# **Inorganic Chemistry**

## Synthesis and Properties of Triarylhalostibonium Cations

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**S** Supporting Information

ABSTRACT: As part of our fundamental interest in the chemistry of main-group Lewis acids, we have decided to target stibonium cations whose Lewis acidity is enhanced by the presence of a halogen substituent directly bound to antimony. Starting from Ph<sub>3</sub>Sb(OTf)<sub>2</sub> (1) and Mes<sub>3</sub>Sb(OTf)<sub>2</sub> (2), we successfully prepared the triflate derivatives  $Ph_3SbF_3$ (OTf) (3) and Mes<sub>3</sub>SbF(OTf) (4). We also synthesized the hexachloroantimonate salt of  $[Mes_3SbCl]^+$  (6), an analogue of the known  $[Ph_3SbCl][SbCl_6]$  (5). The structures of these complexes have been investigated experimentally as well as computationally using density functional theory methods. While direct interaction is observed between the anion and the stibonium center in compounds 3-5, compound 6 exists as an



ionic solid with the four-coordinate [Mes<sub>3</sub>SbCl]<sup>+</sup> cation separated from the [SbCl<sub>6</sub>]<sup>-</sup> anion. The structural difference observed between the two hexachloroantimonate derivatives 5 and 6 is ascribed to the increased steric protection provided by the larger mesityl substituents. To understand how these structural differences affect the properties of these antimony species, we have compared their catalytic activity in two simple reactions, namely, the polymerization of tetrahydrofuran and the Friedel-Crafts dimerization of 1,1-diphenylethylene. These studies show that 5 is the most active catalyst for both reactions, suggesting that the reactivity of these species is controlled by both the coordinating nature of the counteranion and the steric accessibility of the reactive antimony center.

### INTRODUCTION

Electron-deficient group 15 compounds are attracting growing interest in the field of Lewis acid catalysis. While it has been shown that simple phosphonium cations can promote a range of reactions including aldol additions,<sup>1</sup> the cyanosilylation of aldehydes,<sup>2</sup> and hydroformylation reactions,<sup>3</sup> this field of research has attracted a renewed interest prompted by the introduction of highly electron-deficient fluorophosphonium cations such as  $[(C_6F_5)_3PF]^+$  (A<sup>+</sup>; Chart 1)<sup>4</sup> and  $[(SIMes)^-$ 

Chart 1



 $PFPh_2$ <sup>2+</sup> (SIMes = 1,3-dimesitylimidazolidin-2-ylidene).<sup>5</sup> These electrophilic phosphorus cations<sup>6</sup> are highly reactive and catalyze hydrodefluorination,<sup>4</sup> hydrosilylation,<sup>7</sup> hydrodeoxygenation,<sup>8</sup> Friedel-Crafts-type dimerization,<sup>5</sup> and dehydrocoupling reactions.<sup>9</sup>

In parallel to these developments, several groups including ours have become interested in the Lewis acidic properties of antimony(V) compounds<sup>10</sup> and their use in the field of anion

sensing<sup>11</sup> and catalysis. With respect to the latter, it has long been known that simple stibonium cations such as [Ph<sub>4</sub>Sb]<sup>+</sup> can catalyze the addition of isocyanates to epoxides.<sup>12</sup> It has more recently been shown that stibonium cations can also be used to promote hydrosilylation or allylstannation of aldehydes<sup>13</sup> among other reactions.<sup>14</sup> On the basis of the prediction that a higher Lewis acidity could be obtained through the use of electron-withdrawing substituents, we synthesized the stibonium salt  $[Sb(C_6F_5)_4]^+$  (B<sup>+</sup>; Chart 1) and found that it is sufficiently acidic to polymerize tetrahydrofuran (THF) or abstract a fluoride anion from  $[SbF_6]^{-15}$  In a continuation of these studies and inspired by the work of Stephan and co-workers on fluorophosphonium cations,<sup>4,5</sup> we have now decided to investigate the synthesis and properties of stibonium cations whose Lewis acidity is enhanced by a halogen substituent ( $C^+$ ; Chart 1).

