratio. This result indicates non-equivalency of the boron mesityl substituents with free rotation of one and hindered rotation of the other on the NMR timescale. The signal corresponding to the antimony-bound methyl group appears as a singlet at 1.56 ppm. The  $^{11}\text{B}$  NMR spectrum of **1-CN** displays a single peak at  $-11.7$  ppm, in the expected region for a triarylcyanoborate. The IR spectrum of **1-CN**, obtained as a colorless microcrystalline solid by precipitation and washing with anhydrous MeOH, shows a CN stretching band at  $2160\text{ cm}^{-1}$ , in the same region as that reported for similar triarylcyanoborates [41, 63]. The  $^1\text{H}$  NMR spectrum of **1-N<sub>3</sub>** more closely resembles that of **1-F**, exhibiting single resonances for the mesityl *ortho*-CH<sub>3</sub> and CH groups and a singlet at 1.32 ppm corresponding to the antimony-bound methyl group. The  $^{11}\text{B}$  NMR spectrum of **1-N<sub>3</sub>** displays a single peak at  $+0.99$  ppm.

The crystal structures of **1-CN** (Fig. 2) and **1-N<sub>3</sub>** (Fig. 3) have been determined by X-ray diffraction (Tables 1 and 2). Examination of the structure of **1-CN** confirms the formation of a cyanoborate (B(1)–C(38) =  $1.601(8)$  Å) and suggests that the cyanide anion may also be engaged in a weak bridging interaction with the Sb atom. This is indicated by the C(38)–Sb(1) and N(1)–Sb(1) distances of  $2.943(7)$  and  $3.093(5)$  Å, respectively, which are longer than the sum of the covalent radii (Sb–C  $2.08$  Å, Sb–N  $2.10$  Å) [64],

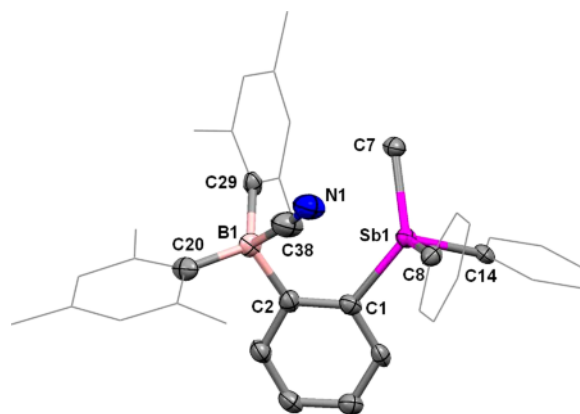


Fig. 2 (color online). Molecular structure of **1-CN** in the crystal. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms have been omitted for clarity, and phenyl and mesityl groups are depicted in wireframe. Pertinent metrical parameters can be found in Table 2.

but shorter than the sum of the van der Waals radii (Sb–C  $3.9$  Å, Sb–N  $3.8$  Å) [65]. On the other hand, the structure of **1-N<sub>3</sub>** clearly shows that the terminal azide N atom is engaged in a B–N–Sb bridging interaction. The B(1)–N(1) bond length ( $1.623(6)$  Å) in **1-N<sub>3</sub>** is very similar to that measured for the phosphonium analog **A-N<sub>3</sub>** ( $1.623(4)$  Å). However, the Sb(1)–N(1) distance ( $2.477(4)$  Å) is significantly shorter than the corresponding P–N bond length ( $2.790(2)$  Å) [40] and only marginally longer than the Sb–N distance

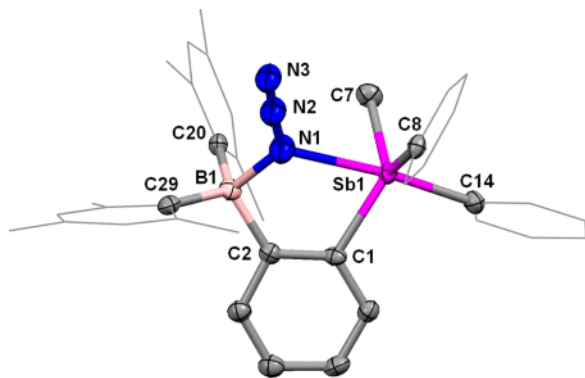


Fig. 3 (color online). Molecular structure of **1-N<sub>3</sub>** in the crystal. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms have been omitted for clarity, and phenyl and mesityl groups are depicted in wireframe. Pertinent metrical parameters can be found in Table 2.

