



Short Communication

Unexpected reaction of antimony pentafluoride with a fluorinated propellane

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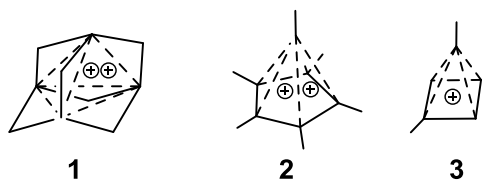
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ABSTRACT

While 1,3-dehydro-5,7-difluoroadamantane **11** reacts with SbF_5 in super acid media (SO_2ClF) to generate the 1,3-dehydroadamant-5,7-diyl dication **1**, 1,3-dehydro-5-fluoroadamantane **12** fails to react analogously to produce the 1,3-dehydroadamant-5-yl cation **9**; instead, the 3,5-difluoro-1-adamantylcation **13** is formed. We present a computational study that explains this surprising behavior by the initial addition of Sb_2F_{10} to the propellane bond present in **12**. This is computed to be highly exothermic and leads to a zwitterionic (or ion-pair) species, which in turn reacts autocatalytically with HF to produce the observed fluorinated cation **13**, SbF_3 , and SbF_6^- .

1. Introduction

The 1,3-dehydro-5,7-adamantyl dication **1** – Schleyer's dication – is a stable species in $\text{SbF}_5/\text{SO}_2\text{ClF}$ -solution characterized by NMR-spectroscopy and extensive theoretical work [1,2]. It contains hyper-coordinated carbon atoms and electron delocalization in three dimensions in line with other non-classical carbonium ions, such as Hogeveen's dication **2** [3] or Masamune's cation **3** [4].



The bridgehead carbon atoms of diamondoid hydrocarbons, such as adamantane and diamantane, are ideally suited to bear positive charges since C—C-hyperconjugation stabilizes the electron-deficient atom, and the rigidity of the hydrocarbon cage prevents rearrangement and decomposition [5]. Placing two positively charged centers in a bicyclic or cage hydrocarbon is only possible if more than two methylene groups separate them – unless “special” stabilization effects are present. Thus, neither the 1,3-adamantyl dication **4** nor the 1,4-bicyclo[2.2.2]octyl dication **5** could be generated. In contrast, the manxyl dication (1,5-bicyclo[3.3.3]undecyl dication) **6** and the 4,9-diamantanyl dication **7**, where three and four carbon atoms separate the cationic centers, were

prepared by Olah and coworkers [6].

Dication **1** is a special case indeed: Although formally a 1,3-carbocation, the positive charges are mainly delocalized over the 12 hydrogens. Substantial overlap exists between the bridgehead carbon orbitals in the center of the cage, forming a four-center-two-electron bond. The work of Richard Pincock on 1,3-dehydroadamantanes [7–9], highly strained molecules with unusual bonding between the inverted bridgehead carbons, where all four valencies point in one hemisphere, probably inspired Paul Schleyer's conception of **1**.

Pincock's group synthesized the 5-bromo-derivative **8** in solution and reacted it *in situ* with cyanide to form 5-cyano-1,3-dehydroadamantane **10**, a relatively stable compound whose molecular structure they determined by X-ray crystallography [10,11]. The formation of **10** from **8** in an $\text{S}_{\text{N}}1$ reaction implies the intermediate cation **9**, containing a 3-center-2-electron bond in a trishomo-cyclopropenium moiety.

Extending the delocalization to the fourth bridgehead carbon leads to dication **1**, which we synthesized in 1987 [1] from 1,3-dehydro-5,7-difluoroadamantane **11**, in analogy to Pincock's work. Fig. 1 compares the highest occupied molecular orbitals of **9** and **1**, showing the two- and three-dimensional electron delocalization.

