Supporting information for:

Complete Deconstruction of SF_6 by an Aluminium(I) Compound

Daniel J. Sheldon[a], Mark R. Crimmin*[a]

*Corresponding author. Email: m.crimmin@imperial.ac.uk

[a]Molecular Sciences Research Hub, Department of Chemistry, Imperial College London, 82 Wood Lane, White City, Shepherds Bush, London, W12 0BZ, UK.

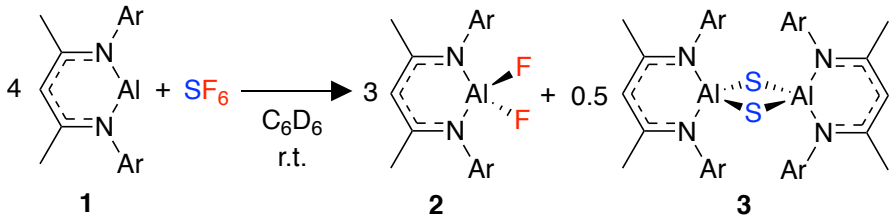
Contents

1. General Experimental

Standard Schlenk line and glovebox techniques were used for all manipulations under an inert atmosphere of dinitrogen or argon unless otherwise stated. NMR scale reactions were performed in J. Young NMR tubes equipped with internal standard capillaries of ferrocene (^{1}H NMR spectroscopy) and prepared in a glovebox. An MBraun Labmaster glovebox was utilised, operating at <0.1 ppm H_2O and <0.1 ppm O_2. ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra were recorded on BRUKER 400 MHz or 500 MHz machines, and referenced against $SiMe_4$ (^{1}H, ^{13}C), $CFCl_3$ (^{19}F) and $EtO{\bullet}BF_3$ (^{11}B). Data were processed using the MestReNova software package. Solvents were dried over activated alumina from a solvent purification system (SPS) based upon the Grubbs design and de-gassed before use. Glassware was dried for >6 h prior to use at 120 °C. Benzene-d_6 and toluene-d_8 were de-gassed and stored over 3 Å molecular sieves before use. All reagents were acquired from Sigma Aldrich (Merck), Honeywell or Fluorochem and used without further purification unless specified. Sulfur Hexafluoride was acquired from Apollo Scientific and used without further purification. Where liquids at 25 °C, reagents were dried over activated 3 Å molecular sieves and freeze-pump-thaw degassed prior to use. [{(ArNCMe)$_2$CH}Al] (**1**, Ar = 2,6-di-isopropylphenyl) was prepared following the literature procedure.[1]

2. Synthetic Procedures

2.1 Activation of Sulfur Hexafluoride with [{(ArNCMe)$_2$CH}Al] (1)



Ar = 2,6-^{i}Pr-C$_6$H$_3$ *67 %* *70 %*

Scheme S1: Activation of SF_6 with **1**.

2.1.1 Isolation of [{(ArNCMe)$_2$CH}AlF$_2$] (2)

In an N_2 filled glovebox, 27 mg (0.06 mmol) of **1** was dissolved in 0.6 mL of C_6D_6, added to a J. Young NMR tube equipped with a ferrocene capillary internal standard, and a t=0 ^{1}H NMR spectrum was recorded. The solution was degassed once *via* freeze-pump-thaw and SF_6 (1 bar, 22 °C) was added. The J. Young tube was inverted multiple times and the red solution turned pale yellow within seconds. The formation of a colourless precipitate was also observed. After 15 minutes, t=1 ^{1}H and ^{19}F NMR spectra were recorded. The 67 % yield of the product [{(ArNCMe)$_2$CH}AlF$_2$] (**2,** Ar = 2,6-di-isopropylphenyl) was determined *in situ* by integral comparison to the ferrocene internal standard in the ^{1}H NMR spectrum. No other species were determined by NMR spectroscopy. The product **2** can be isolated by filtration, removal of C_6D_6 *in vacuo*, and crystallisation from a concentrated *n*-hexane solution.[2]

[{(ArNCMe)$_2$CH}AlF$_2$]: (matching that of literature reports)[2]

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.10 (d, 12H, CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$ = 6.8 Hz), 1.42 (d, 12H, CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$ = 6.8 Hz), 1.53 (s, 6H, C$\underline{H}_3$), 3.31 (sept, 4H, C$\underline{H}$(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz), 4.94 (s, 1H, C(CH$_3$)C$\underline{H}$C(CH$_3$)), 7.05-7.15 (m, 6H, Ar$\underline{H}$); ^{19}F NMR (376.5 MHz, C_6D_6, 298 K): δ -173.6 (2F, Al$\underline{F}$)

SF_6:

^{19}F NMR (376.5 MHz, C_6D_6, 298 K): δ 58.4 (6F)

2.1.2 Isolation of [{(ArNCMe)$_2$CH}Al(μ-S)]$_2$ (3)

The reaction was carried out in the same manner but with no agitation of the NMR tube after addition of the gas, allowing for slow diffusion of SF_6 into the C_6D_6 solution of **1**. Single-crystals

of the insoluble product **3** grew over a period of 2 days, in a 70 % isolated yield. These crystals were suitable for single-crystal x-ray diffraction, allowing the confirmation of the structure of **3**. It is noted that **3** was found to be insoluble in all common laboratory solvents, consistent with the findings of the original literature report.[3]

IR Data: (matching very closely to that of the literature report)[3]

v(cm^{-1}): 3056 (vw), 2956 (m), 2924 (str), 2849 (m), 1587 (vw), 1531 (str), 1461 (m), 1436 (m), 1382 (str), 1316 (str), 1291 (vw, shoulder of peak), 1249 (m), 1174 (w), 1103 (vw), 1056 (vw), 1021 (w), 936 (vw), 867 (w), 804 (w), 775 (w), 763 (w)

X-ray Crystal Structure of 3

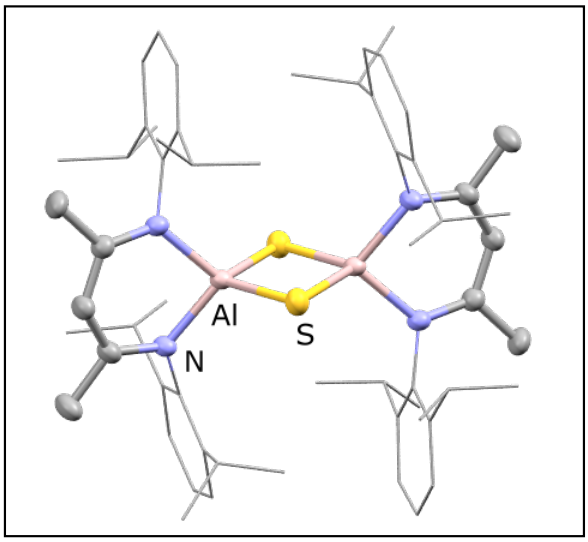


Figure S1: X-ray crystal structure of **3**. Hydrogen atoms omitted for clarity.