in  $\text{Ph}_4\text{Sb}(\text{N}_3)$  (2.373(3) Å) [66]. Similar to **1-F**, the antimony atom in **1-N<sub>3</sub>** adopts a distorted trigonal-bipyramidal geometry defined by  $\text{C}(14)\text{-Sb}(1)\text{-N}(1) = 174.1(2)^\circ$  and  $\Sigma(\text{C}_{\text{eq}}\text{-Sb}\text{-C}_{\text{eq}}) = 350.8^\circ$ .

The geometries of **1-CN** and **1-N<sub>3</sub>** were optimized using density functional theory (DFT) methods (B3LYP functional with the mixed basis set: aug-cc-pVTz-pp for Sb, 6-31+g(d') for B, N, and F, 6-31g for C, H). The resulting geometries closely matched those determined experimentally, and no imaginary frequencies were calculated at the optimized structures. To probe the role of the stibonium group in assisting cyanide and azide anion binding, Atoms in Molecules (AIM) analysis and Natural Bond Order (NBO) calculations were performed at the optimized geometries. For **1-CN**, the AIM calculation located a bond path between Sb and the N atom of the boron-bound cyanide anion with an electron density of  $\rho(r) = 0.132 e \text{ \AA}^{-3}$  at the bond critical point (labeled as bcp1 in Fig. 4). In the case of **1-N<sub>3</sub>**, the AIM calculation identified the bond path between Sb and the bridging azide N atom with  $\rho(r) = 0.290 e \text{ \AA}^{-3}$  at the bond critical point (labeled as bcp1 in Fig. 4). Although the electron density at the bond critical point of the Sb–N bond in **1-N<sub>3</sub>** is comparable to that calculated for the Sb–F bond in **1-F** ( $0.287 e \text{ \AA}^{-3}$ ), these values are a factor of two greater than that calculated at the bond critical point between Sb and N in **1-CN**. This observation is in line with the long Sb–C<sub>CN</sub> and Sb–N<sub>CN</sub> distances observed in the solid-state structure of **1-CN**, as well as with the absence of a nonbonding lone pair on the cyanide anion.

Table 1. Crystal structure data for **1-CN** and **1-N<sub>3</sub>**.

	<b>1-CN</b>	<b>1-N<sub>3</sub></b>
Empirical formula	C <sub>38</sub> H <sub>39</sub> BNSb	C <sub>37</sub> H <sub>39</sub> BN <sub>3</sub> Sb
$M_r$	642.26	658.27
Crystal size, mm <sup>3</sup>	0.14 × 0.10 × 0.07	0.20 × 0.10 × 0.05
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
$a$ , Å	16.247(7)	17.154(8)
$b$ , Å	9.307(4)	11.271(5)
$c$ , Å	25.233(8)	19.904(7)
$\beta$ , deg	124.732(19)	124.47(3)
$V$ , Å <sup>3</sup>	3136(2)	3173(2)
$Z$	4	4
$D_{\text{calcd.}}$ , g cm <sup>-3</sup>	1.36	1.38
$\mu(\text{MoK}\alpha)$ , cm <sup>-1</sup>	0.9	0.9
$F(000)$ , $e$	1320	1352
$hkl$ range	±20, ±11, ±31	±20, ±13, ±23
$((\sin \theta)/\lambda)_{\text{max}}$ , Å <sup>-1</sup>	0.617	0.596
Refl. measured	31 589	26 214
Refl. unique/ $R_{\text{int}}$	6160/0.0754	5566/0.0517
Param. refined	364	367
$R1(F)/wR2(F^2)^{a,b}$ , all refl.	0.0676/0.1514	0.0536/0.1261
GoF ( $F^2$ ) <sup>c</sup>	1.023	1.029
$\Delta\rho_{\text{fin}}$ (max/min), $e \text{ \AA}^{-3}$	1.26/−1.09	1.95/−1.80

<sup>a</sup>  $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ; <sup>b</sup>  $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$  and  $a = 0.0951$  (**1-CN**), 0.0773 (**1-N<sub>3</sub>**);  $b = 0$  (**1-CN**), 3.4228 (**1-N<sub>3</sub>**); <sup>c</sup>  $\text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$ .