#### **RESULTS AND DISCUSSION**

Triarylfluorostibonium Triflates. Realizing the stabilizing influence of the counteranion, we decided to first consider halostibonium salts with anions of intermediate coordinative ability. Based on the knowledge that stibonium triflates

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sometimes adopt molecular rather than ionic structures in the solid state, we investigated the reaction of  $Ar_3SbF_2$  (Ar = Ph, Mes)<sup>16</sup> with a stoichiometric amount of trimethylsilyl triflate (TMSOTf). In situ <sup>19</sup>F NMR measurements confirmed the formation of fluorostibonium triflates, as indicated by the presence of a SbF resonance at -156 ppm for Ph<sub>3</sub>SbF(OTf) (3) and -145 ppm for Mes<sub>3</sub>SbF(OTf) (4) in CH<sub>2</sub>Cl<sub>2</sub>. Efforts to isolate the pure salts from these mixtures were complicated by the oily nature of the residue, which impeded purification. Faced with these difficulties, we considered an alternative approach based on ligand redistribution starting from Ar<sub>3</sub>SbF<sub>2</sub> and the corresponding  $Ar_3Sb(OTf)_2$ . This approach was inspired by the elegant work of Burford and co-workers, who recently described Ph<sub>3</sub>Sb(OTf)<sub>2</sub> (1).<sup>10d,e</sup> For the purpose of this study, we synthesized the mesityl analogue, namely,  $Mes_3Sb(OTf)_2$  (2). This new compound, which could be conveniently obtained by the reaction of Mes<sub>3</sub>SbBr<sub>2</sub> with AgOTf in CH<sub>2</sub>Cl<sub>2</sub>, has been spectroscopically characterized. Gratifyingly, we found that 1 and 2 react with their

Scheme 1. Synthesis of the Ditriflate and Fluorotriflate Derivatives

Ar <sub>3</sub> SbCb	AgOTf	Ar <sub>3</sub> Sb(OTf) <sub>2</sub> -	Ar <sub>3</sub> SbF <sub>2</sub>	Ar <sub>3</sub> SbF(OTf)
° 2	CH <sub>2</sub> Cl <sub>2</sub>	<b>0</b> ( ) <u>1</u>	CH <sub>2</sub> Cl <sub>2</sub>	• • •
		<b>1</b> , Ar = Ph		<b>3</b> , Ar = Ph
		<b>2</b> , Ar = Mes		<b>4</b> , Ar = Mes

corresponding difluorides to afford 3 and 4 (Scheme 1). The <sup>19</sup>F NMR spectra of both 3 and 4 display two sets of resonances, which correspond to the triflate CF<sub>3</sub> and SbF moieties, respectively. These two signals, which appear at -78and -156 ppm for 3 and -78 and -145 ppm for 4, show the expected 3:1 intensity ratio. It is interesting to note that the chemical shifts of the antimony-bound fluorine atoms are distinctly more upfield than those measured for  $Ph_3SbF_2$  (-148 ppm) and  $Mes_3SbF_2$  (-100 ppm). The origin of the larger change observed in the chemical shift of the antimony-bound fluorine atom upon conversion of Mes<sub>3</sub>SbF<sub>2</sub> into 4 has not been elucidated. Compounds 3 and 4 have also been investigated by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Clean spectra of compound 3 could not be obtained even when starting from thoroughly dried CD<sub>2</sub>Cl<sub>2</sub> and recrystallized materials. We assign these difficulties to the reactive nature of this compound.

By contrast, <sup>1</sup>H and <sup>13</sup>C NMR of 4 show the expected resonances, with no sign of impurities or decomposition, suggesting that 4 is kinetically stabilized by the bulky mesityl ligands. Despite the asymmetry introduced by the presence of two different axial ligands in 4, the *o*-methyl groups from the mesityl substituents are not differentiated, giving rise to a single <sup>1</sup>H NMR resonance at 2.50 ppm in CD<sub>2</sub>Cl<sub>2</sub>. The equivalence of these resonances is rationalized by invoking the rapid rotation of the mesityl substituents about the Sb–C<sub>ipso</sub> bonds. In agreement with this view, we observed a single aromatic CH resonance at 7.10 ppm.