*Crystal Data for **3*** ($C_{58}H_{82}Al_2N_4S_2$), M =953.35, monoclinic, space group C2/c (no. 15), a = 22.3453(5) Å, b = 14.7350(3) Å, c = 16.3947(3) Å, β = 90.3187(18)°, V = 5398.01(18) $Å^3$, Z = 4, $\rho_{calc}g/cm^3$ = 1.173, μ(Cu Kα) = 1.507 mm^{-1}, T = 173.10(14), clear light colourless blocks, F^2 refinement, R_1(obs) = 0.0564, wR_2(all) = 0.1734, 5181 independent observed reflections (R_{int} = 0.0285), 4243 independent measured reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 146.876], 308 parameters. CCDC deposition number: 2084888. Data were collected using Agilent Xcalibur PX Ultra A diffractometer.

3 was found to crystallise in the space group (C2/c). There was no solvent or disorder to be modelled. The structure we report is a different polymorph to that previously reported in the literature, which crystallised in the space group C2/m, although both are monoclinic.[3] The

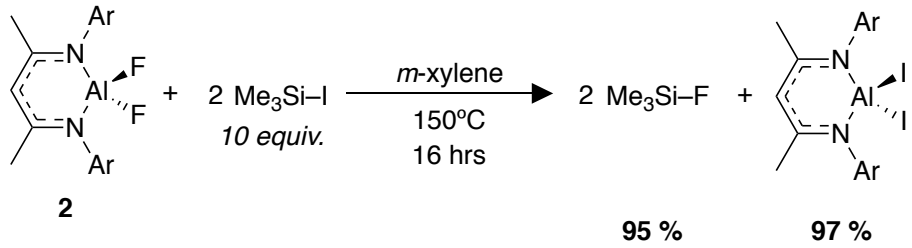
bonding metrics are found to be almost identical (Table S1), crucially both suggesting an almost planar and symmetrical Al_2S_2 ring.

	Literature Report (see reference 3)	Crystal Data Reported Here
Al-N	1.928(2)	1.944(2)/1.939(2)
Al-S	2.237(1)	2.2136(9)
Al-S1	2.245(1)	2.2171(9)
S-Al-S	96.5(1)	97.52(3)
Al-S-Al	83.5(1)	82.48(3)
N-Al-N	94.9(1)	93.92(9)

Table S1: Comparison of bond metrics to literature report.

2.2 Reactivity of [{(ArNCMe)$_2$CH}AlF$_2$] (2)

2.2.1 Reactivity of [{(ArNCMe)$_2$CH}AlF$_2$] (2) with a Silicon Electrophiles



2

95 % **97 %**

Scheme S2: Conditions for reaction of **2** with a silicon electrophile

In an N_2 filled glovebox, 51.8 µL of a 0.2 M stock solution (0.010 mmol) of **2** in *m*-xylene was added to a J Young NMR tube along with a further 530 µL of *m*-xylene, 20 µL of a 0.1 M stock solution of 1,2-difluorobenzene (internal standard) in C_6D_6, and 0.10 mmol (10 equiv.) of the relevant electrophile. The J Young NMR tube was equipped with a capillary internal standard containing ferrocene in C_6D_6, and t=0 ^{1}H and ^{19}F NMR spectra were recorded. The NMR tube was then placed in a 150°C oil bath for a set amount of time, before further ^{1}H and ^{19}F spectra were recorded. Quantitative ^{19}F integration was performed using the 1,2-difluorobenzene triplet at δ -138.0 ppm, while quantitative ^{1}H integration was performed using the ferrocene singlet at δ 4.0 ppm, or through external addition of 1,3,5-trimethoxybenzene and comparison of singlet at δ 6.33 in *m*-xylene (this peak comes at δ 6.26 in C_6D_6).

NMR Characterisation of Products:

Fluorotrimethylsilane: (in very close agreement with literature reports)[4]

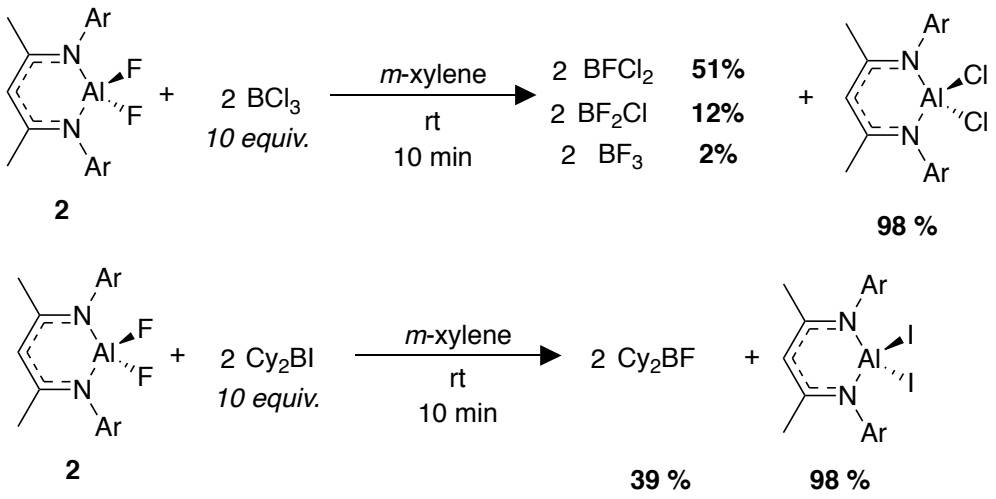
^{19}F NMR (C_6D_6, 100 MHz, 298K): -157.2 (sept, $^3J_{HH}$ = 7.0 Hz).

^{1}H NMR (*m*-xylene, C_6D_6 insert, 400 MHz): 0.11 (d, $^3J_{HH}$ = 7.0 Hz).

[{(ArNCMe)$_2$CH}AlI$_2$]: (in very close agreement with literature reports)[1]

^{1}H NMR (C_6D_6, 400 MHz, 298 K): 7.1-7.2 (m, 6 H, Ph), 5.05 (s, 1 H, *γ*–C<u>H</u>), 3.59 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, C<u>H</u>Me$_2$), 1.49 (s, 6 H, Me), 1.43 (d, 12 H, $^3J_{HH}$ = 6.80 Hz, CH<u>Me$_2$</u>), 1.08 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH<u>Me$_2$</u>).The formation of this compound was confirmed by independent synthesis.

2.2.2 Reactivity of [{(ArNCMe)$_2$CH}AlF$_2$] (2) with Boron Electrophiles



Scheme S3: Conditions for reaction of **2** with boron electrophiles

In an N_2 filled glovebox, 51.8 µL of a 0.2 M stock solution (0.010 mmol) of **2** in *m*-xylene was added to a J Young NMR tube along with a further 530 µL of *m*-xylene, 20 µL of a 0.1 M stock solution of 1,2-difluorobenzene in C_6D_6, and the J Young NMR tube was equipped with a capillary internal standard containing ferrocene in C_6D_6. Then, on the Schlenk line, 0.10 mmol (10 equiv.) of the relevant boron electrophile was added under a N_2 atmosphere. ^{1}H, ^{19}F and ^{11}B NMR spectra were recorded. Quantitative ^{19}F integration was performed using the 1,2-difluorobenzene triplet at δ -138.0 ppm, while quantitative ^{1}H integration was performed using the ferrocene singlet at δ 4.0 ppm, or through external addition of 1,3,5-trimethoxybenzene and comparison of singlet at δ 6.33 in *m*-xylene (peak comes at δ 6.26 in C_6D_6).