2. Results and discussion

Encouraged by the successful synthesis of **1**, we envisaged that 1,3-dehydro-5-fluoroadamantane **12** [12] should efficiently ionize to cation **9** when reacted with SbF_5 in SO_2ClF . To our surprise and disappointment, **9** did not form, and we observed the 3,5-difluoroadamantyl

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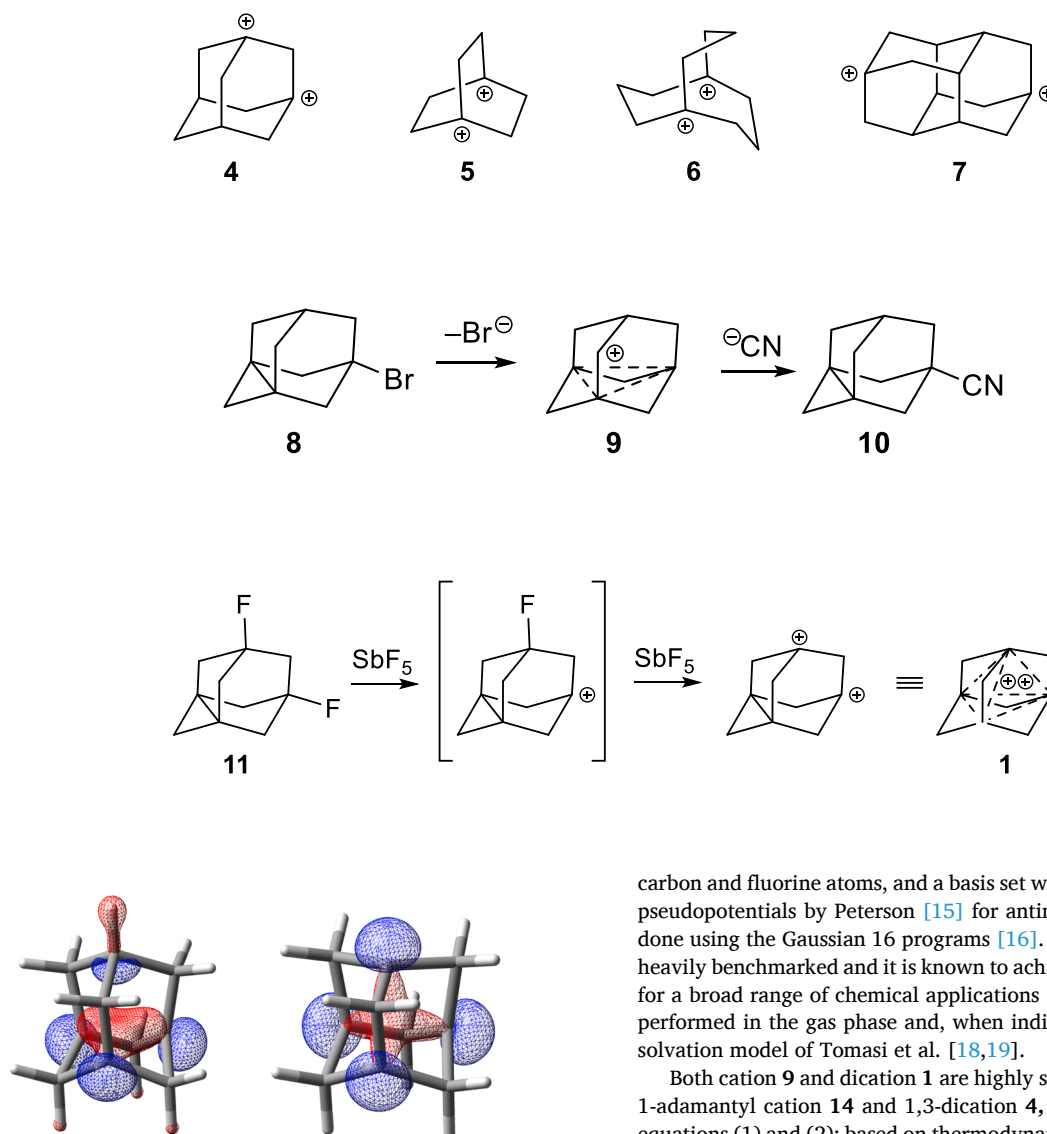


Fig 1. The highest occupied molecular orbitals (HOMOs) of **9** (left) and **1** (right) show the 3-center-2-electron- and 4-center-2-electron bonds.

cation **13** instead [12].

This result clearly called for a theoretical study, but in the late 1980s, computations on molecules the size of adamantane derivatives were limited to the Hartree-Fock level of theory with a 6-31G(d)-basis set. Quantum chemical computations involving heavy elements, such as antimony, were not feasible. After more than 30 years, we have now revisited this work and explain the failure to generate **9** based on modern Density Functional Theory (DFT) computations.

