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Radical Cation of Dibenzothiophene Fully Annelated with Bicyclo[2.2.2]octene Units: X-ray Crystal Structure and Electronic Properties

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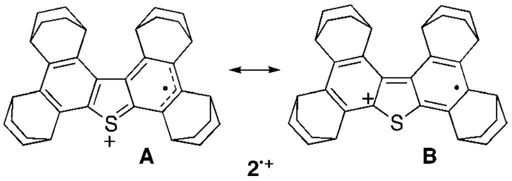
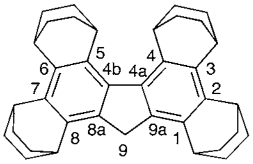
ABSTRACT



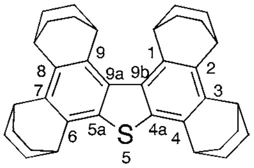
New dibenzothiophene 2 fully annelated with bicyclo[2.2.2]octene units was synthesized and oxidized to stable radical cation salt $2^{\bullet+}SbCl_6^-$, whose structure was determined by X-ray crystallography. Although the intrinsic electronic structure of $2^{\bullet+}$ is predicted to be close to structure A, an interaction with the counteranion makes structure B contribute significantly. A part of the salt $2^{\bullet+}SbCl_6^-$ underwent rearrangement to arenium ion 6^+, whose structure was also clarified by X-ray crystallography.

Elucidation of electronic properties for radical cations of π-conjugated systems is quite important in clarifying their chemical reactivity[1] as well as their role in the operating mechanism of organic molecular devices.[2] For this purpose, X-ray structural analysis is a particularly powerful means. Although a growing number of such studies has been reported, the examples are still limited because of the general instability of the radical cations.[3] On the other hand, we have developed a technique to stabilize the radical cations of various π-conjugated systems by annelation with bicyclo-[2.2.2]octene (abbreviated as BCO) units so that even their isolation as stable single crystals becomes possible.[4]

By virtue of this technique, we recently succeeded in the first X-ray structural determination of the radical cation salt of fluorene **1**, which can be regarded as a derivative of biphenyl planarized by a methylene-bridge connecting the two ortho and ortho′ carbons.[5] The study demonstrated a great contribution of a quinoidal form to the electronic structure of radical cation $\mathbf{1}^{\bullet+}$. However, there has been no report on the X-ray structure of radical cation salts of dibenzothiophene (DBT), which is a sulfur-bridged analogue of fluorene, although the radical cation salts of tetraalkoxy derivatives have been obtained by electrochemical oxidation.[6] Here, we report the first X-ray structure of radical cation salt of DBT annelated with BCO units **2**, to be compared with that of $\mathbf{1}^{\bullet+}$. Also we report the isolation and X-ray structure determination of novel arenium ion obtained by rearrangement of $\mathbf{2}^{\bullet+}$.



1



2

DBT **2** was synthesized in three steps from bis-BCO-annelated bromobenzene **3**[5] as shown in Scheme 1. Lithiation of **3** followed by reaction with $(C_6H_5SO_2)_2S$[7] provided sulfide

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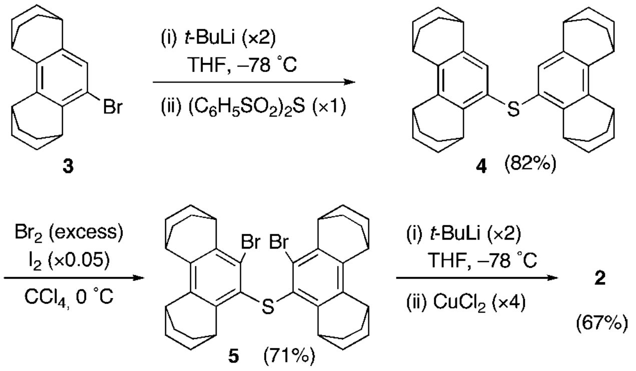
(1) For a review see: Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2550−2589.