NMR Characterisation of Products:

[{(ArNCMe)$_2$CH}AlI$_2$]: (in very close agreement with literature reports)[1]

^{1}H NMR (C_6D_6, 400 MHz, 298 K): 7.1-7.2 (m, 6 H, Ph), 5.05 (s, 1 H, *γ*–C<u>H</u>), 3.59 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, C<u>H</u>Me$_2$), 1.49 (s, 6 H, Me), 1.43 (d, 12 H, $^3J_{HH}$ = 6.80 Hz, CH<u>Me$_2$</u>), 1.08 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH<u>Me$_2$</u>). The formation of this compound was confirmed by independent synthesis.

[{(ArNCMe)$_2$CH}AlCl$_2$]: (in very close agreement with literature reports)[5]

^{1}H NMR (C_6D_6, 400 MHz, 298 K): 7.1-7.2 (m, 6 H, Ph), 4.91 (s, 1 H, *γ*–C<u>H</u>), 3.44 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, C<u>H</u>Me$_2$), 1.50 (s, 6 H, Me), 1.42 (d, 12 H, $^3J_{HH}$ = 6.80 Hz, CH<u>Me$_2$</u>), 1.10 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH<u>Me$_2$</u>).

BCl$_2$F: (in very close agreement with literature reports)[6]

^{19}F NMR (*m*-xylene, C_6D_6 insert, 100 MHz, 298 K): -27.7, 1:1:1:1 quartet, $^1J_{BF}$ = 72 Hz)

^{11}B NMR (*m*-xylene, C_6D_6 insert, 128 MHz, 298 K): 32.6, d, $^1J_{BF}$ = 74 Hz)

$BClF_2$: (in very close agreement with literature reports)[6]

^{19}F NMR (*m*-xylene, C_6D_6 insert, 100 MHz, 298 K): -74.4, 1:1:1:1 quartet (coupling poorly resolved), $^1J_{BF}$ = 35 Hz)

^{11}B NMR (*m*-xylene, C_6D_6 insert, 128 MHz, 298 K): 20.0, tr, $^1J_{BF}$ = 33 Hz)

BF_3: (in very close agreement with literature reports)[6]

^{19}F NMR (*m*-xylene, C_6D_6 insert, 100 MHz, 298 K): -125.8, 1:1:1:1 quartet (coupling poorly resolved), $^1J_{BF}$ = 10 Hz)

^{11}B NMR (*m*-xylene, C_6D_6 insert, 128 MHz, 298 K): 9.9, q, coupling unresolved)

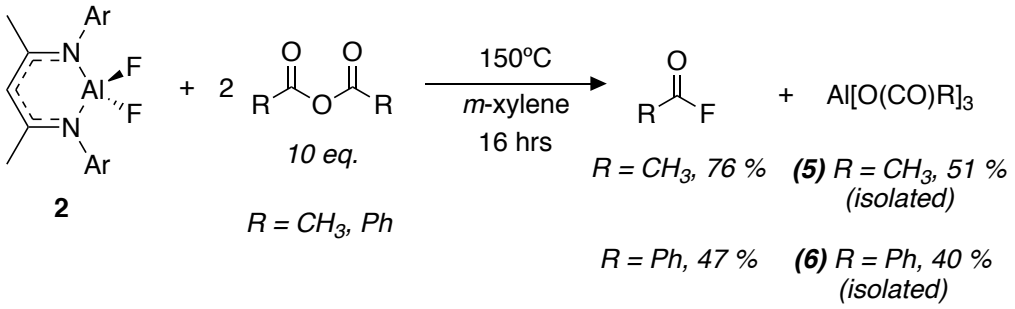
Cy_2BF:

^{19}F NMR (C_6D_6, 100 MHz, 298 K): -42.2, m (br)

^{11}B NMR (C_6D_6, 128 MHz, 298 K): 58.2, m (br)

^1H NMR (C_6D_6, 400 MHz, 298 K): 0.88 – 1.88, m, cyclohexyl). *^1H spectrum was contaminated with a very minor amount of* ***[{(ArNCMe)$_2$CH}AlI$_2$].***

2.2.3 Reactivity of [{(ArNCMe)$_2$CH}AlF$_2$] (2) with Carbon Electrophiles



Scheme S4: Conditions for reaction of **2** with carbon electrophiles

NMR Procedure: In an N_2 filled glovebox, 51.8 µL of a 0.2 M stock solution (0.010 mmol) of **2** in *m*-xylene was added to a J Young NMR tube along with a further 530 µL of *m*-xylene, 20 µL of a 0.1 M stock solution of 1,2-difluorobenzene (internal standard) in C_6D_6 and 0.10 mmol (10 equiv.) of the relevant electrophile. The J Young NMR tube was equipped with a capillary internal standard containing ferrocene in C_6D_6, and t=0 ^{1}H and ^{19}F NMR spectra were recorded. The NMR tube was then placed in a 150°C oil bath for a set amount of time, before further ^{1}H and ^{19}F spectra were recorded. Quantitative ^{19}F integration was performed using the 1,2-difluorobenzene triplet at δ -138.0 ppm, while quantitative ^{1}H integration was performed using the ferrocene singlet at δ 4.0 ppm, or through external addition of 1,3,5-trimethoxybenzene and comparison of singlet at δ 6.33 in *m*-xylene (this peak comes at δ 6.26 in C_6D_6). It was noted that a colourless precipitate also formed in the NMR tube, which was found to be insoluble in NMR solvents (see below for preparative procedure).

NMR Characterisation of Products:

Benzoyl Fluoride: (in very close agreement with literature reports)[7]

^{1}H NMR (C_6D_6, 400 MHz, 298 K): 7.67 (d, 2H, $^3J_{HH}$ = 7.7 Hz, o-CH), 6.99 (t, 1H, $^3J_{HH}$ = 7.5 Hz, p-CH), 6.82 (t, 2H, $^3J_{HH}$ = 8.6 Hz, m-CH). ^{19}F NMR (C_6D_6, 100 MHz, 298 K): 18.0 (s).

Acetyl Fluoride: (in very close agreement with literature reports)[7]

^{19}F NMR (C_6D_6, 100 MHz, 298 K): 50.6 (s).

Preparative Procedure:

Reaction with Acetic Anhydride:

In an N_2 filled glovebox, 200 mg (0.41 mmol) of **2** was added to a J Young ampoule equipped with a stirrer bar, along with 423 mg (4.1 mmol, 10 equivs.) of acetic anhydride, and 5 mL of *m*-xylene. The reaction mixture was stirred and heated to 150°C in a silicon oil bath overnight. A colourless precipitate was observed to form, as observed on the NMR scale. The mixture was left to settle, before the solid precipitate was isolated by filtration of the liquid fraction, washed with n-hexane (3 x 5 mL) and toluene (3 x 5 mL), and dried *in vacuo* for 6 hours (43 mg, 0.21 mmol, 51 %). This compound (Scheme S4, compound **5**), was found to be insoluble in NMR solvents, and thus was subjected to IR spectroscopy for analysis (see below).