Colorless single crystals of compounds 2-4 could be obtained by layering a CH<sub>2</sub>Cl<sub>2</sub> solution of the stibonium salt with hexanes at -20 °C. The structure of 2 resembles that reported for 1 (Figure 1 and Table 1). The antimony center adopts a trigonal-bipyramidal geometry, with the triflate anions occupying the apical sites. It is interesting to note that the Sb-O distances in 2 [2.178(2) Å] are almost equal to those in 1  $[2.1708(14) \text{ Å}]^{10d}$  despite the larger steric demand of the mesityl substituents. The structures of 3 and 4 (Figure 1) are again best described as trigonal-pyramidal, with the fluoride and triflate anions spanning the apical sites. However, the Sb-O distances of 2.2493(15) Å in 3 and 2.325(9) Å in 4 are longer than those in 1 and 2, thus indicating that the triflate anions are more loosely coordinated to the antimony atom. This lengthening is distinctly more acute in the case of 4, a factor that we assign to the bulk of the mesityl substituents. The structures of 1-4 have been optimized using density functional theory (DFT) methods, as implemented in *Gaussian*  $09.^{17}$ These optimizations were carried out using the M06 functional<sup>18</sup> and mixed basis set [6-31g(d) for carbon, hydrogen, and oxygen, 6-31g(d') for fluorine,  $6-311g^*$  for sulfur and chlorine, and cc-pVTZ-PP<sup>19</sup> with Stuttgart relativistic small-core effective core potential (ECP)<sup>20</sup> for antimony] to produce structures that closely match those determined by X-ray diffraction. The optimized structures were also subjected to natural bond orbital (NBO) analysis to extract natural population analysis (NPA) charges (Table 2). These charges, combined with the Sb-F and Sb-O Wiberg bond indices (WBIs), are in good agreement with the structural results and show that the antimony centers of 3 and 4 have greater cationic character while forming a weaker bond with the triflate anion.

Triarylchlorostibonium Hexachloroantimonates. Following the observation that the triflate anions remain



**Figure 1.** Structures of **2** (left), **3** (middle), and **4** (right) in the crystal. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The asymmetric unit of **4** contains two independent molecules, one of which resides about the  $C_3$  axis. The molecule of **4** shown in the figure does not reside in a crystallographic special position.

Та	ble	1.	Sele	cted	Sti	ructural	ŀ	Parameters	for	C	om	pour	ıds	51	-4	1
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compd	Sb1-O1 (Å)	Sb1-F1/O4 (Å)	avg. Sb–C (Å)	∠O1-Sb-F1/O4 (deg)	avg. ∠C−Sb−C (deg)	avg. ∠O1−Sb−C (deg)	avg. ∠F1/O4−Sb−C (deg)
1 <sup>10d</sup>	2.1716(14)	2.1708(14)	2.084	173.21(5)	120.0	89.8	89.8
2	2.173(2)	2.178(2)	2.123	174.91(9)	120.0	89.3	90.7
3	2.2493(15)	2.0003(15)	2.085	177.75(6)	119.9	87.9	92.1
4 <sup><i>a</i></sup>	2.325(9) [2.344(15)]	1.948(7) [1.958(12)]	2.096 [2.142]	176.5(3) [175.2(7)]	119.9 [120.0]	88.2 [88.9]	91.8 [91.8]
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"The metrical parameters given in square brackets correspond to the molecule that resides about the  $C_3$  axis.

Table 2. Calculated NBO Partial Charges (NPA) and WBIs of Compounds 1-4 in the Gas Phase

		WBI		
compd	NPA on Sb	Sb-O	Sb-F	
1	2.2926	0.2976		
2	2.3226	0.2778		
3	2.5806	0.2646	0.4601	
4	2.3635	0.2297	0.4232	

coordinated to the antimony center of 3 and 4, we decided to investigate the use of a more weakly coordinating counteranion. A review of the literature shows that monohalostibonium cations such as  $[Ph_3SbCl]^+$  have been previously isolated as hexachloroantimonate ( $[SbCl_6]^-$ ) salts. Given the weakly coordinating nature of this anion, we decided to revisit some aspects of this chemistry. While it has been shown previously that  $Ph_3SbCl_2$  reacts with  $SbCl_5$  in  $CCl_4$  to afford  $[Ph_3SbCl]$ -[ $SbCl_6$ ] (5; Scheme 2),<sup>21</sup> we found that this synthesis could be