The presence of a weak  $\pi_{(\text{CN})} \rightarrow \sigma^*_{(\text{S-C})}$  interaction in **B-CN** has been proposed to contribute to the high cyanide affinity of the *o*-sulfonium borane **B<sup>+</sup>**, suggesting that the Sb–N<sub>CN</sub> bond path calculated for **1-CN** may be due to a similar  $\pi_{(\text{CN})} \rightarrow \sigma^*_{(\text{Sb-C})}$  interaction [41].

An NBO analysis performed on **1-CN** confirms the presence of a weak  $\pi_{(\text{CN})} \rightarrow \sigma^*_{(\text{Sb-C})}$  interaction whose deletion affords an increase in the energy of the molecule by 3.5 kcal mol<sup>-1</sup> (Fig. 4). In **1-N<sub>3</sub>**, NBO analysis located a  $lp_{(\text{N})} \rightarrow \sigma^*_{(\text{Sb-C})}$  donor-acceptor interaction whose deletion resulted in an increase in the total energy of the molecule by 15.15 kcal mol<sup>-1</sup>. This value is very close to that calculated from deletion of the  $lp_{(\text{F})} \rightarrow \sigma^*_{(\text{Sb-C})}$  ( $E_{\text{del}} = 15.2$  kcal mol<sup>-1</sup>) interaction in **1-F** and is significantly greater than the  $lp_{(\text{N})} \rightarrow \sigma^*_{(\text{P-C})}$  ( $E_{\text{del}} = 5.8$  kcal mol<sup>-1</sup>) donor-acceptor interaction in the phosphonium analog **A-N<sub>3</sub>** [40].

In summary, we have shown that the stibonium borane **1<sup>+</sup>** reacts with the toxic cyanide and azide anions to afford the zwitterionic Lewis acid-base adducts **1-CN** and **1-N<sub>3</sub>**, respectively. The Lewis acidity of the stibonium center allows it to engage the azide in

Table 2. Selected bond lengths (Å) and angles (deg) for **1-CN** and **1-N<sub>3</sub>**.

	<b>1-CN</b>	<b>1-N<sub>3</sub></b>
Distances		
Sb(1)–C(1)	2.113(5)	2.110(4)
Sb(1)–C(7)	2.103(5)	2.096(5)
Sb(1)–C(8)	2.088(5)	2.100(4)
Sb(1)–C(14)	2.119(5)	2.121(4)
Sb(1)–N(1)	3.093(5)	2.477(4)
Sb(1)–C(38)	2.943(7)	
B(1)–C(2)	1.650(7)	1.627(6)
B(1)–C(20)	1.636(8)	1.666(6)
B(1)–C(29)	1.663(7)	1.640(6)
B(1)–C(38)	1.601(8)	
B(1)–N(1)		1.623(6)
N(1)–C(38)	1.147(7)	
Angles		
C(1)–Sb(1)–N(1)	87.3(2)	74.0(2)
C(1)–Sb(1)–C(38)	68.9(2)	
C(14)–Sb(1)–N(1)	168.5(2)	174.1(2)
C(14)–Sb(1)–C(38)	169.8(2)	
N(1)–B(1)–C(2)		99.7(3)
C(38)–B(1)–C(2)	101.9(4)	