(2) For a review, see: Baumgaten, M.; Müllen, K. *Top. Curr. Chem.* **1994**, *169*, 1−103.

(3) For a review, see: Nishinaga, T.; Komatsu, K. *Org. Biomol. Chem.* Submitted.

10.1021/ol0483605 CCC: \$27.50

Scheme 1



4. Then, dibromination, dilithiation, and intramolecular oxidative coupling afforded **2**. The π-system of **2** was anticipated to be more strained than fluorene **1** because of the longer C−S bond than the corresponding C−C bond in the central five-membered ring and, furthermore, due to increased steric repulsion between BCO bridgehead hydrogens close to C1 and C9. In fact, the X-ray crystallography on **2**[8] showed that the π-system is twisted, with the dihedral angle between the mean planes of the two benzene rings being 16°. This angle is larger than that of **1** (12°),[5] with elongation of the C9a−C9b bond (1.487(3) Å) as compared with that of parent DBT[9] (1.450(2) Å).[10]

The cyclic voltammetry of **2** was conducted in CH_2Cl_2 at room temperature to give a reversible first oxidation wave ($E_{1/2} = +0.67$ V vs Fc/Fc$^+$) and a quasireversible second oxidation wave ($E_{pa} = +1.23$ V). The first oxidation potential of **2** is 0.1 V higher than that of **1** ($E_{1/2} = +0.56$ V).[5] This is possibly because of the slightly larger twisting of the π-system of **2**, since similar values are reported for parent DBT ($E_{1/2} = +1.22$ V vs Fc/Fc$^+$ in acetonitrile)[6,11] and fluorene ($E_{1/2} = +1.28$ V).[12] The first oxidation potential of **2** is much lower (by 0.55 V) than that of parent DBT due to the annelation with BCO units, which raises the HOMO level by $\sigma-\pi$ conjugation and inductive effects.[4]

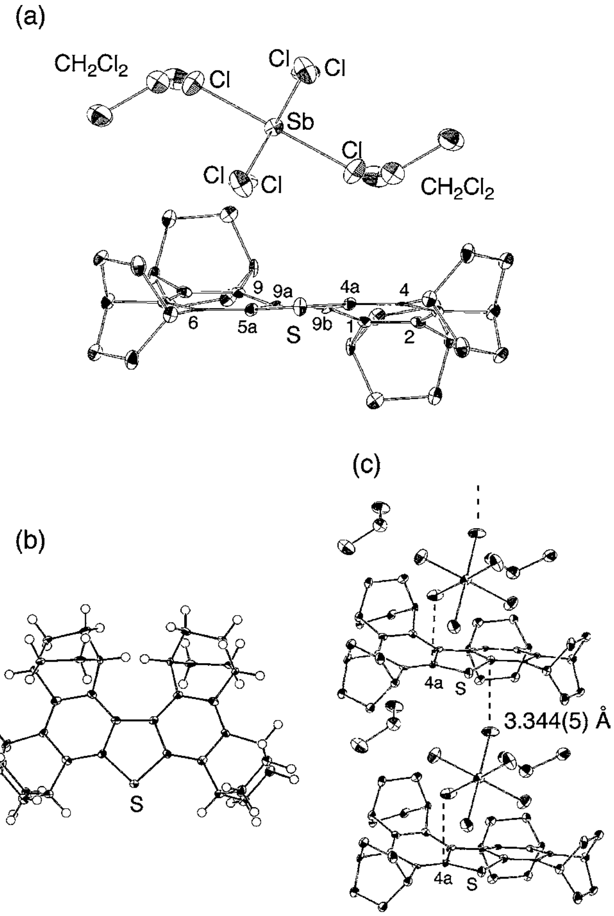


Figure 1. ORTEP drawings showing (a) $\mathbf{2}^{\bullet+}\mathrm{SbCl}_6^-(\mathrm{CH_2Cl_2})_2$, (b) a top view of the $\mathbf{2}^{\bullet+}$ moiety only, and (c) the parking structure. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity in a and c.

