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Daniel J. Sheldon and Mark R. Crimmin

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Complete deconstruction of SF_6 by an aluminium(I) compound†

Daniel J. Sheldon and Mark R. Crimmin*

The room-temperature activation of SF_6, a potent greenhouse gas, is reported using a monovalent aluminium(I) reagent to form well-defined aluminium(III) fluoride and aluminium(III) sulfide products. New reactions have been developed to utilise the aluminium(III) fluoride and aluminium(III) sulfide as a nucleophilic source of F^- and S^{2-} for a range of electrophiles. The overall reaction sequence results in the net transfer of fluorine or sulfur atoms from an environmentally detrimental gas to useful organic products.

Sulfur hexafluoride (SF_6) is widely used as an electrical insulating gas in circuit breakers.[1] SF_6 possesses unique chemical and physical inertness and excellent thermal conductivity; properties that result from its high dielectric constant, high heat capacity and high density.[1–3] However, SF_6 is a potent greenhouse gas with a global warming potential (GWP_{100}) 23 900 times greater than CO_2 and a long atmospheric lifetime of 3200 years.[4–7] As a result, its emission is restricted through the Kyoto protocol as one of the six most prominent greenhouse gases.[6–8] Specific attention has been directed towards its control as in many cases there are no suitable alternatives or drop-in replacements for SF_6.[4,6,9] Typical methods for its destruction are energy intensive and often produce toxic and corrosive products.[10–12] Efficient methods for recycling or destroying SF_6 are therefore highly sought after.[13]

A challenge remains to transform SF_6 into non-toxic, high-value compounds under mild reaction conditions.[12] Not only does this offer an attractive method for its depletion, but it opens up the potential to use SF_6 as a source of S and F atoms through the deconstruction of this molecule to its elemental components. In particular, there has been recent interest in using SF_6 as a fluorinating agent in organic synthesis. Fluorinated building blocks are increasingly crucial in the pharmaceutical, agrochemical and materials industries, where fluorine substitution is used to improve the quality and efficiency of new products.[14–16]

The activation and chemical deconstruction of SF_6 has been achieved with strong reducing agents or low-valent transition metal complexes.[9,17–26] The latter approach results in the formation of transition metal fluorides and sulfides. Metal-free approaches have also been reported in which strong nucleophiles directly attack SF_6.[27] In recent years, these synthetic approaches have been developed further and reactions that allow the onwards use of the fluorine content of SF_6 in organic synthesis have been targeted. Particular attention has been given to the use of SF_6 in the deoxyfluorination of alcohols.[18,28–34] In one example, Braun and co-workers developed a photochemical protocol in which SF_6 is reduced by an NHC to form a difluoroimidazolidine, which was then successfully applied in the deoxyfluorination of a range of alcohols.[30]

For some time we have been interested in using main group nucleophiles to activate the C–F bonds in environmentally persistent fluorocarbons.[35–42] Herein we report the extension of this methodology to the rapid, room temperature activation of SF_6 by a monovalent aluminium(I) species. This reaction results in the complete deconstruction of SF_6 to its reduced elemental components, forming well-defined aluminium(III) fluoride and sulfide products. The fluoride species can be used as a nucleophile in onward synthesis, while the sulfide species is shown to act as a sulfide source in the formation of a heterocycle, thus allowing the elemental fluorine and sulfur content of SF_6 to be re-used.

An excess of sulfur hexafluoride (1 bar) was added to a C_6D_6 solution of [{(ArNCMe)$_2$CH}Al] (**1**, Ar = 2,6-di-isopropylphenyl). The red solution rapidly turned pale yellow. Monitoring the reaction by ^{1}H and ^{19}F NMR spectroscopy revealed the complete consumption of **1** and the formation of [{(ArNCMe)$_2$CH}AlF$_2$] (**2**) within 15 min at 22 °C (Scheme 1).

2 is a known compound and the data match that reported in the literature.[37] Although no further products were detected by

Molecular Sciences Research Hub, Department of Chemistry, Imperial College London, London, W12 0BZ, UK. E-mail: m.crimmin@imperial.ac.uk

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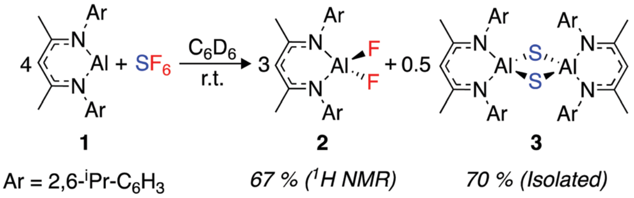

Scheme 1 Reaction scheme for SF_6 activation by **1**. ^{1}H NMR yields are reported against a ferrocene internal standard.