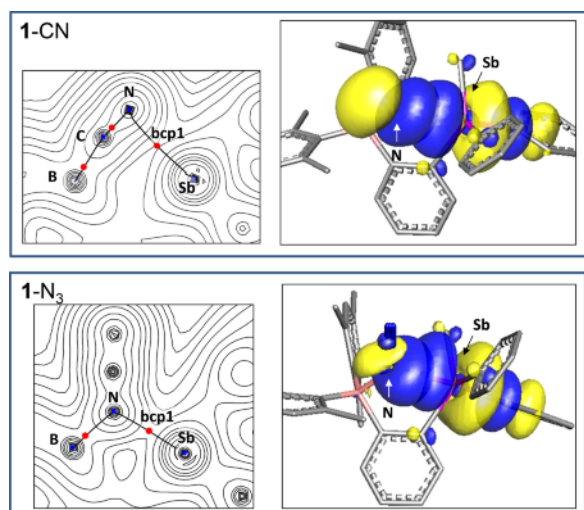


Fig. 4 (color online). Left: AIM electron density maps with relevant bond paths and bond critical points for the B–CN→Sb and B–N<sub>3</sub>→Sb interactions in **1-CN** (top) and **1-N<sub>3</sub>** (bottom), respectively. Right: Plots of the NBO donor-acceptor interactions calculated for **1-CN** (top) and **1-N<sub>3</sub>** (bottom). Density isovalues are set to 0.03 e Å<sup>-3</sup>, and hydrogen atoms have been omitted for clarity.

a strong donor-acceptor interaction similar to that observed for the fluoride adduct **1-F**, making **1<sup>+</sup>** a potent bidentate Lewis acid for chelation of both anions. Although **1<sup>+</sup>** effectively binds cyanide anions

via complexation to the boron atom, chelation effects are minimal and limited to a weak  $\pi_{(\text{CN})} \rightarrow \sigma^*_{(\text{Sb}-\text{C})}$  interaction. Altogether, these results support the notion of an increased Lewis acidity of bifunctional onium/boron anion receptors upon moving to heavier main group onium ions, an effect which can be attributed to a greater energetic/spatial accessibility of the accepting  $\sigma^*_{(\text{E}-\text{C})}$  orbital.

## Experimental Section

### General considerations

Tetrabutylammonium cyanide (TBACN) and tetrabutylammonium azide (TBAN<sub>3</sub>) were purchased from Aldrich and used as received. CHCl<sub>3</sub> and CDCl<sub>3</sub> were dried by refluxing and distilling over P<sub>2</sub>O<sub>5</sub> under an atmosphere of N<sub>2</sub>. Methanol was distilled from NaOMe and stored over Linde-type 4 Å molecular sieves. All other solvents were ACS reagent grade and used as received. Air-sensitive compounds were handled under an N<sub>2</sub> atmosphere using standard Schlenk and glovebox techniques. Elemental analyses were performed at Atlantic Microlab (Norcross, GA, USA). NMR spectra were recorded on a Varian Unity Inova 400 FT NMR (399.59 MHz for <sup>1</sup>H, 128.19 MHz for <sup>11</sup>B, 100.45 MHz for <sup>13</sup>C) spectrometer at ambient temperature unless otherwise stated. Chemical shifts  $\delta$  are given in ppm and are referenced against external Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C) and BF<sub>3</sub>·Et<sub>2</sub>O (<sup>11</sup>B). [1]OTf was synthesized as previously reported [45].

### Crystallography

Single crystals of **1-CN** and **1-N<sub>3</sub>** were obtained by addition of 1 equiv. of TBACN, or TBAN<sub>3</sub>, respectively, to solutions of [1]OTf in CHCl<sub>3</sub> and subsequent layering with anhydrous methanol. Details of the data collection and structure refinement are included in Table 1. The crystallographic measurements were performed using a Bruker APEX-II CCD area detector diffractometer, with graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å). A specimen of suitable size and quality was selected and mounted onto a nylon loop. The semiempirical method SADABS [67] was applied for absorption correction. The structures were solved by Direct Methods and refined by the full-matrix least-squares techniques against  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms. All H atoms were geometrically placed and refined in a riding model approximation. Data reduction and further calculations were performed using the Bruker SAINT+ [68] and SHELXTL NT [69] program packages.

CCDC 1016159 and 1016160 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Theoretical calculations

Density functional theory (DFT) calculations (full geometry optimization) were carried out on **1-CN**, and **1-N<sub>3</sub>** starting from the crystal structure geometries with GAUSSIAN 09 [70] and utilizing the gradient-corrected Becke exchange functional (B3LYP) and the Lee-Yang-Parr correlation functional [71, 72]. A 6-31+g(d') basis set was used for B, N, and F [73] and 6-31g basis set for C, H [74]. An aug-cc-pvTz-pp basis set [75] was used for Sb. Frequency calculations were also carried out on the optimized geometry and showed no imaginary frequencies. The electron density of the DFT-optimized structures of **1-CN**, and **1-N<sub>3</sub>** were subjected to Atoms In Molecules analysis [76] using AIM2000 [77]. The Natural Bond Orbital (NBO) analysis of **1-CN** and **1-N<sub>3</sub>** was carried out using the NBO v3.1 program implemented in GAUSSIAN [78, 79].