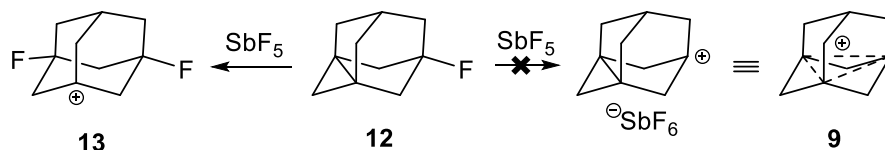
The computations were performed using the range separated general gradient approximation (GGA) density functional ω B97X-D including dispersion corrections [13]. The correlation consistent polarized valence triple zeta basis sets (cc-pVTZ) by Dunning [14] were used for hydrogen,

carbon and fluorine atoms, and a basis set with relativistic effective core pseudopotentials by Peterson [15] for antimony. All calculations were done using the Gaussian 16 programs [16]. This methodology has been heavily benchmarked and it is known to achieve a high level of accuracy for a broad range of chemical applications [17]. The calculations were performed in the gas phase and, when indicated, using the continuum solvation model of Tomasi et al. [18,19].

Both cation **9** and dication **1** are highly stabilized with respect to the 1-adamantyl cation **14** and 1,3-dication **4**, as shown by the isodesmic equations (1) and (2); based on thermodynamics, there is no reason why **9** should not form. The extension of electron delocalization from two into three dimensions yields an additional stabilization of -11.8 kcal/mol according to equation (1).

Starting with Schindler's work in 1987 [20], the prediction of ^{13}C NMR chemical shifts has proven extremely useful in elucidating detailed structures of carbocations by comparing theoretical and experimental data [21]. The IGLO method was first applied to various carbocations [20] and later to dication **1**, establishing its computed structure [1]. Table 1 summarizes computed and (available) experimental chemical shifts for **1**, **9**, and **13**. We used the GIAO method implemented in the Gaussian program [22].

The chemical shift of the bridgehead carbons in **1** appears surprising when compared to the 1-adamantyl cation **14** (300 ppm) [5] and **13** (272 ppm) [12]. It is, however, quite usual for hyper-coordinated carbons where the shifts can even be negative with respect to TMS, e.g.,



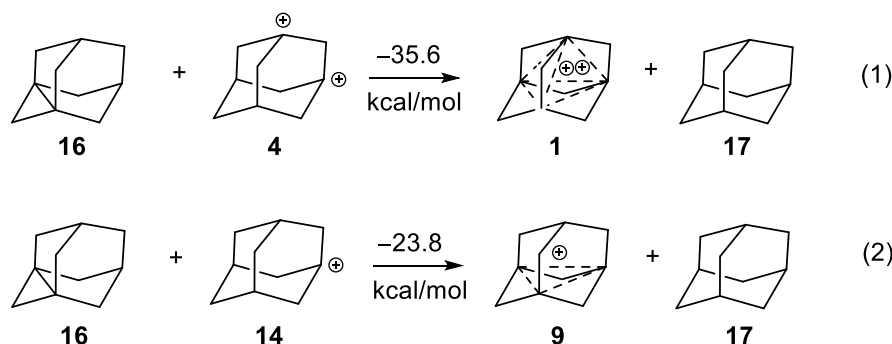


Table 1
Calculated and experimental ^{13}C NMR chemical shifts for cations **1**, **9** and **13**.

Cation Carbon	1		13		9	
	Expt [1]	Calc	Expt [12]	Calc	Expt	Calc
C1	6.6	4.9	272.2	283.9		80.2
C2	35.6	35.7	70.9	73.2		40.7
C3			112.8	121.4		45.4
C4			43.6	47.5		39.7
C5						
C6			37.7	41.4		
C7			50.2	52.7		
C8			66.5	69.4		

Hogeveen's dication **2** [3] (-2 ppm for the apical methyl group). The calculated shifts for the C3 and C4 carbons of the tris-homocyclopropenium unit of **9** are less shielded than in **1** and compared to the parent trishomocyclopropenium cation C_6H_9^+ (4.7 and 17.3 ppm) [23].