Scheme 2. Synthesis of the Triarylchlorostibonium Hexachloroantimonates



easily carried out in  $CH_2Cl_2$ , leading to a moderate yield (55%) of this salt. This approach also proved to be well adapted to the synthesis of [Mes<sub>3</sub>SbCl][SbCl<sub>6</sub>] (6), which was obtained in 75% yield by the reaction of Mes<sub>3</sub>SbCl<sub>2</sub> with SbCl<sub>5</sub> in  $CH_2Cl_2$ . In the <sup>1</sup>H NMR spectrum, the methyl groups of 6 give rise to two resolved resonances at 2.45 ppm (6H) and 2.42 ppm (3H), respectively. Similar to compound 4, we propose that the detection of only two methyl resonances originates from the rapid rotation of the mesityl substituents about the Sb- $C_{ipso}$  bonds. In agreement with this view, we observe a single aromatic *CH* resonance at 7.22 ppm (2H). We also note that this resonance is more downfield than that measured for the ditriflate derivative 1 (7.11 ppm) and the fluorotriflate derivative 4 (7.09 ppm).

In the crystal, we observe that **6** exists as a salt with no short contact between the  $[SbCl_6]^-$  anion and the stibonium cation (Figure 2). This is in contrast to the previously reported structure of **5** in which the  $[SbCl_6]^-$  anion interacts with the stibonium center via a long Sb–Cl bond of 3.231(6) Å.<sup>21</sup> Congruent with the different degrees of cation–anion interactions observed in **5** and **6**, we find that the  $[Mes_3SbCl]^+$ 



**Figure 2.** Structure of **6** in the crystal. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **6**: Sb1–Cl1 = 2.322(2), Sb1–C1 = 2.112(9), Sb1–C10 = 2.092(10), Sb1–C19 = 2.105(9), average  $\angle$ C–Sb–C = 116.3, and average  $\angle$ Cl–Sb–C = 101.2.

cation of **6** is closer to a tetrahedral geometry than the  $[Ph_3SbCl]^+$  cation of **5**, with  $\tau_4$  values<sup>22</sup> of 0.84 for **5** and 0.89 for **6**, respectively. We attribute the absence of such short contacts between the  $[SbCl_6]^-$  anion and the stibonium center of **6** to the protection offered by the *o*-methyl groups of the mesityl substituents, as illustrated in Figure 3. The antimony



Figure 3. Space-filling model of cations  $[Ph_3SbCl]^+$  (left) and  $[Mes_3SbCl]^+$  (right).

atom is 0.30 Å above the plane defined by the three *ipso*-carbon atoms in the structure of **5** and 0.41 Å in that of **6**. The distorted tetrahedral geometry of **6** is further characterized by average  $\angle$ Cl–Sb–C and  $\angle$ C–Sb–C angles of 101.2° and 116.3°, respectively. The Sb–Cl bond distance in [Mes<sub>3</sub>SbCl]<sup>+</sup> [2.322(2) Å] is as short as that in [Ph<sub>3</sub>SbCl]<sup>+</sup> [2.325(7) Å],<sup>21</sup> pointing to a very electrophilic antimony center. This view is corroborated by the fact that this bond distance is shorter than that measured in  $(C_6F_5)_4$ SbCl (2.45 Å),<sup>15</sup> Ph<sub>3</sub>SbCl<sub>2</sub> (av. 2.49 Å),<sup>23</sup> and Ph<sub>4</sub>SbCl (2.69 Å).<sup>24</sup>

On the basis of the knowledge that the Lewis acidity of group 15 compounds originates from low-lying  $\sigma^*$  orbitals centered on the pnictogen atom,<sup>15</sup> we examined the molecular orbitals of both [Ph<sub>3</sub>SbCl]<sup>+</sup> and [Mes<sub>3</sub>SbCl]<sup>+</sup>. The geometries of the cations were optimized with the M06 functional and mixed basis sets [6-31+g(d') for carbon, hydrogen, and chlorine and cc-pVTZ-PP<sup>19</sup> with Stuttgart relativistic small-core ECP<sup>20</sup> for antimony]. The lowest unoccupied molecular orbital (LUMO) of both [Ph<sub>3</sub>SbCl]<sup>+</sup> and [Mes<sub>3</sub>SbCl]<sup>+</sup> is centered on the antimony atom and is dominated by  $\sigma^*(Sb-Cl)$  character. Smaller components of the LUMO reside on the ortho and para positions of the arene substituents, suggesting a small degree of  $\sigma^* - \pi$  conjugation (Figure 4). The LUMO energy of



Figure 4. LUMO of  $[Ph_3SbCl]^+$  (left) and  $[Mes_3SbCl]^+$  (right). Isovalue = 0.02.