NMR spectroscopy, the reaction was accompanied by the production of a colourless precipitate, suggesting the formation of an insoluble by-product. Repeating the reaction with slow diffusion of the SF_6 into a C_6D_6 solution of **1** led to the formation of single crystals of the insoluble product suitable for X-ray diffraction. The side-product was determined as $[\{(ArNCMe)_2CH\}Al(\mu\text{-}S)]_2$ (**3**) (Scheme 1).[43] **3** is also a known compound, and crystallised as a polymorph (monoclinic, *C*2/*c*) of a previously reported structure (monoclinic, *C*2/*m*). Crystalline samples of **3** were found to be insoluble in common laboratory solvents.

The mechanism for SF_6 activation was investigated by DFT calculations (Fig. 1). The reaction sequence is likely initiated by nucleophilic attack of **1** at a fluorine atom of SF_6, proceeding *via* **TS-1** ($\Delta G_1^{\ddagger}$ = 10 kcal mol^{-1}), to give **2** and SF_4 (**Int-1**). A further equivalent of **1** then reacts with SF_4 in a similar nucleophilic manner *via* **TS-2** ($\Delta G_2^{\ddagger}$ = 11 kcal mol^{-1}) to form SF_2 and **2** (**Int-2**). SF_4 possess a see-saw structure where the axial and equatorial fluorine atoms are inequivalent. The calculations suggest that the most favourable pathway involves attack of **1** at the equatorial fluorine of SF_4 as this is the most electrophilic (least electronegative) site. Another equivalent of **1** then reacts in a similar fashion with SF_2 *via* **TS-3** ($\Delta G_3^{\ddagger}$ = 11 kcal mol^{-1}) to form **Int-3**. **Int-3** is subsequently attacked by a final equivalent of **1**, leading to **Int-4** *via* **TS-4** ($\Delta G_4^{\ddagger}$ = 3 kcal mol^{-1}). A rearrangement to form the experimentally observed products **2** and **3** is calculated to be thermodynamically feasible. When following the reaction by NMR spectroscopy, no reaction intermediates could be detected and the reaction proceeds to completion within 15 minutes at room temperature. These observations are consistent with the small activation barriers calculated for these elementary steps.

Numerous mechanistic analyses of SF_6 activation propose a first step involving single electron transfer to SF_6 from a transition metal, alkali metal or photocatalyst.[9,19,23,25,28–30] Dielmann and co-workers have proposed an alternative mechanism involving nucleophilic attack at the fluorine atom of SF_6 by a strongly nucleophilic phosphine, in a pathway similar to the one calculated here.[27]

NBO analysis of the transition states was carried out. **TS-1**, **TS-2** and **TS-3** are calculated to involve the nucleophilic attack of **1** at a fluorine atom of SF_x (x = 6, 4, 2). The *NPA* charges show a trend of increasing negative charge at the sulfur atom as the maxima associated with the transition state is traversed, and conversely an accumulation of positive charge at aluminium. This implies electron density is transferred from aluminium to sulfur, consistent with nucleophilic attack, rather than a fluoride abstraction mechanism (see ESI† for NBO data). Wiberg Bond Indices are consistent with a decrease in the S–F bond order in **TS-1** relative to SF_6 itself (ESI† Table S3).