Reaction with Benzoic Anhydride:

In an N_2 filled glovebox, 200 mg (0.41 mmol) of **2** was added to a J Young ampoule equipped with a stirrer bar, along with 937 mg (4.1 mmol, 10 equivs.) of benzoic anhydride, and 5 mL of *m*-xylene. The reaction mixture was stirred and heated to 150°C in a silicon oil bath overnight. A colourless precipitate was observed to form, as observed on the NMR scale. The mixture was left to settle, before the solid precipitate was isolated by filtration of the liquid fraction, washed with n-hexane (3 x 5 mL) and toluene (3 x 5 mL), and dried *in vacuo* for 6 hours (66 mg, 0.17 mmol, 40 %). This compound (Scheme S4, compound **6**), was found to be insoluble in NMR solvents, and thus was subjected to IR spectroscopy for analysis (see below).

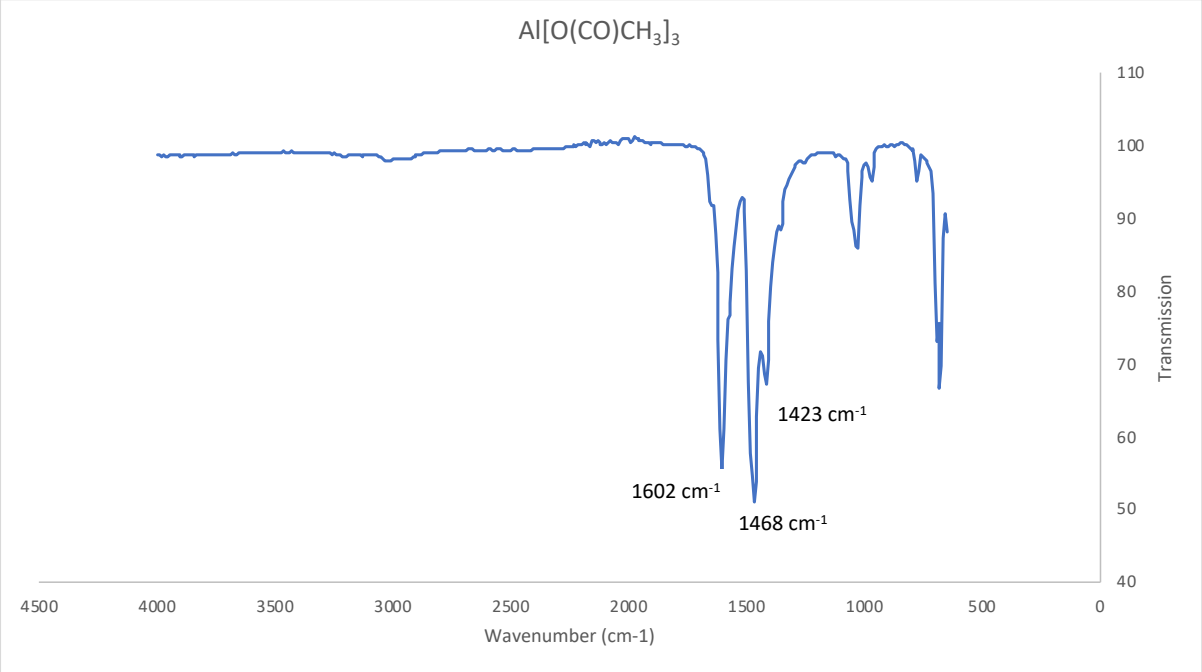


Figure S2: IR spectrum of $Al[O(CO)CH_3]_3$, **5**

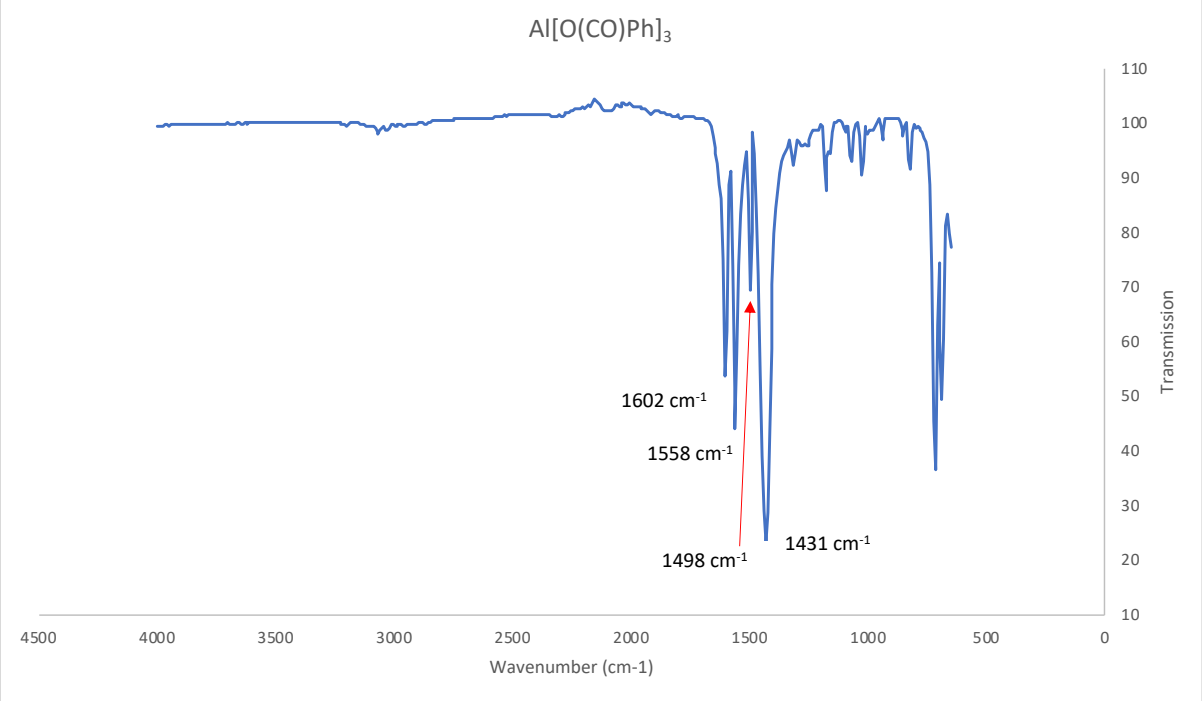
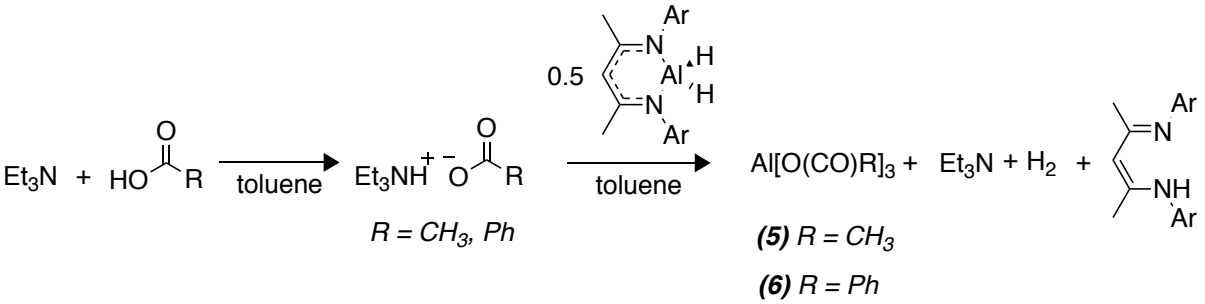


Figure S3: IR spectrum of $Al[O(CO)Ph]_3$, **6**

Compound **5** and **6** show a similar pattern (compound 6 data in parenthesis): a strong peak at 1602 cm^{-1} (1602 cm^{-1}) and 1468 cm^{-1} (1558 cm^{-1}), and then a weaker peak at 1423 cm^{-1} (1498 cm^{-1}). These stretches fall in the typical region for asymmetric and symmetric COO^- stretches, based on similar stretches observed for other metal carboxylates in the literature.[8,9] We propose the products are tris-carboxylates of the form $Al(O(CO)CH_3)_3$ **(5)** and $Al(O(CO)Ph)_3$

(6). Although it is difficult to say with certainty whether the bonding mode is unidentate or bidentate, previous work suggests that presence of a symmetric COO^- stretch indicates a bidentate bonding mode.[9] The proposed compound **5** has some precedence in the literature, albeit with very limited data.[10,11] It was found to be insoluble in benzene and dioxane. It was characterised only by CHN analysis. A similar lack of experimental data was found for **6** or similar compounds.