Since the stable radical cation of DBT **2** was expected to be generated as the result of electrochemistry, the chemical one-electron oxidation of **2** was attempted by the reaction with 1.5 equiv of $SbCl_5$ in CS_2 at −78 °C for 30 min. The resulting precipitates were redissolved in CH_2Cl_2 at −78 °C, and then hexane was slowly diffused at −78 °C. After 7 days at −78 °C, there appeared two kinds of crystals, which were deep green and reddish purple. The two kinds were separated using tweezers. The weight ratio of the former and latter crystals was 2:1. (The total yield calculated by assuming all the crystals as $\mathbf{2}^{\bullet+}\mathrm{SbCl}_6^-$ was 20% (however, see below).)

The ESR spectrum of a solution of the mixed crystals in CH_2Cl_2 showed a broad single-line signal ($g = 2.0057$), indicating the presence of a stable radical species.

In fact, the result of X-ray crystallography of the deep green crystal demonstrated that it was the radical cation salt of DBT, $\mathbf{2}^{\bullet+}\mathrm{SbCl}_6^-$, as shown in Figure 1.[13] This is the first

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(4) (a) Nishinaga, T.; Wakamiya, A.; Yamazaki, D.; Komatsu, K. *J. Am. Chem. Soc.* **2004**, *126*, 3163−3174. (b) Wakamiya, A.; Nishinaga, T.; Komatsu, K. *Chem. Commun.* **2002**, 1192−1193. (c) Matsuura, A.; Nishinaga, T.; Komatsu, K. *J. Am. Chem. Soc.* **2000**, *122*, 10007−10016. (d) Nishinaga, T.; Wakamiya, A.; Komatsu, K. *Tetrahedron Lett.* **1999**, *40*, 4375−4378. (e) Nishinaga, T.; Komatsu, K.; Sugita, N.; Lindner, H. J.; Richter, J. *J. Am. Chem. Soc.* **1993**, *115*, 11642−11643.

(5) Nishinaga, T.; Inoue, R.; Matsuura, A.; Komatsu, K. *Org. Lett.* **2002**, *4*, 4117−4120.

(6) Cariou, M.; Douadi, T.; Simonet, J. *New J. Chem.* **1995**, *19*, 65−76.

(7) De Jong, F.; Janssen, M. J. *J. Org. Chem.* **1971**, *36*, 1645−1648.

(8) Crystal data for **2**: $C_{36}H_{40}S$, orthorhombic; space group *Fdd*2; $a = 22.321(5)$ Å, $b = 23.158(5)$ Å, $c = 10.204(5)$ Å, $V = 5275(3)$ Å^3, $Z = 8$. The final *R* values and GOF were $R_1 = 0.0406$, w$R_2 = 0.0903$ ($I > 2\sigma(I)$), and GOF = 1.000.

(9) Schaffrin, R. M.; Trotter, J. *J. Chem. Soc. A.* **1970**, 1561−1565.

(10) X-ray crystallography on DBT was reconducted in the present work. Crystal data: $C_{12}H_8S$, monoclinic; space group *P*2(1)/*n*; $a = 8.551(5)$ Å, $b = 5.956(5)$ Å, $c = 16.994(5)$ Å, $\beta = 94.393(5)$°, $V = 863.0(9)$ Å^3, $Z = 4$. The final *R* values and GOF were $R_1 = 0.0346$, w$R_2 = 0.0882$ ($I > 2\sigma(I)$), and GOF = 1.002.

(11) Original value determined versus Ag/Ag$^+$ (+1.26 V)[6] was converted to the value versus Fc/Fc$^+$ by subtracting 0.04 V: Gagné, R. R.; Allison, J. L.; Gall, R. S.; Koval, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7170−7178.

(12) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2867−2872.

(13) Crystal data for $\mathbf{2}^{\bullet+}\cdot\mathrm{SbCl}_6^-\cdot(\mathrm{CH_2Cl_2})_2$: $C_{38}H_{44}Cl_{10}SSb$, orthorhombic; space group *Pccn*; $a = 22.182(5)$ Å, $b = 9.474(5)$ Å, $c = 19.654(5)$ Å, $V = 4130(3)$ Å^3, $Z = 4$. The final *R* values and GOF were $R_1 = 0.0412$, w$R_2 = 0.0504$ ($I > 2\sigma(I)$), and GOF = 0.908.