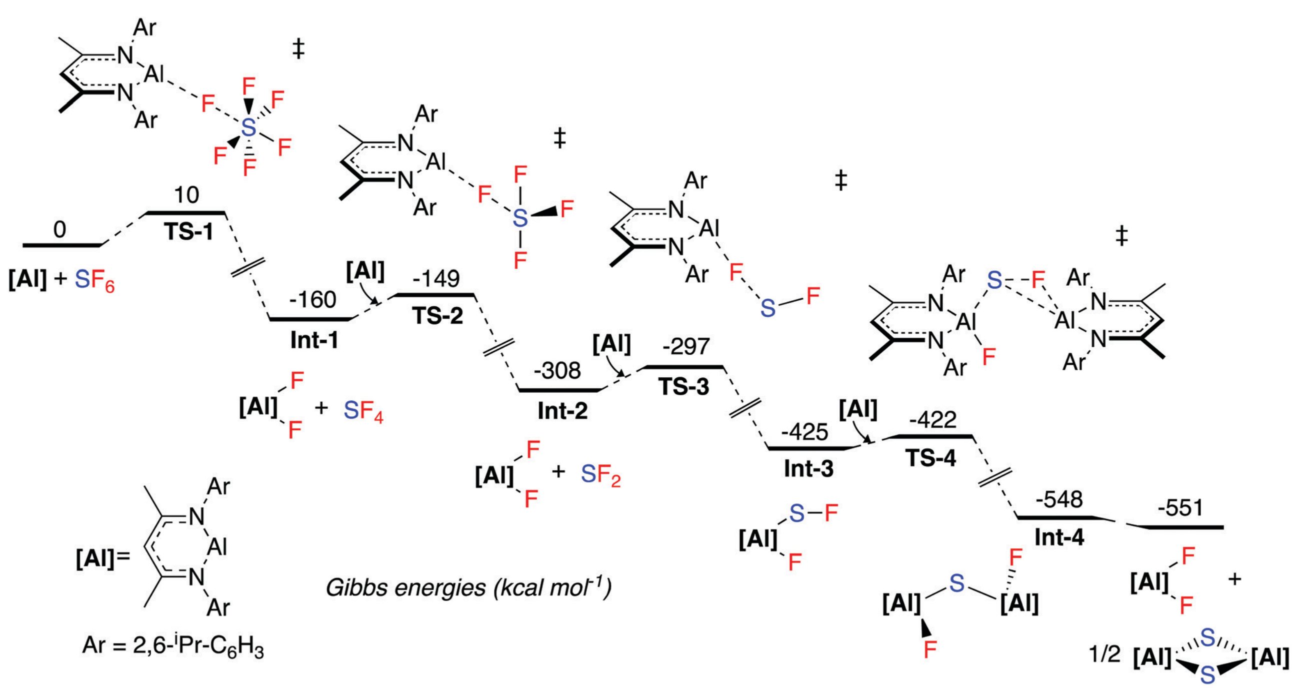

Fig. 1 Calculated potential energy surface for SF_6 activation. The M06-2X functional was used with a hybrid basis set, 6-31g**(C,H)/6-311+g*(N,F,S). The SDDAll pseudopotential was used for Al. Dispersion and solvent effects were included *via* single-point corrections, using Grimme's D3 correction for dispersion and the PCM (solvent = benzene) model for solvent.

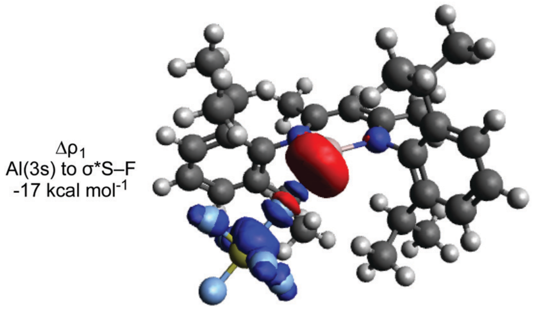

Fig. 2 ETS-NOCV deformation density plot for **TS-1**. Charge flow is from red to blue.

An IRC calculation connects **TS-1** directly to **2** and SF_4 (**Int-1**), where a second fluorine transfer has also occurred. This suggests that the second fluorine transfer step is a barrierless process somewhere on the pathway between **TS-1** and **Int-1**. A very similar process is found for **TS-2**. Second-order perturbation analysis of **TS-1** reveals donation of electron density from the aluminium lone pair into σ*(S–F) (17 kcal mol^{-1}), with simultaneous donation of electron density from the same fluorine atom into the empty p-orbital of the aluminium atom (14 kcal mol^{-1}). Similar donor–acceptor interactions, albeit of slightly different magnitudes are found for **TS-2**, **TS-3** and **TS-4**.

ETS-NOCV calculations were performed to further probe the postulated nucleophilic attack mechanism.[44] The largest contributor ($\Delta\rho_1$) to the orbital interaction (ΔE_{orb}) for **TS-1**, **TS-2** and **TS-3** involves donation from the aluminium lone pair to σ* (S–F) (Fig. 2).