 $[Ph_3SbCl]^+$  is 42 kJ/mol lower that of  $[Mes_3SbCl]^+$ , consistent with the greater electron-withdrawing ability of Ph versus Mes as well as with the experimental observation that  $[Ph_3SbCl]^+$  strongly interacts with the  $[SbCl_6]^-$  anion in the solid state. Hence, electronic effects may also be partly responsible for the absence of a direct interaction between the mesitylstibonium  $[Mes_3SbCl]^+$  cation and the  $[SbCl_6]^-$  anion in the solid state of **6**.

**Reactivity Studies.** We have investigated the reactivity of all compounds described above, with the exception of **3**, whose <sup>1</sup>H and <sup>13</sup>C NMR spectra showed that it could not be reliably handled in solution (*vide supra*). We first decided to assess the relative reactivity of these derivatives by investigating their ability to polymerize THF (Chart 2). With a catalyst loading of 0.1 mol % in neat THF, we observed that **1**, **2**, and **4** were almost inactive, with only 0.1% of the monomer polymerized

Chart 2. Catalytic Reactions Investigated



after 2 h, as established by <sup>1</sup>H NMR spectroscopy. By contrast, 5 and 6 were significantly more active, leading to conversions of 17% [turnover frequency (TOF) = 1.6 min<sup>-1</sup>] for 5 and 15%  $(TOF = 1.3 \text{ min}^{-1})$  for 6 in 2 h. Letting the reaction run for longer periods gave viscous polymer solutions, thereby complicating NMR analysis. These results point to the inhibitory role played by the triflate anion, which may coordinate too strongly to the Lewis acidic antimony center. Such limitations do not seem to affect 5 and 6, in accordance with the more weakly coordinating nature of the [SbCl<sub>6</sub>]<sup>-</sup> counteranion. The higher activity displayed by 5 most likely originates from steric effects, with the smaller phenyl substituents affording a more exposed and thus more reactive antimony center. This argument is supported by the observed catalytic activity of these compounds in the Friedel-Crafts dimerization of 1,1-diphenlyethylene (Chart 2). Compound 5 was the only one to show any activity, leading to a 99% yield of 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene after 20 min. with a catalyst loading of only 5%. Compounds 1, 2, 4, and 6 showed no activity even after 1 day. The fact that 6 was inactive also ruled out the possibility of the hexachloroantimonate anion being responsible for the catalytic properties of 5. While a similar reactivity has been reported for electrophilic phosphoniums and fluorosulfoxonium cations,<sup>5,25</sup> this is the first use of a stibonium catalyst for this reaction.

#### CONCLUSION

Our results demonstrate that halostibonium cations of the general formula [Ar<sub>3</sub>SbX]<sup>+</sup> can be readily synthesized using either anion-exchange or anion-abstraction reactions. The high electrophilic character of the antimony center in these species is reflected by the tendency of these stibonium cations to interact with the counteranion as in the case of 3 and 4, which exist as molecular rather than ionic solids. The formation of halostibonium salts necessitates the use of the more weakly coordinating hexachloroantimonate anion as well as the steric protection of the antimony center, as in the case of 6. Computational studies show that the [Ph<sub>3</sub>SbCl]<sup>+</sup> present in 5 is the most electron-deficient cation investigated in this study. This view is supported by the highest reactivity that 5 displays in the polymerization of THF and the Friedel-Crafts dimerization of 1,1-diphenlyethylene. These results show that the reactivity of such species is controlled by the coordinating nature of the counteranions, the steric accessibility of the reactive antimony center, and possibly the greater electronwithdrawing ability of the phenyl substituents present in 5.