Table 1. Observed and Calculated Bond Lengths (Å)[a] of DBT **2** and Its Radical Cation Salt $\mathbf{2}^{\bullet+}\mathrm{SbCl_6}^-$

compd	method	C4a−S	C9a−C9b	C1−C9b	C1−C2	C2−C3	C3−C4	C4−C4a	C4a−C9b
2	X-ray[a]	1.756(2)	1.487(3)	1.416(2)	1.409(2)	1.401(2)	1.395(2)	1.388(2)	1.412(2)
	calcd[b]	1.765	1.482	1.418	1.412	1.400	1.402	1.391	1.424
$\mathbf{2}^{\bullet+}$	X-ray[a]	1.733(4)	1.448(7)	1.391(5)	1.408(6)	1.384(5)	1.409(5)	1.395(5)	1.433(5)
	calcd[b]	1.734	1.485	1.402	1.439	1.397	1.406	1.403	1.430

[a] Averaged values are shown. ESDs of mean values given in parentheses are calculated from the following equation: $\sigma(l) = (\Sigma(1/\sigma_i^2))^{-1/2}$. [b] B3LYP/6-31G(d).

example for the X-ray crystallography of the DBT radical cation salt. The observed and calculated[14] π-bond lengths for both neutral **2** and radical cation $\mathbf{2}^{\bullet+}$ are given in Table 1.

As shown in Figure 2, the shapes of HOMO and HOMO-1 of DBT **2** are quite similar to those of HOMO-1 and HOMO of fluorene **1**, respectively. In general, upon removal of an electron from the HOMO to generate the radical cation, bonds with antibonding (out-of-phase) character in the HOMO should become shortened, while those with bonding (in-phase) character should be elongated.[4c,5] This has been well represented by the quinoidal structure in the π-system of the radical cation of **1**.[5] In the case of DBT **2**, C4a−S and C1−C9b bonds having antibonding character in the HOMO are actually shortened upon one-electron oxidation, and bonds such as C4−C4a and C4a−C9b are elongated (see X-ray data in Table 1). This fact suggests that an electronic structure such as **A** is contributing as an intrinsic structure of radical cation of DBT, $\mathbf{2}^{\bullet+}$. The fairly good agreement of observed lengths for these bonds with calculated values supports this assumption.

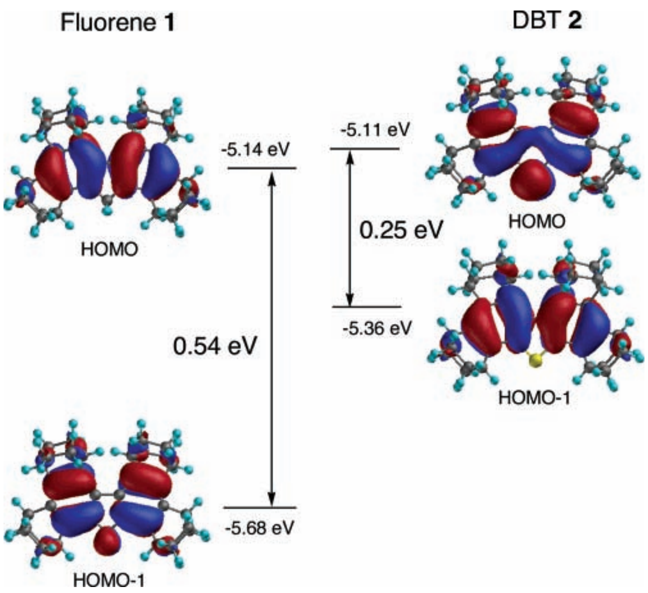
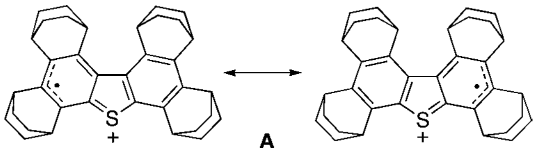


