

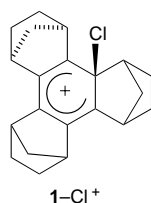
X-Ray structure of bridged 2,2'-bi(adamant-2-ylidene) chloronium cation and comparison of its reactivity with a singly-bonded chloroarenium cation

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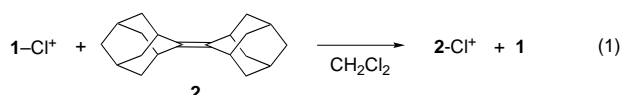
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The unsymmetrically bridged 2,2'-bi(adamant-2-ylidene) chloronium hexachloroantimonate shows distinctive electrophilic (transfer) chlorination reactivity in comparison with the singly-bonded chloroarenium cation.

We recently reported¹ the isolation and structural characterization of a novel cationic chlorine–aromatic complex in which the chlorine atom is directly bonded to a single aromatic carbon atom in a manner similar to that qualitatively described for Wheland intermediates in electrophilic aromatic chlorinations.² The lability of the C–Cl bond in the highly colored (red) chloroarenium cation (**1**–Cl⁺) is demonstrated by its ready



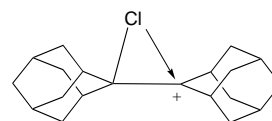
ability to transfer the positive chlorine (Cl⁺) to a variety of aromatic and olefinic donors.¹ For example, an ice-cold solution of 2,2'-bi(adamant-2-ylidene)³ (**2**) reacts with an equimolar amount of **1**–Cl⁺ SbCl₆[–] in CH₂Cl₂ and immediately leads to the bleaching of the red color. The addition of cold hexane affords a colorless microcrystalline precipitate of **2**–Cl⁺ SbCl₆[–] in quantitative yield [eqn. (1)]. The identity of **2**–Cl⁺ SbCl₆[–] is



confirmed by spectral (IR and NMR) comparison with an authentic sample prepared from olefin **2** and SbCl₅ according to the procedure of Nugent.⁴ Note that the chloronium salt **2**–Cl⁺ SbCl₆[–] is extremely robust (if protected from moisture), and it may be stored at room temperature for several days without any decomposition. However despite its remarkable stability,⁴ the structural proof for the nature of bonding in the olefin–chloronium complex **2**–Cl⁺ has not been forthcoming. Accordingly, we now report (a) the single-crystal structure analysis of **2**–Cl⁺ SbCl₆[–] and (b) its reactivity with various aromatic and olefinic donors in comparison with that of the chloroarenium cation **1**–Cl⁺ SbCl₆[–].

A colorless crystal suitable for X-ray crystallography was grown by slow diffusion of hexane into a CH₂Cl₂ solution of **2**–Cl⁺ SbCl₆[–] at –23 °C. Single crystal analysis[‡] by X-ray crystallography established its molecular structure, and the ORTEP diagram in Fig. 1 shows that the chlorine atom is bonded to both olefinic carbon atoms, resulting in a bridged structure akin to that of the corresponding bromonium cation reported previously by Brown and co-workers.⁵ The attachment of a positive chlorine (Cl⁺) to the olefinic bond [C(1)–C(11)] in

2 generates an unsymmetrical cyclopropane ring system in which the C(1)–C(11) bond (2.08 Å) is significantly longer than the C(1)–C(17) bond (1.92 Å); the C(1)–C(11) bond (1.49 Å) is close to a normal single C–C bond. [Note that the hexachloroantimonate anion is only weakly coordinated to C(17).]⁶



We ascribe the unique features of **2**–Cl⁺ to an unsymmetrical structure in which chlorine is σ bonded to a single carbon center [C(11)], and the cationic charge on the adjacent center (C1) is stabilized (solvated) by the chlorine lone pair (acting as an n-donor). The bridged structure of **2**–Cl⁺ is reminiscent of that described for the stabilization of carbocations by neighboring group participation.⁷ Such a 'non-classical' structure of **2**–Cl⁺ leads to a highly stabilized chloronium cation in comparison to the singly-bonded chloroarenium cation **1**–Cl⁺ that readily transfers its positive chlorine to a variety of aromatic and olefinic donors [eqn. (1) and Table 1].