In order to further this identification, independent syntheses of the aluminium products were carried out (Scheme S5).



Scheme S5: Independent syntheses of aluminum by-products

Independent Synthesis of Al-containing Side product 5: Triethylamine (172 mg, 1.7 mmol) and acetic acid (102 mg, 1.7 mmol) were stirred in a toluene solution (3 mL) for 1 hour. The solvent was removed *in vacuo*. The residue was redissolved in toluene (3 mL) and 0.5 equiv of [{(ArNCMe)$_2$CH}AlH$_2$] (380 mg, 0.85 mmol) (synthesised as per ref. 12) was added.[12] Immediately a colourless precipitate formed. The reaction was stirred for 30 minutes. The solid precipitate was isolated by decanting the liquid fraction, before washing with hexane (3 x 1 mL). The solid was investigated by IR spectroscopy (see below), which was found to be in close agreement with the IR data above, and thus also assigned as compounds **5**. ^{1}H NMR spectroscopy of the liquid fraction from this reaction revealed the parent, protonated, β-diketiminate ligand.[13]

Independent Synthesis of Al-containing Side product 6: Triethylamine (172 mg, 1.7 mmol) and benzoic acid (207 mg, 1.7 mmol) were stirred in a toluene solution (3 mL) for 1 hour. The solvent was removed *in vacuo*. The residue was redissolved in toluene (3 mL) and 0.5 equiv of [{(ArNCMe)$_2$CH}AlH$_2$] (380 mg, 0.85 mmol) (synthesised as per ref. 12) was added.[12] Immediately a colouress precipitate formed and the reaction was stirred for 30 minutes. The solid precipitate was isolated by decanting the liquid fraction, before washing with hexane (3 x 1 mL). The solid was investigated by IR spectroscopy (see below), which was found to be in close agreement with the IR data above, and thus also assigned as compounds **6.** ^{1}H NMR spectroscopy of the liquid fraction from this reaction revealed the parent, protonated, β-diketiminate ligand.[13]