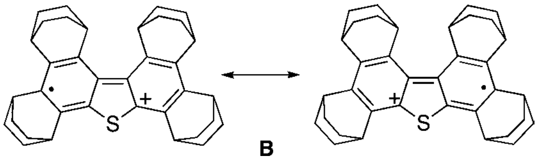
Figure 2. Energy diagrams of KS-HOMO and HOMO-1 of **1** and **2** calculated at the B3LYP/6-31G(d) level.



A

However, in the X-ray crystal structure of $\mathbf{2}^{\bullet+}\mathrm{SbCl_6}^-$, it is noticed that the bond C9a−C9b, which has bonding character in HOMO, is remarkably *shortened* as compared with neutral state (**2**, 1.487(3) Å; $\mathbf{2}^{\bullet+}$, 1.448(7) Å) in contradiction to the prediction and in disagreement with the value predicted by calculation (1.485 Å). This shortening is quite strange since this should bring about larger steric repulsion between the BCO units at 1,2- and 8,9-positions. In fact, it causes larger twisting with a dihedral angle of 22° between mean planes of the two six-membered rings in $\mathbf{2}^{\bullet+}$ than that in neutral **2**.

To interpret this observation it is necessary to take an external factor into consideration. Upon close examination of the packing structure (Figure 1c), the Sb−Cl···C4a distance (3.344(5) Å) is found to be significantly shorter than the sum of van der Waals radii (3.51 Å). Therefore, the electrostatic interaction would induce greater positive charge density on the C4a atom, and this would have made an electronic structure such as **B** contribute to the unexpected shortening of C9a−C9b bond in the crystal of salt $\mathbf{2}^{\bullet+}\mathrm{SbCl_6}^-$.[15]



B

As the second possibility, we may consider the mixing of HOMO-1 into HOMO positioned with such a small energy

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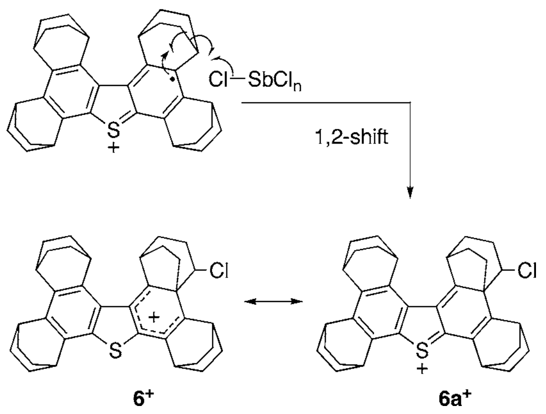
[14] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

[15] This tendency is also observed for C1−C2 bond.

Scheme 2



gap (0.25 eV) for **2**. If one-electron removal is to take place from HOMO-1, a quinoid-type structure such as **B** would be formed as has been shown in the case of **1**.[5]

On the other hand, another kind of crystal with reddish purple color, separated from the product mixture, was found to be the arenium ion salt $\mathbf{6}^{+}\mathrm{SbCl}_6^{-}\cdot(\mathrm{CH_2Cl_2})$ by X-ray crystal structure analysis.[16] A possible reaction pathway for the formation of $\mathbf{6}^{+}$ is shown in Scheme 2. Thus, a 1,2-shift of the methylene carbon of BCO's ethano-bridge to the C2 carbon possessing relatively high spin density (0.1568)[14] would have taken place with concomitant abstraction of a chlorine atom from chloroantimony species[17] (Scheme 2).

From the values of bond lengths shown in Figure 3c, the arenium ion $\mathbf{6}^{+}$ would be better described as the sulfonium ion $\mathbf{6a}^{+}$ with strong $n-\pi$ interaction of the sulfur atom.