The electrophilic (transfer) chlorination of various aromatic donors with **2**–Cl⁺ SbCl₆[–] was carried out as follows. A solution of **2**–Cl⁺ SbCl₆[–] (0.02 M) in CH₂Cl₂ was treated with pentamethylbenzene (3 equiv.) at room temperature under an argon atmosphere. The colorless reaction mixture was stirred for 3 h, during which the solution took on a pale brown coloration. Aqueous workup of the reaction mixture and GC and GC–MS analysis indicated that only a trace amount of chloropentamethylbenzene (<1%) was formed. The decom-

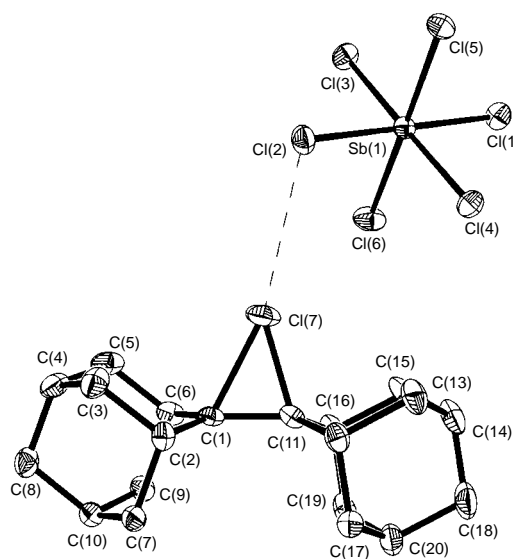


Fig. 1 ORTEP diagram of chloronium cation **2**–Cl⁺ SbCl₆[–]

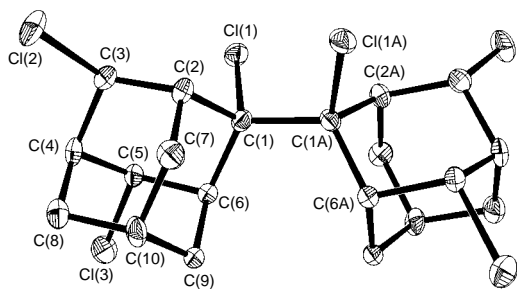


Fig. 2 ORTEP diagram of 2,2',4,4',9,9'-hexachloro-2,2'-biadamantane

position products of $2\text{-Cl}^+ \text{SbCl}_6^-$ were identified as the recovered olefin **2** (27%), the rearranged spiroketone (58%) and several unidentified products.⁸ Similarly, the reaction of $2\text{-Cl}^+ \text{SbCl}_6^-$ with various other aromatic donors listed in Table 1 yielded mainly the decomposition products of 2-Cl^+ .⁸ Furthermore, the treatment of excess cyclohexene (3 equiv.) with $2\text{-Cl}^+ \text{SbCl}_6^-$ in CH_2Cl_2 afforded only the decomposition products of 2-Cl^+ , and no chlorinated product derived from cyclohexene was detected. This remarkable absence of transfer chlorination toward various aromatic and olefinic donors by 2-Cl^+ is in sharp contrast to the corresponding bromonium (or iodonium) cation which readily transfers its positive halogen (Br^+ or I^+) to a variety of olefinic donors.⁹ The insufficient reactivity of 2-Cl^+ towards various electron donors is consistent with our proposal of rather tight σ -bonded character to the bridged chloronium cation (*vide supra*). On the other hand, the enhanced reactivity of the corresponding 2-Br^+ (or 2-I^+) may be attributed to a more loose bromonium-olefin complex with predominant π -character.¹⁰

Although 2-Cl^+ is an ineffective Cl^+ -transfer agent, it readily oxidizes electron-rich aromatic donors to the corresponding cation radicals in its capacity as a one-electron oxidant. For example, treatment of a hexasubstituted aromatic donor (CRET)¹¹ with a solution of 2-Cl^+ in CH_2Cl_2 at 25 °C yields the orange cation radical $[\text{CRET}^+]$, $\lambda_{\text{max}} = 518, 486$ (sh) nm¹¹ in close to quantitative yield during the course of a 3 h period.