Why did **9** fail to form under conditions where **1** was smoothly generated? 1,3-Dehydroadamantanes [24,25] possess nucleophilic properties at the bridgehead propellane carbons, and, instead of ionizing to the desired cations and SbF_6^- -anion, could also react with the Lewis acid SbF_5 to form zwitterionic adducts. Using a continuum solvation model [18,19] (PCM, acetonitrile), these reactions are computed to be strongly exothermic for **11** (-40.8 kcal/mol) and **12** (-47.9), with a difference of 7.1 kcal/mol in favor of the formation of **15**. To the best of our knowledge this is novel chemistry for SbF_5 , although its scope must rather be limited to zwitterionic species where the cationic part is highly stabilized, as in the adamantane skeleton.

The zwitterionic adduct **15** (Fig. 2) can rearrange to cation **13** and SbF_4^- -anion, which gets further stabilized by reacting with excess SbF_5 to form SbF_3 and SbF_6^- -anion. The overall result is the oxidative fluorination of **12** by SbF_5 via an unusual mechanism.

Computations on the rearrangement of **15** to **13** did not identify an energetically viable pathway, probably because the transition structure between **15** and **13** has appreciable 1,3-dicationic character with strong Coulombic repulsion [26].

SbF_5 is known to extensively aggregate in the liquid state, and even in the gas phase; the dimer Sb_2F_{10} is a stronger Lewis acid than SbF_5

itself [27]. This is reproduced by the computations shown in Scheme 1 which summarize the thermodynamics for the parent 1,3-dehydroadamantane **16** and its mono- and difluoro derivatives **12** and **11**.

The formation of zwitterions **18–20** is surprisingly exothermic. It is due to ring strain relief in the propellane moiety, attractive Coulombic intramolecular interactions, and the stability of the carbocationic parts of the molecules:

Increasing the number of bridgehead fluorine atoms destabilizes the cations by roughly 8 kcal/mol per fluorine (Scheme 2), and this is reflected in the heats of reaction for zwitterion formation (Scheme 1). The putative next step is the reaction with HF yielding the corresponding adducts. This is also exothermic but a lot less so (Scheme 1). In the case of **21** there is no stationary point after HF-addition and the adduct fragments without a barrier to form 3-fluoro-1-adamantyl cation **24**, SbF_3 and SbF_6^- -anion. Transition structures could be located for **22** and **23** (Fig. 3) but the barriers are very small (Fig. 4). Intrinsic reaction coordinate computations for **22** and **23** show that the transition structures connect the educts and products **13** and **25**, and the reactions are exothermic. Overall, the processes are autocatalytic in HF, which is

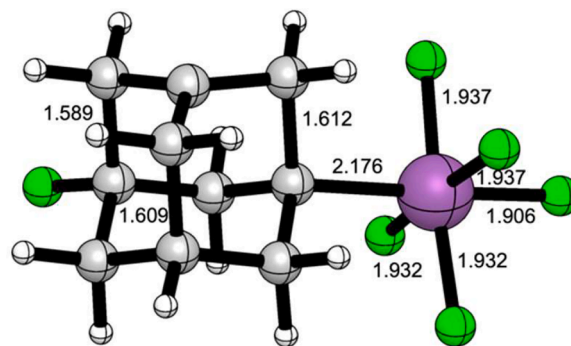
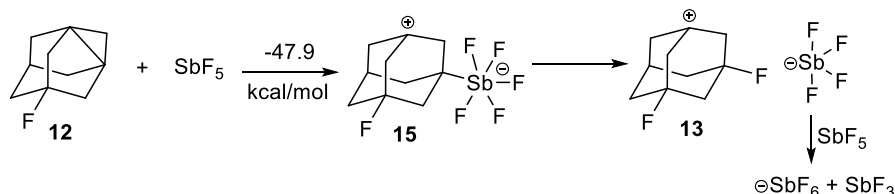
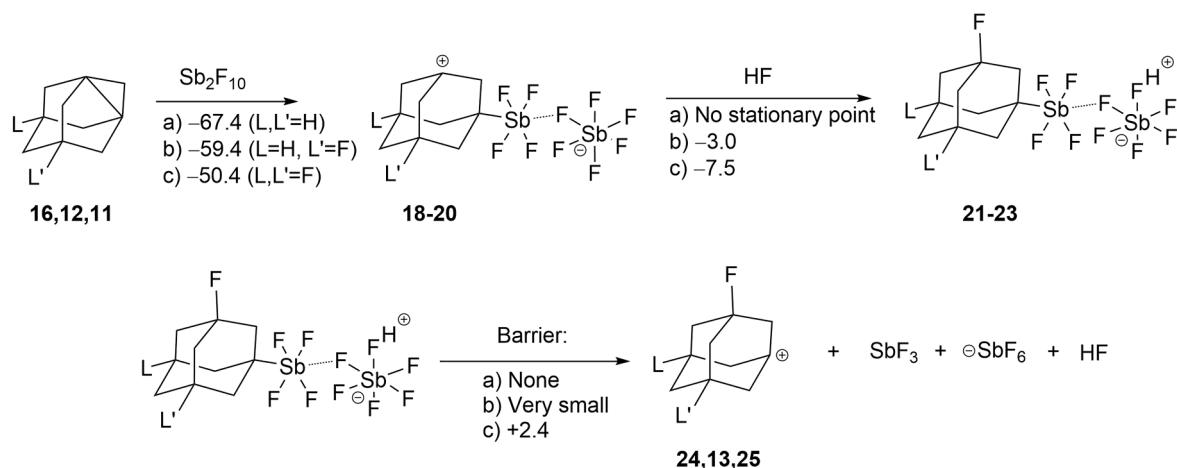
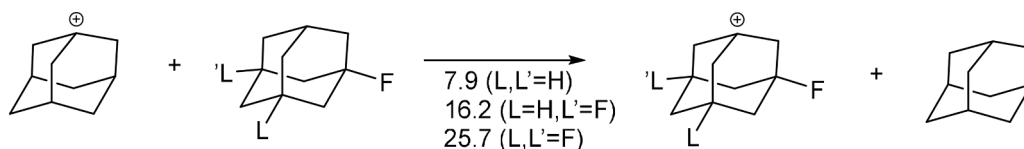