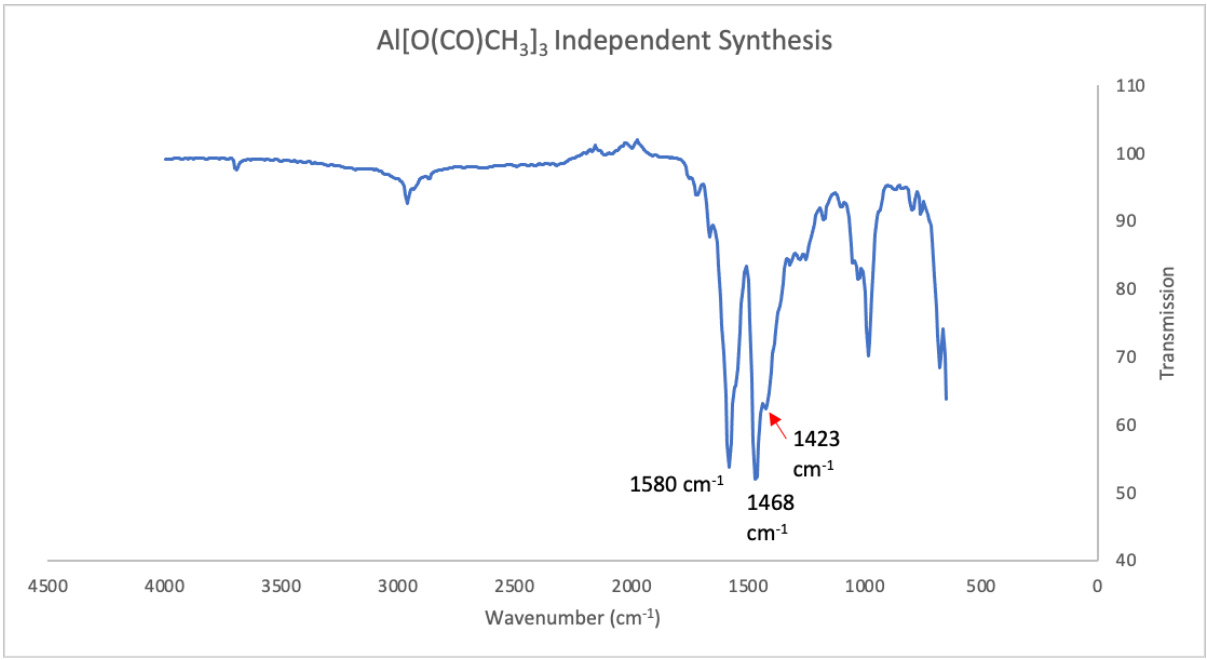


Figure S4: IR spectrum of independently synthesised Al[O(CO)CH_3]$_3$, **5**

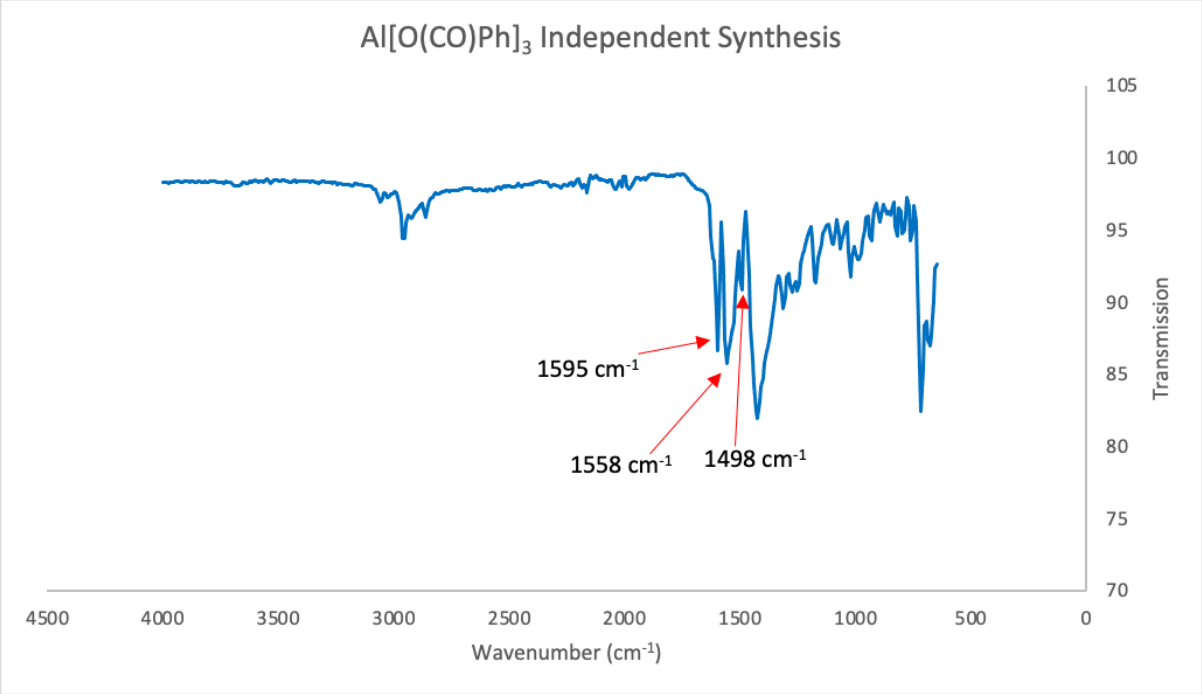
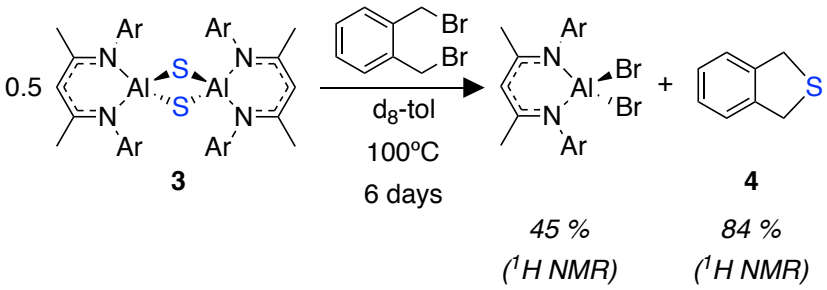


Figure S5: IR spectrum of independently synthesised Al[O(CO)Ph]$_3$, **6**

2.3 Reactivity of [{(ArNCMe)$_2$CH}Al(μ-S)]$_2$ (3)



Scheme S6: Reaction conditions for the sulfide transfer from **3** to form heterocycle **4**.

Reaction of 3 with α,α′-dibromo-o-xylene: 10 mg (0.01 mmol) of **3** was added to a J Young NMR tube, along with 27.7 mg (0.10 mmol) of α,α′-dibromo-*o*-xylene, and 0.6 mL toluene-d$_8$. The J Young NMR tube was placed in a silicon oil bath at 100°C for 6 days. ^{1}H NMR spectroscopy revealed the formation of [{(ArNCMe)$_2$CH}AlBr$_2$] in a 45 % yield,[14] and the sulfur heterocycle 1,3-dihydrobenzothiophene in an 84 % yield.[15,16] Yields were determined by integral comparison to 1,3,5-trimethoxybenzene internal standard (6.16, s, 3H, C<u>H</u>).

[{(ArNCMe)$_2$CH}AlBr$_2$]: (in very close agreement with literature reports)[14]
^{1}H NMR (toluene-d$_8$, 400 MHz, 298 K): 7.01-7.15 (m, 6 H, Ph), 4.93 (s, 1 H, γ–C<u>H</u>), 3.46 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, C<u>H</u>Me$_2$), 1.50 (s, 6 H, Me), 1.40 (d, 12 H, $^3J_{HH}$ = 6.80 Hz, CH<u>Me$_2$</u>), 1.10 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH<u>Me$_2$</u>).

1,3-dihydrobenzothiophene: (in very close agreement with literature reports)[16]
^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): 7.27-7.14 (m, Ar, 4H), 4.28 (s, C<u>H$_2$</u>, 4H). *^{1}H NMR spectrum also contained some of the excess starting material α,α′-dibromo-o-xylene: 7.40-7.36 (m, 2H), 7.34-7.30 (m, 2H), 4.68 (s, 4H).*

3. Computational Methods

DFT calculations were run using Gaussian 09 (Revision D.01)[17] using the M06-2X Minnesota functional and an ultrafine integration grid (keyword int=ultrafine).[18] Al centres were described with Stuttgart SDDAll RECPs and associated basis sets, while a hybrid basis set was used for the other atoms: 6-31g**(C, H)/6-311+g*(S, N, F).

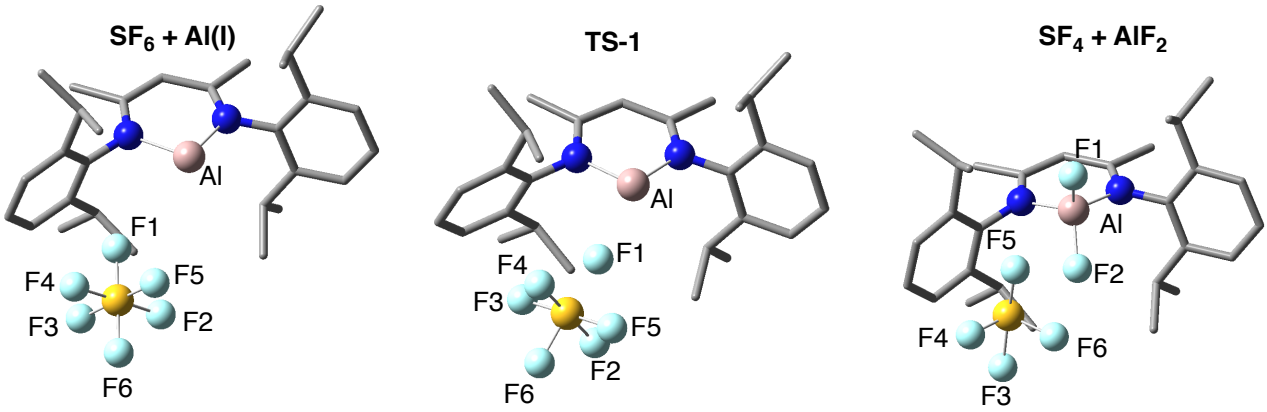
Geometry optimisation calculations were performed without symmetry constraints. The Gaussian 09 default optimisation criteria were tightened to 10^{-9} on the density matrix and 10^{-7} on the energy matrix. The default numerical integration grid was also improved using a pruned grid with 99 radial shells and 590 angular points per shell. Frequency analyses for all stationary points were performed using the enhanced criteria to confirm the nature of the structures as either minima (no imaginary frequency) or transition states (only one imaginary frequency). Single point solvent corrections (benzene, $\varepsilon = 2.2706$) were applied using the polarizable continuum model (PCM) to free energies.[19] Single point dispersion corrections using Grimme's D3 correction were applied to free energies.[20] Intrinsic reaction coordinate (IRC) calculations followed by full geometry optimisations on final points were used to connect transition states and minima located on the potential energy surface allowing a full energy profile (calculated at 298.15 K, 1 atm) of the reaction to be constructed.[21,22] The graphical user interface used to visualise the various properties of the intermediates and transition states was GaussView 5.0.9.[23] Natural Bond Orbital analysis was carried out using NBO 6.0.[24]

ETS-NOCV[25] calculations were performed using DFT as implemented in Orca 4.2.1.[26,27] Optimised geometries from the Gaussian 09 calculations detailed above were used. Single-point calculations were performed using the M06-2X functional[18] with Grimme's D3 dispersion correction[20] applied, and an ultrafine (99,950) grid (grid6). The def2-tzvpp basis set was used for all atoms.