#### EXPERIMENTAL SECTION

**General Considerations.** *Caution!* Antimony compounds are potentially toxic and should be handled accordingly. Air-sensitive experiments were carried out using standard glovebox or Schlenk techniques in the absence of oxygen and moisture. All glassware was dried in an oven and cooled under vacuum before use. Triphenylantimony and potassium fluoride were purchased from EMD Millipore, 2-bromomestyliene, *n*-butyllithium (2.2 M in hexanes), and 1,1-diphenlyethylene were purchased from Alfa Aesar, and antimony pentachloride was purchased from Acros Organics. All commercially available chemicals were used without further purification. SbMes<sub>3</sub><sup>26</sup> PhICl<sub>2</sub><sup>27</sup> Ph<sub>3</sub>SbCl<sub>2</sub><sup>28</sup> Ph<sub>3</sub>SbBr<sub>2</sub><sup>29</sup> Ph<sub>3</sub>Sb-(OTf)<sub>2</sub> (1),<sup>10d</sup> and Mes<sub>3</sub>SbBr<sub>2</sub><sup>26</sup> were prepared according to reported procedures. The solvents were dried by passing through an alumina column (pentane and CH<sub>2</sub>Cl<sub>2</sub>), distillation under N<sub>2</sub> over Na/K (Et<sub>2</sub>O, *n*-hexane, and THF), or distillation under N<sub>2</sub> over CaH<sub>2</sub> (CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, CD<sub>3</sub>CN, and CH<sub>3</sub>CN). All other solvents were ACS

reagent grade and were used as received. NMR spectra were recorded on a Varian Unity Inova 400 FT NMR (399.52 MHz for <sup>1</sup>H, 375.92 MHz for <sup>19</sup>F, 161.74 MHz for <sup>31</sup>P, and 100.46 MHz for <sup>13</sup>C) or a Varian Unity Inova 500 FT NMR (499.42 MHz for <sup>1</sup>H, 469.86 MHz for <sup>19</sup>F, 202.18 MHz for <sup>31</sup>P, and 125.60 MHz for <sup>13</sup>C) at ambient temperature. Chemical shifts ( $\delta$ ) are given in ppm and are referenced against residual solvent signals (<sup>1</sup>H and <sup>13</sup>C) or external standards [BF<sub>3</sub>:Et<sub>2</sub>O for <sup>19</sup>F (-153 ppm) and 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P (0 ppm)]. Elemental analyses were performed at Atlantic Microlab (Norcross, GA).

Synthesis of Mes<sub>3</sub>Sb(OTf)<sub>2</sub> (2). A suspension of AgOTf (720 mg, 2.80 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to a solution of Mes<sub>3</sub>SbBr<sub>2</sub> (883 mg, 1.38 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) in a 50 mL Schleck tube. After stirring in the dark for 1 h, the solution was filtered with a cannula and transferred to another Schlenk tube. Next, a large amount of hexanes (~40 mL) was added to the solution, and the resulting suspension was left to stand at -40 °C overnight. The supernatant was discarded by cannula filtration, affording a white precipitate, which was dried in vacuo. This precipitate was identified as 2 (800 mg, 75% yield). Single crystals were grown at -40 °C in 3-5 days after a CH<sub>2</sub>Cl<sub>2</sub> solution of 2 was layered with hexanes. <sup>1</sup>H NMR (399 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.11 (s, 2H, m-Mes), 2.38 (s, 6H, o-CH<sub>3</sub>), 2.36 (s, 3H, p- $CH_3$ ). <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -79.50 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 145.43 (s), 143.41 (s, o-Mes), 131.90 (s), 130.83 (s, m-Mes), 119.84 (q,  $J_{C-F}$  = 318.3 Hz, OTf), 24.07 (s, o-CH<sub>3</sub>), 21.36 (s, p-CH<sub>3</sub>). Elem anal. Calcd for 2·CH<sub>2</sub>Cl<sub>2</sub>: C, 41.78; H, 4.09. Found: C, 42.09; H, 4.67.