To further examine the differences in reactivities of 2-Cl^+ and 2-Br^+ , we carried out the reaction of olefin **2** with dichlorine in CH_2Cl_2 .¹² Thus, the addition of a cooled (−30 °C) solution of **2** to a yellow solution of chlorine in CH_2Cl_2 rapidly led to bleaching; and the careful subsequent addition of hexane led to colorless crystals during the course of a three day period. The crystalline material was filtered, and X-ray structure determination[§] of a colorless single crystal revealed the molecular structure of the chlorinated product to be 2,2',4,4',9,9'-hexachloro-2,2'-biadamantane **3** as illustrated in Fig. 2. Removal of solvent from the filtrate revealed the presence of several other unidentified (chlorinated) products. The irreversible reaction of gaseous chlorine with **2** is to be contrasted with the corresponding reaction with bromine, in which **2** reacts reversibly with Br_2 resulting in a variety of intermediates together with 2-Br^+ . However, removal of the solvent and gaseous bromine *in vacuo* led to the quantitative recovery of olefin **2**.¹³

Further experiments are underway to determine the electron-density distribution in various aromatic and olefinic halonium complexes,¹⁰ in order to more precisely characterize the nature of the bonding in these complexes.

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Notes and References

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‡ *Crystal data* for 2,2'-bi(adamant-2-ylidene) chloronium hexachloroantimonate $[(\text{C}_{20}\text{H}_{28}\text{Cl})^+ \text{SbCl}_6^- \cdot \text{CH}_2\text{Cl}_2]$. X-Ray quality crystal ($0.40 \times 0.15 \times 0.04$ mm) was obtained from a $\text{CH}_2\text{Cl}_2\text{-C}_6\text{H}_{14}$ mixture at −23 °C. $M = 723.25$, orthorhombic, space group $P2_12_12_1$, $a = 10.3394(1)$, $b = 16.0104(1)$ and $c = 16.0930(1)$ Å, $D_c = 1.803$ mg m^{−3}, $V = 2664$ Å³, $Z = 4$. Data collection was carried out on a Siemens SMART diffractometer equipped with a CCD detector, using Mo-K α radiation ($\lambda = 0.71073$ Å), at −150 °C. The total number of reflections measured was 34 182, of which 12 224 reflections were symmetrically non-equivalent. The structure was solved by direct methods and refined by full-matrix least-squares procedure. Final residuals were $R1 = 0.054$ and $wR2 = 0.103$ for 8640 reflections with $I > 2\sigma(I)$.

§ *Crystal data* for 2,2',4,4',9,9'-hexachloro-2,2'-biadamantane $[(\text{C}_{20}\text{H}_{24}\text{Cl}_6)]_2$. Bi(adamantylidene) was added to a solution of chlorine in CH_2Cl_2 at −30 °C and the resulting pale yellow solution was layered with prechilled (−30 °C) hexane. A well-formed crop of crystals was obtained after a three day period at −23 °C. A colorless crystal with dimensions ($0.1 \times 0.1 \times 0.15$ mm) was used for X-ray structural study. $M = 477.09$, monoclinic, space group $C2/c$, $a = 14.116(2)$, $b = 6.8734(8)$ and $c = 19.537(3)$ Å, $D_c = 1.686$ mg m^{−3}, $V = 1879.4$ Å³, $Z = 4$. Data collection was carried out as described above and the total number of reflections measured was 4085, of which 2679 reflections were symmetrically non-equivalent. The structure was solved by direct methods and refined by full-matrix least-squares procedure. Final residuals were $R1 = 0.074$ and $wR2 = 0.136$ for 1727 reflections with $I > 2\sigma(I)$. (Note that this crystal also contained ~8% of 2,2',9,9',10,10'-hexachloro-2,2'-biadamantane as an isomeric impurity.)

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- In various 2-X^+ cations, the disposition of counteranion with respect to X^+ may be viewed as an indicator of the degree of the positive charge on the halogen atom. Thus the hexachloroantimonate anion in 2-Cl^+ is only weakly coordinated ($\text{Cl}^+ \text{ClSbCl}_5^- = 3.51$ Å) whereas the tribromide in 2-Br^+ ($\text{Br}^+ \text{Br}_3^- = 3.10$ Å) and a water molecule in 2-I^+ ($\text{I}^+ \text{OH}_2 = 2.63$ Å) are strongly coordinated to the halonium cation.
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- In order to determine the decomposition products from 2-Cl^+ , a 0.02 M solution of $2\text{-Cl}^+ \text{SbCl}_6^-$ in CH_2Cl_2 was stirred at 25 °C and aqueous sodium hydrogen carbonate (~5%) was added. The mixture was further stirred for 10 min and the CH_2Cl_2 layer was separated. Analysis by GC and GC-MS indicated the presence of **2** (10%), spiroketone (60%) and several unidentified products.
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