### Preparation of **1-CN** and **1-N<sub>3</sub>**

Addition of 1 equiv. of TBACN or TBAN<sub>3</sub> to solutions of [1]OTf in CDCl<sub>3</sub> resulted in quantitative conversion to the adducts **1-CN**, and **1-N<sub>3</sub>**, respectively, as determined by multinuclear NMR experiments. The solid products could be precipitated as colorless, microcrystalline solids by addition of anhydrous MeOH to these samples.

Data for **1-CN**: <sup>1</sup>H NMR (399.9 MHz, CDCl<sub>3</sub>): δ = 1.52 (brs, 3H, *o*-Mes-CH<sub>3</sub>), 1.56 (s, 3H, Sb-CH<sub>3</sub>), 1.72 (brs, 3H, *o*-Mes-CH<sub>3</sub>), 2.22 (brs, 6H, *p*-Mes-CH<sub>3</sub>), 2.27 (brs, 6H, *o*-Mes-CH<sub>3</sub>), 6.61 (brs, 1H, Mes-CH), 6.66 (brs, 1H, Mes-CH), 6.76 (brs, 1H, Mes-CH), 6.79 (brs, 1H, Mes-CH),

7.09 (t, 1H, *o*-C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz), 7.21 (m, 2H, *o*-C<sub>6</sub>H<sub>4</sub>), 7.36 (brm, 2H, SbPh), 7.40 (d, 1H, *o*-C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz), 7.44–7.53 (m, 8H, SbPh) ppm. – <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>): δ = 9.57 (Sb-CH<sub>3</sub>), 20.79 (*p*-Mes-CH<sub>3</sub>), 24.57 (*o*-Mes-CH<sub>3</sub>), 24.76 (*o*-Mes-CH<sub>3</sub>), 25.65 (*o*-Mes-CH<sub>3</sub>), 25.98 (*o*-Mes-CH<sub>3</sub>), 125.63, 127.53, 129.01, 129.23, 129.45, 130.00, 130.26, 130.55, 131.13, 131.68, 131.89, 133.11, 133.80, 134.34, 134.75, 139.07, 140.92, 142.86, 143.54, 145.37, 150.25(br), 166.00 (br) ppm. – <sup>11</sup>B NMR (128.2 MHz, CDCl<sub>3</sub>): δ = –11.67 ppm. – Anal. for C<sub>38</sub>H<sub>39</sub>BNSb: calcd. C 71.06, H 6.12; found C 70.54, H 6.12.

Data for **1-N<sub>3</sub>**: <sup>1</sup>H NMR (399.9 MHz, CDCl<sub>3</sub>): δ = 1.32 (s, 3H, Sb-CH<sub>3</sub>), 1.83 (brs, 12H, *p*-Mes-CH<sub>3</sub>), 2.20 (s, 6H, *o*-Mes-CH<sub>3</sub>), 6.67 (s, 4H, Mes-CH), 7.02 (dd, 1H, *o*-C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, <sup>4</sup>J<sub>H-H</sub> = 0.9 Hz), 7.08 (ddd, 1H, *o*-C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.7 Hz), 7.25 (ddd, 1H, *o*-C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.3 Hz), 7.32 (d, 4H, SbPh, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 7.43–7.53 (m, 1H *o*-C<sub>6</sub>H<sub>4</sub>+ 6H SbPh) ppm. – <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>): δ = 6.28 (Sb-CH<sub>3</sub>), 20.76 (*p*-Mes-CH<sub>3</sub>), 24.67 (*o*-Mes-CH<sub>3</sub>), 125.95, 128.53, 129.34, 129.75, 131.03, 131.25, 133.82, 133.91, 134.16, 138.65, 142.42, 147.52, 167.96, (1 *ipso*-C not observed) ppm. – <sup>11</sup>B NMR (128.2 MHz, CDCl<sub>3</sub>): δ = 0.99 ppm. – Anal. for C<sub>37</sub>H<sub>39</sub>BN<sub>3</sub>Sb: calcd. C 67.51, H 5.97; found: C 67.30, H 6.03.

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