Synthesis of Ph<sub>3</sub>SbF(OTf) (3). A solution of 1 (187 mg, 0.28 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to a solution of Ph<sub>3</sub>SbF<sub>2</sub> (141 mg, 0.36 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) in a 50 mL Schleck tube. The reaction mixture was allowed to stir for 10 min, at which point a large amount (~40 mL) of hexanes was added while the reaction was still stirring. The resulting suspension was left to stand at -40 °C overnight. The supernatant was discarded by cannula filtration, affording a white precipitate, which was dried in vacuo. This precipitate was identified as impure 3 (250 mg). Single crystals were grown at -40 °C in 4 days after a CH<sub>2</sub>Cl<sub>2</sub> solution of 3 was layered with hexanes. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.06-8.02 (m, 2H), 7.74-7.65 (m, 3H). <sup>19</sup>F NMR (470 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -78.57 (s, 3F, OTf), -156.27 (s, 1F, SbF). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 134.16 (d, o-Ph, J = 2.9 Hz), 133.42 (s, p-Ph), 130.35 (s, m-Ph), 119.04 (q,  $J_{C-F}$  = 318.3 Hz, OTf). Elem anal. Calcd: C, 43.79; H, 2.90. found: C, 44.06; H, 2.97. Note: Despite repeated recrystallizations under multiple conditions, the <sup>1</sup>H and <sup>13</sup>C NMR spectra showed the presence of other species, leading to the conclusion that this compound could not be isolated or handled confidently in solution.

Synthesis of Mes<sub>3</sub>SbF(OTf) (4). A solution of 2 (235 mg, 0.30 mmol) in  $CH_2Cl_2$  (5 mL) was added to a solution of  $Mes_3SbF_2$  (154 mg, 0.30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) in a 50 mL Schleck tube. The reaction mixture was allowed to stir for 10 min, at which point a large amount (~40 mL) of hexanes was added while the reaction was still stirring. The resulting suspension was left to stand at -40  $^\circ C$ overnight. The supernatant was discarded by cannula filtration, affording a white precipitate, which was dried in vacuo. This precipitate was identified as 4 (285 mg, 74% yield). Single crystals were grown at -40 °C in 3-5 days after a CH<sub>2</sub>Cl<sub>2</sub> solution of 4 was layered with hexanes. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.10 (s, 2H, m-Mes), 2.50 (s, 6H, o-CH<sub>3</sub>), 2.35 (3H, p-CH<sub>3</sub>). <sup>19</sup>F NMR (470 MHz,  $CD_2Cl_2$ ):  $\delta$  -78.52 (s, 3F, OTf), -144.66 (s, br, 1F, SbF). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz,  $CD_2Cl_2$ ):  $\delta$  143.69 (s), 143.56 (s), 137.70 (s), 131.38 (s, m-Mes), 119.93 (q,  $J_{C-F}$  = 319.6 Hz, OTf), 23.60 (s, o-CH<sub>3</sub>), 21.30 (s, p-CH<sub>3</sub>). Elem anal. Calcd: C, 51.95; H, 5.14. Found: C, 51.67; H, 5.09.

**Synthesis of [Ph<sub>3</sub>SbCl][SbCl<sub>6</sub>] (5).** This procedure is a variant of that available in the literature.<sup>21</sup> A solution of SbCl<sub>5</sub> (396 mg, 1.33 mmol) was slowly added to a solution of Ph<sub>3</sub>SbCl<sub>2</sub> (563 mg, 1.33 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) in a 50 mL Schleck tube. The resulting yellow solution was allowed to stir for 10 min, at which point a large amount (~40 mL) of hexanes was added while the reaction was still stirring. The resulting suspension was left to stand at -40 °C

overnight. The supernatant was discarded by cannula filtration, affording a yellow precipitate, which was dried in vacuo. This precipitate was identified as **5** (558 mg, 55% yield). The product was stored in the -40 °C freezer in the glovebox. Single crystals were grown at -40 °C in 3–5 days after a CH<sub>2</sub>Cl<sub>2</sub> solution of **5** was layered with pentanes. The unit cell matches the reported data. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.97–7.94 (m, 2H), 7.93–7.89 (m, 1H), 7.88–7.83 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  135.80 (s, *p*-Ph), 134.96 (s, *o*-Ph), 132.37 (s, *m*-Ph), 127.31 (quaternary). Elem anal Calcd: C, 29.90; H, 2.09. Found: C, 29.52; H, 2.40.