Fig. 2. The computed structure of the zwitterion **15**. Bond lengths are in Ångströms. The cationic part of the molecule shows the typical hyperconjugative bond lengthening of the $\text{C}_\beta\text{-C}_\gamma$ -bonds that are parallel to the empty orbital at C_α indicating the presence of appreciable positive charge in the adamantane cage. Carbon and hydrogen atoms are shaded in gray, fluorine in green and antimony in violet.





Scheme 1. Computed heats of reaction and barriers (kcal/mol) for zwitterion formation and subsequent fragmentation (ω B97X-D/cc-pVTZ, PCM solvent model for acetonitrile). For **22** the barrier becomes *negative* when zero-point vibrational corrections are added to the SCF-energies.



Scheme 2. Relative stabilities (kcal/mol) for 1-adamantyl cations (ω B97X-D/cc-pVTZ, gas phase).

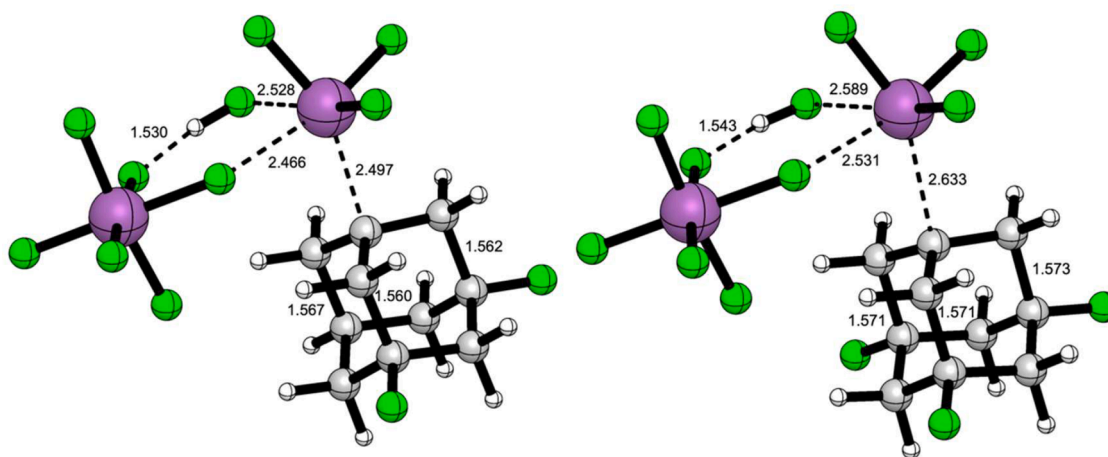


Fig. 3. Transition structures from **22** (left) and **23** (right) to cations **13** and **25**. Carbon and hydrogen atoms are shaded in gray, fluorine in green and antimony in violet. The elongation of the β - γ -carbon-carbon bonds shows the presence of significant charge in the adamantyl moiety already in the transition states.