It is evident that attack of the aluminium occurs at the fluorine atom of the S–F bond. Along with the orbital interactions discussed, this is likely also due to the electrostatic interaction between Al and F (see ESI† for *NPA* charges), and the fluorophilic nature of aluminium. There is a contrast here to halocarbon reactivity where 'frontside' S_N2X attack at the halogen atom is rare, although has been proposed in some recent examples with other fluorophilic nucleophiles.[38,45,46]

We were interested in the utility of the fluorinated aluminium species **2** as a nucleophile for onward synthesis. Organoaluminium fluorides have been the subject of previous reviews.[47,48] The use of these compounds as a nucleophilic source of fluorine is very rare owing to the thermodynamic stability of the Al–F bond.[49,50] We report here a fluoride metathesis reaction of **2** with various electrophiles (Fig. 3).

Reaction of **2** with organic anhydrides resulted in the formation of acyl fluorides. Acyl fluorides are becoming increasingly important and valuable fluorinating agents due to their unique balance of stability and reactivity.[51–54] Furthermore, the reaction of **2** with trimethysilyl iodide produces trimethylsilyl fluoride, a silylating agent for ketones, alcohols, terminal alkynes and various lithiated precursors.[55–59] **2** also reacted with BCl_3 to produce a series of commercially relevant Lewis acids.[60,61] Finally, despite its lack of solubility, we were able to demonstrate the transfer of sulfide (S^{2-}) from **3** to α,α′-dibromo-*o*-xylene to form the sulfur heterocycle **4** (Fig. 3).[62] These fluoride (F^-) and sulfide (S^{2-}) transfer reactions represent a formal re-use of

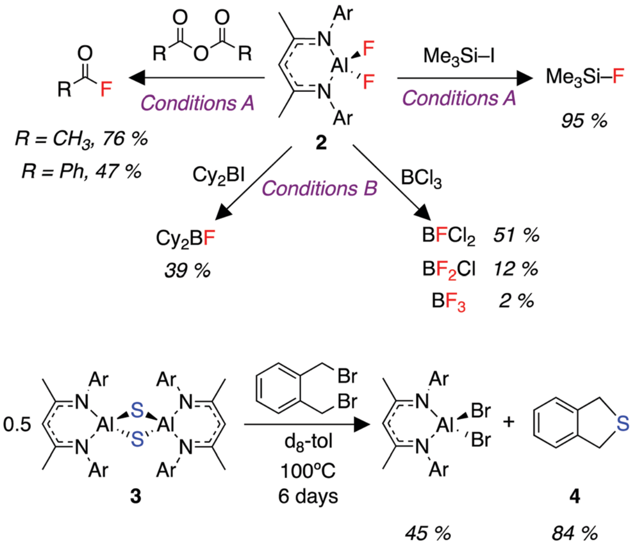

Fig. 3 Fluoride and sulfide transfer reactions. Conditions (A): heat at 150 °C for 16 hours in *m*-xylene solvent. Conditions (B): room temperature for 10 minutes in *m*-xylene solvent. 10 equiv. of electrophile used for all the above reactions. Yields are determined by quantitative ^{1}H or ^{19}F NMR spectroscopy against a ferrocene, 1,3,5-trimethoxybenzene or 1,2-difluorobenzene internal standard.

the atoms derived from SF_6, and thus the overall reaction sequence describes the transfer of fluorine and sulfur from a potent greenhouse gas to highly useful organic products.

In conclusion, we have developed a transition metal free process to deconstruct the potent greenhouse gas SF_6 to its elemental components (F^- and S^{2-}) using a monovalent aluminium(I) compound under ambient conditions. The aluminium(III) fluoride and sulfide products of the reaction are well-defined and easy to separate by virtue of their differing solubilities. We have undertaken DFT calculations to propose a viable pathway for SF_6 activation through nucleophilic attack by the Al(I) fragment at the σ*(S–F) orbital of an S–F bond. We have demonstrated the utility of the aluminium difluoride product (**2**) as a nucleophilic source of fluorine for organic substrates, and we have shown the ability of **3** to transfer it's sulfide content. Overall, the complete activation of SF_6 to its elemental components has been developed in a system where the fluorine and sulfur content can be re-used in the synthesis of valuable compounds.

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Conflicts of interest

There are no conflicts to declare.

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