This rearrangement to form $\mathbf{6}^{+}$ brings about the release of the severe steric congestion between the BCO bridgehead hydrogens in $\mathbf{2}^{\bullet+}$ as well as the twisting of the π-system. The dihedral angle between mean planes of the two six-membered rings is decreased from 22° in $\mathbf{2}^{\bullet+}$ to 11° in $\mathbf{6}^{+}$. This overall release of steric strain would be the driving force of this rearrangement.

In summary, we succeeded in the first X-ray crystal structural study of the radical cation salt of dibenzothiophene derivative $\mathbf{2}^{\bullet+}\mathrm{SbCl}_6^{-}$ by the use of cation-stabilization technique with BCO units. The experimentally observed structure was interpreted by molecular orbital consideration. Furthermore, we invoked an external factor such as an interaction with a counteranion in our reasoning. Also, a novel stabilized arenium-ion salt was obtained by a rearrangement from $\mathbf{2}^{\bullet+}$, which was driven by release of molecular strain.

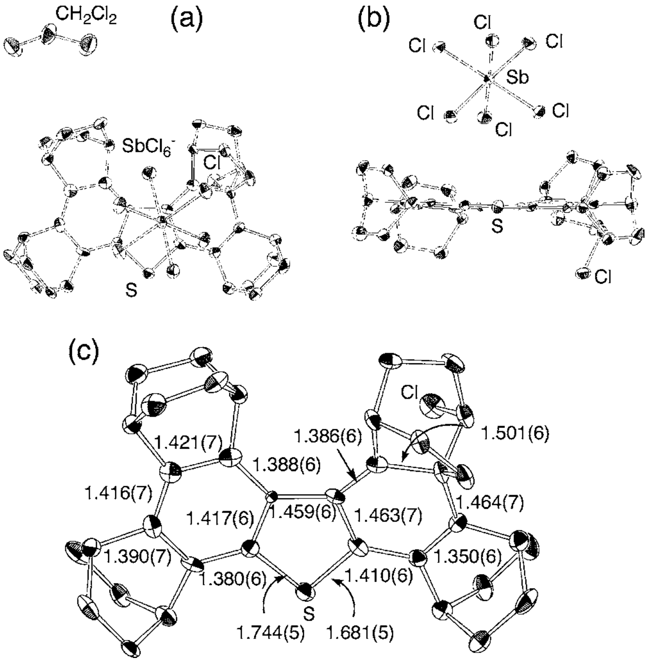


Figure 3. ORTEP drawings of $\mathbf{6}^{+}\mathrm{SbCl}_6^{-}(\mathrm{CH_2Cl_2})_2$; hydrogen atoms are omitted for clarity: (a) top view, (b) side view with solvent molecule omitted, and (c) structure of moiety $\mathbf{6}^{+}$ with π-bond lengths. Thermal ellipsoids are drawn at the 50% probability level.

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Supporting Information Available: Detailed experimental procedures, including spectral data and CIF data of dibenzothiophene, **2**, $\mathbf{2}^{\bullet+}\mathrm{SbCl}_6^{-}\cdot(\mathrm{CH_2Cl_2})_2$, and $\mathbf{6}^{+}\mathrm{SbCl}_6^{-}\cdot(\mathrm{CH_2Cl_2})$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Crystal data for $\mathbf{6}^{+}\cdot\mathrm{SbCl}_6^{-}\cdot(\mathrm{CH_2Cl_2})$: $\mathrm{C_{37}H_{42}Cl_9SSb}$, orthorhombic; space group *Pbca*; $a = 21.228(5)$ Å, $b = 13.527(5)$ Å, $c = 27.025(5)$ Å, $V = 7760(4)$ Å^3, $Z = 8$. The final *R* values and GOF were $R_1 = 0.0430$, $wR_2 = 0.0530$ ($I > 2\sigma(I)$), and GOF = 0.858.

[17] For the arrangement with similar chlorine atom abstraction from chloroantimony species, see: Nishinaga, T.; Inoue, R.; Matsuura, A.; Komatsu, K. *Org. Lett.* **2002**, *4*, 1435–1438.