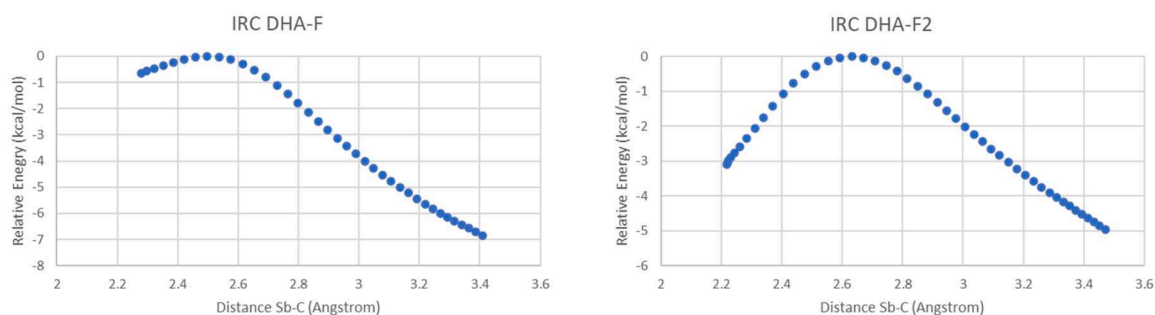
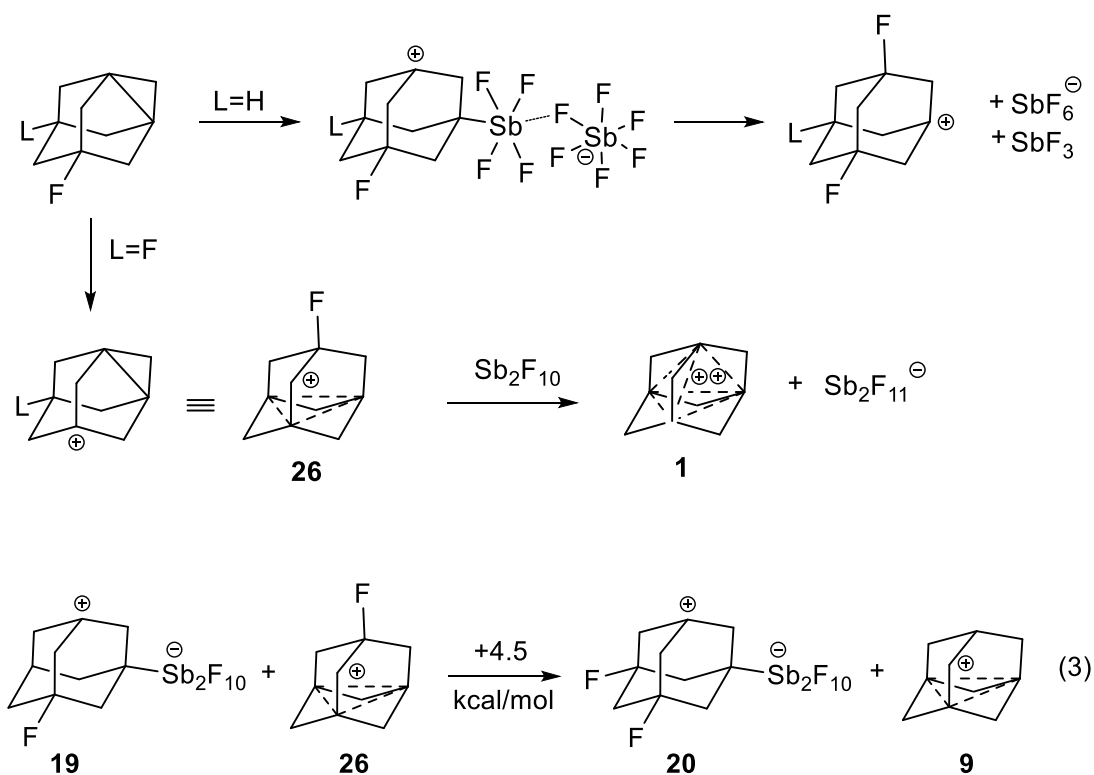


Fig. 4. Results from Intrinsic Reaction Coordinate computations for **22** (DHA-F) and **23** (DHA-F2).



certainly present in the reaction mixture, albeit in trace amounts.