3.1 NBO Data and Analysis

A full NBO analysis was carried out and the relevant NPA charges and Wiberg Bond Indices are tabulated below.

It is noted in the manuscript that for **TS-1** and **TS-2**, the second S–F cleavage occurs after the transition state has been surmounted. An IRC calculation connects **TS-1** directly to SF_4 and [{(ArNCMe)$_2$CH}AlF_2], suggesting a barrierless process for the second bond cleavage. Likewise for **TS-2**, an IRC calculation connects **TS-2** directly to SF_2 and [{(ArNCMe)$_2$CH}AlF_2].

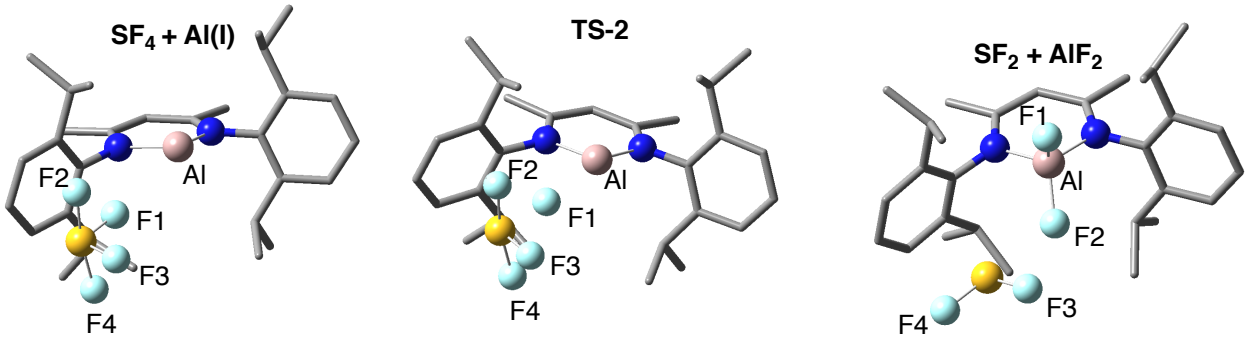


NPA Charge	SF_6 + Al(I)	TS-1	Al-F_2 + SF_4
S	+2.61	+2.46	+2.00
F1	-0.41	-0.51	-0.81
F2	-0.43	-0.47	-0.82
Al	+0.83	+1.13	+2.30

Table S2: NPA charges for TS-1

WBI	SF_6 + Al(I)	TS-1	Al-F_2 + SF_4
S–F1	0.71	0.49	0.00
S–F2	0.69	0.63	0.02
S–F3	0.70	0.64	0.60
S–F4	0.69	0.64	0.76
S–F5	0.69	0.64	0.62
S–F6	0.69	0.69	0.78
Al–F1	0.02	0.16	0.32
Al–F2	0.00	0.04	0.28

Table S3: WBI indices for TS-1

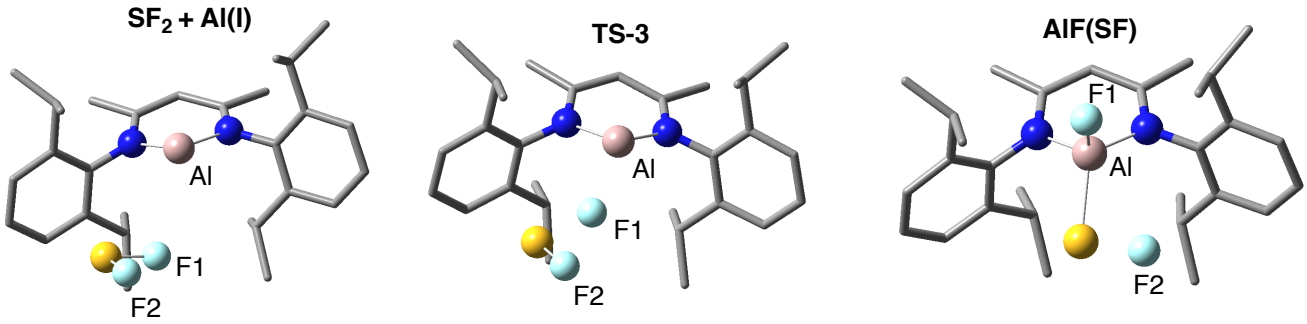


NPA Charge	Al(I) + SF_4	TS-2	Al-F_2 + SF_2
S	1.95	1.75	0.97
F1	-0.41	-0.53	-0.81
F2	-0.55	-0.56	-0.81
F3	-0.44	-0.44	-0.47
F4	-0.56	-0.57	-0.49
Al	0.84	1.15	2.30

Table S4: NPA charges for TS-2

Wiberg Bond Index	Al(I) + SF_4	TS-2	Al-F_2 + SF_2
S–F1	0.79	0.50	0.001
S–F2	0.63	0.60	0.03
S–F3	0.77	0.76	0.79
S–F4	0.61	0.59	0.76
Al–F1	0.02	0.19	0.32
Al–F2	0.001	0.001	0.28

Table S5: WBI Indices for TS-2

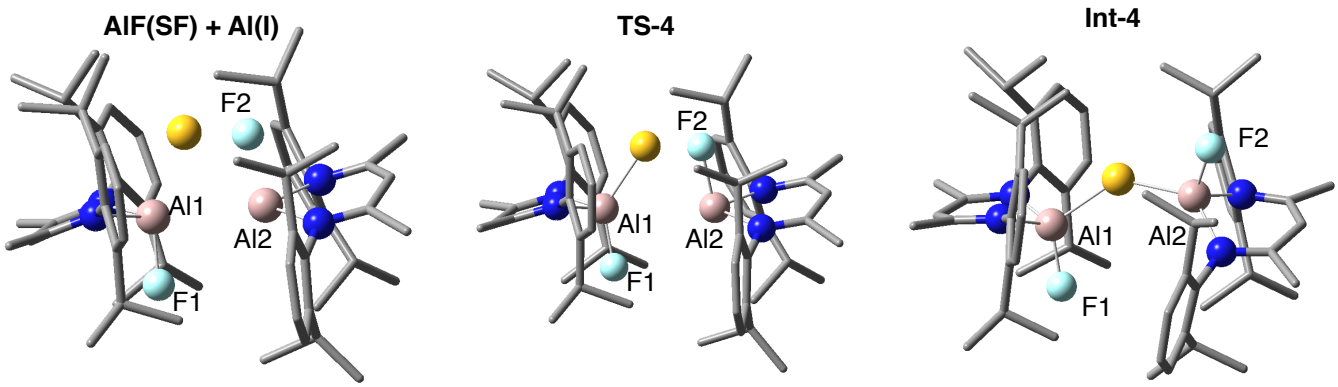


NPA charge	Al(I) + SF_2	TS-3	Al(F)(SF)
S	0.95	0.78	-0.04
F1	-0.47	-0.60	-0.80
F2	-0.46	-0.47	-0.48
Al	0.83	1.08	2.00