**Synthesis of [Mes<sub>3</sub>SbCl][SbCl<sub>6</sub>] (6).** A solution of SbCl<sub>5</sub> (179 mg, 0.59 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was slowly added to a solution of Mes<sub>3</sub>SbCl<sub>2</sub> (304 mg, 0.59 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) in a 50 mL Schleck tube. The reaction mixture was allowed to stir for 10 min, at which point a large amount (~40 mL) of hexanes was added while the reaction was still stirring. The resulting suspension was left to stand at -40 °C overnight. The supernatant was discarded by cannula filtration, affording a white precipitate, which was dried in vacuo. This precipitate was identified as 6 (380 mg, 75% yield). Single crystals were grown at -40 °C in 3-5 days after a CH<sub>2</sub>Cl<sub>2</sub> solution of 6 was layered with hexanes. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.22 (*s*, 2H, *m*-Mes), 2.45 (*s*, 6H, *o*-CH<sub>3</sub>), 2.42 (*s*, 3H, *p*-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  146.30 (*s*, *p*-Mes), 142.84 (*s*, *o*-Mes), 132.41 (*s*, *m*-Mes), 131.27 (*s*, quaternary), 24.60 (*s*, *o*-CH<sub>3</sub>), 21.05 (*s*, *p*-CH<sub>3</sub>). Elem anal. Calcd: C, 38.19; H, 3.92. Found: C, 37.90; H, 3.80.

**Catalytic Polymerization of THF.** In the glovebox, the antimony catalyst (0.01 mmol) was dissolved in THF (1 mL) in a vial. Aliquots from the reaction mixture were transferred into NMR tubes, mixed with CDCl<sub>3</sub>, and analyzed by <sup>1</sup>H NMR. The progress of the reaction was derived from the integrated signals of the monomer and polymer.

**Catalytic Friedel–Crafts Dimerization of 1,1-Diphenylethylene.** In the glovebox, a NMR tube was charged with a  $CH_2Cl_2$ solution (0.6 mL) of the antimony catalyst (0.025 mmol). Next, 1,1diphenlyethylene (64  $\mu$ L, 0.49 mmol) was added to the NMR tube via a microsyringe. The reaction was monitored by in situ <sup>1</sup>H NMR.

**Crystallographic Measurements.** All crystallographic measurements were performed at 110(2) K using a Bruker SMART APEX II diffractometer with a CCD area detector (graphite-monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) at 110 K. In each case, a specimen of suitable size and quality was selected, coated with paratone oil, and mounted onto a nylon loop. Crystals of **3** and **4** were mounted on a nylon loop over dry ice to avert decomposition. The semiempirical method *SADABS* was applied for absorption correction. The structures were solved by direct methods and refined by a full-matrix least-squares technique against  $F^2$  with anisotropic temperature parameters for all non-hydrogen atoms. All hydrogen atoms were geometrically placed and refined using the riding model approximation. Data reduction and further calculations were performed using the Bruker *SAINT* and *SHELXTL-NT* program packages.<sup>30</sup>

**Theoretical Calculations.** All structures were optimized starting from the crystal structure geometries, using the program and level of theory specified in the Results and Discussion section. Cartesian coordinates of the optimized structures are provided in the Supporting Information. For compounds 2 and 4, weakly negative frequencies associated with methyl group rotation were observed. Because these rotations affect peripheral groups, efforts to carry out additional optimization cycles were not considered. None of the other structures displayed imaginary frequencies, indicating that a local minimum on its potential energy hypersurface had been reached. The optimized structures were also subjected to NBO<sup>31</sup> analysis. The molecular orbitals were visualized and plotted in the *Jimp2* program.<sup>32</sup>

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00293.

Additional experimental data (synthesis of  $Ph_3SbF_2$ , Mes<sub>3</sub>SbCl<sub>2</sub>, and Mes<sub>3</sub>SbF<sub>2</sub>), NMR spectra for com-

pounds 2, 3, and 6, and Cartesian coordinates of the optimized structures (PDF)  $% \left( PDF\right) =0$ 

X-ray crystallographic data of compounds 2-4, 6, and Mes<sub>3</sub>SbF<sub>2</sub> in CIF format (CIF)

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#### Notes

The authors declare no competing financial interest.

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