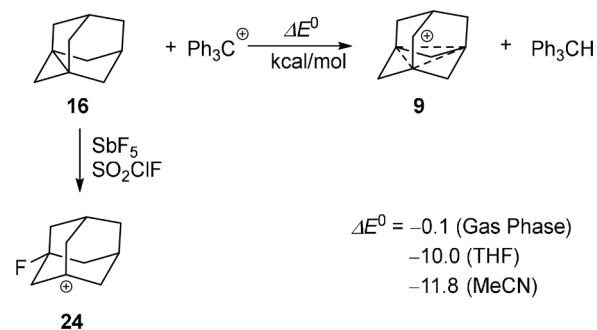
Now, can we answer the question of why dication **1** is smoothly formed and **9** is not? The overall reaction sequence of zwitterion formation, addition of HF, and fragmentation to the adamantyl cations, SbF_3 and SbF_6^- -anion is exothermic by -94.6 kcal/mol for 1,3-dehydroadamantane **16**, -86.3 kcal/mol for the 5-fluoro-1,3-dehydroadamantane **11** and -74.8 kcal/mol for 5,7-difluoro-1,3-dehydroadamantane **12**. Since dication **1** is strongly stabilized with respect to cation **9**, it seems plausible to assume that a second ionization takes place as soon as cation **26** is formed.

The isodesmic equation (3) compares localized and delocalized cations depending on the degree of fluorination: If two fluorine atoms are present, the delocalized structure **26** is favored, with only one fluorine the localized structure **19** will form.

The key isodesmic equation (3) was used to benchmark the performance of the computational model employed in this paper (i.e. $\omega\text{B97X-D/cc-pVTZ}$) against the M06-2X density functional of Truhlar and Zhao [28] and the def2-TZVP basis set of Ahlrichs and Weigend [29] (i.e. M06-2X/def2-TZVP). The result is $+3.8$ kcal/mol, thus nicely corroborating the validity of the theoretical level employed.

We conclude that with Sb_2F_{10} **11** will likely ionize to **26** under fluoride abstraction, but **12** will react to form the addition product **19**. The second ionization **26** to **1** unfortunately is not amenable to calculations, because of the presence of a second positive charge. Here, we must rely on the experimental result.

If the theoretical predictions presented in this paper are correct, cation **9** cannot be formed by fluoride abstraction from **11** using SbF_5 since the competing zwitterion formation is more favorable. But what about a classical cation exchange reaction? Computations ($\omega\text{B97X-D/cc-pVTZ}$) on the reaction of trityl cation with 1,3-dehydroadamantane are thermoneutral in the gas phase but *exothermic* in a polar environment. This could easily be checked experimentally: One only needs to react a suitable salt of triphenylmethyl cation with 1,3-dehydroadamantane **16** in SO_2ClF , and record NMR-spectra. A similar second experiment would be the reaction of **16** with SbF_5 in SO_2ClF which should yield the 3-



Scheme 3. Predicted reactions of **16** with trityl cation or SbF_5 .

fluoro-1-adamantyl cation **24** (Scheme 3).

3. Conclusion

The apparently analogous reactions of **11** to **1** and **12** to **9** are actually very different. With one fluorine substituent in **12**, the stable zwitterion **19** is formed under addition of Sb_2F_{10} and it fragments in the presence of HF to yield the classical cation **13**; in contrast, **11** does not form a zwitterionic species but ionizes first to cation **26** and then to dication **1**. What appeared as a straightforward analogy turned out to be an unpleasant surprise and a challenging riddle to solve. Without computational methods, this problem would have been hard to understand. We now know that a successful synthesis of cation **9** must take a different synthetic route, avoiding the presence of SbF_5 , and we strongly encourage experiments.

CRedit authorship contribution statement

Matthias Bremer: Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jfluchem.2024.110281](https://doi.org/10.1016/j.jfluchem.2024.110281).

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