Table S6: NPA charges for TS-3

WBI	Al(I) + SF_2	TS-3	Al(F)(SF)
S–F1	0.76	0.48	0.02
S–F2	0.79	0.78	0.75
Al-F1	0.03	0.17	0.33
Al-F2	0.01	0.02	0.03
Al-S	0.06	0.39	0.67

Table S7: WBI Indices for TS-3



NPA charge	Al(l) + Al-(F)(SF)	TS-4	Int-4
S	-0.08	-0.23	-1.21
F1	-0.84	-0.83	-0.82
F2	-0.59	-0.66	-0.81
Al1	1.57	1.81	2.10
Al2	1.41	1.41	2.08

Table S8: NPA charges for TS-4

WBI	Al(l) + Al-(F)(SF)	TS-4	Int-4
Al1-S	0.46	0.63	0.61
Al1-F1	0.24	0.26	0.31
S-F2	0.56	0.43	0.02
Al2-F2	0.11	0.18	0.31
Al2-S	0.15	0.35	0.64

Table S9: WBI Indices for TS-4

NPA charge	SF_6	SF_4	SF_2
S	2.61	1.93	0.91
F	-0.43	-0.54 (axial)	-0.46
F	-0.43	-0.54 (axial)	-0.46
F	-0.43	-0.42 (equatorial)	
F	-0.43	-0.42 (equatorial)	
F	-0.43		
F	-0.43		

Table S10: NPA charges for SF_6, SF_4 and SF_2

WBI	SF_6	SF_4	SF_2
S–F	0.70	0.64 (axial)	0.81
S–F	0.70	0.64 (axial)	0.81
S–F	0.70	0.79 (eq.)	
S–F	0.70	0.79 (eq.)	
S–F	0.70		
S–F	0.70		

Table S11: WBI Indices for SF_6, SF_4 and SF_2

3.2 ETS-NOCV

ETS-NOCV calculations were carried out on **TS-1**, **TS-2** and **TS-3** (Table S12). They suggest that the major contribution ($\Delta\rho_1$) to the orbital interaction energy of the two fragments (**1** and SF_x (x=6,4,2) is from the Al lone pair to the σ* S–F orbital. The interpretation of this data is taken with caution due to the limitations of using DFT generated orbitals to depict the electronic structure of transition states. However, the calculations still suggest a qualitative understanding of the flow of electron density.

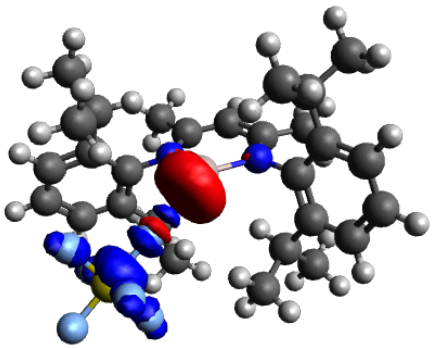
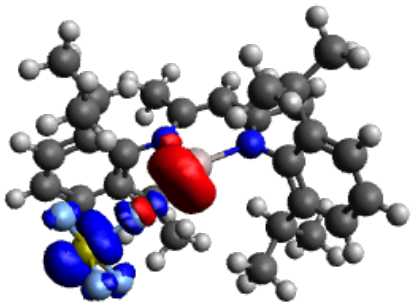
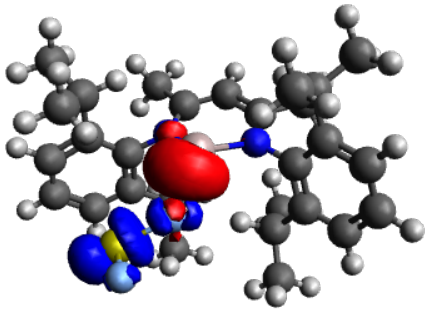
Transition-State ΔE_{orb}	$\Delta\rho_1$
TS-1 ***-21 kcal mol^{-1}***	$\Delta\rho_1$ Al(3s) to σ*S–F -17 kcal mol^{-1} 
TS-2 **-25 kcal mol^{-1}**	$\Delta\rho_1$ Al(3s) to σ*S–F - 18 kcal mol^{-1} 
TS-3 **-37 kcal mol^{-1}**	$\Delta\rho_1$ Al(3s) to σ*S–F - 22 kcal mol^{-1} 

Table S12: Selected deformation density data on transition states **TS-1**, **TS-2**, **TS-3**. Charge flow from red to blue.

3.3 Functional Benchmarking

An assessment of the computational methodology was carried out by a series of functional benchmarking calculations (Table S13). The functionals tested were the Minnesota hybrid-meta functional M06-2X,[18] the long-range corrected functional ω-B97X,[28] and with Grimme's D2 dispersion correction ω-B97X-D.[29] The same basis set and pseudopotential combination were maintained throughout. Single point solvent corrections (benzene, ε = 2.2706) were applied using the polarizable continuum model (PCM) to free energies.[19] Single point

dispersion corrections using Grimme's D3 correction were applied to free energies in the cases of M06-2X and ω-B97X (noting that ω-B97X-D has Grimme's D2 dispersion correction built into the functional).[20] Consistent results were found across the different functionals (Table S13).

	M06-2X	ω-B97X	ω-B97X-D
$\Delta G_{TS\text{-}1}^{\ddagger}$	10	9	10
$\Delta G_{TS\text{-}2}^{\ddagger}$	11	13	14
$\Delta G_{TS\text{-}3}^{\ddagger}$	11	15	15
$\Delta G_{TS\text{-}4}^{\ddagger}$	3	8	7

Table S13: Relative free-energy barriers for the four transition states calculated for various density functionals. Free-energies in kcal mol^{-1}.

3.4 XYZ Coordinates

1.log

SCF (M062X) = -1240.85289427

E(SCF)+ZPE(0 K)= -1240.209482

H(298 K)= -1240.173426

G(298 K)= -1240.275279

Lowest Frequency = 20.8423cm-1

Al	10.188542	1.553179	3.544343
N	9.056951	2.897809	4.542831
N	10.522811	2.991042	2.162315
C	8.945094	4.209605	4.348456
C	9.519203	4.877777	3.260244
H	9.357249	5.945679	3.201947
C	10.211486	4.283235	2.196774
C	8.128099	5.034415	5.315415
H	7.069061	4.765572	5.242332
H	8.235270	6.098778	5.107843
H	8.434032	4.831717	6.345193
C	10.611746	5.175546	1.045003

H	10.234433	4.772050	0.101297
H	11.701789	5.216367	0.955804
H	10.230096	6.186713	1.182798
C	8.292211	2.296262	5.598995
C	6.945880	1.957301	5.351260
C	6.230752	1.303923	6.354027
H	5.194582	1.030347	6.180311
C	6.824651	0.991522	7.572245
H	6.253647	0.479588	8.340124
C	8.148220	1.336505	7.801424
H	8.609363	1.092473	8.754719
C	8.905528	1.992207	6.826316
C	6.293304	2.251468	4.008091
H	6.846558	3.065703	3.528522
C	6.395111	1.027017	3.089380
H	7.436341	0.712383	2.955962
H	5.971879	1.246849	2.103061
H	5.848655	0.181181	3.519692
C	4.835770	2.703616	4.137949
H	4.732474	3.530444	4.847074
H	4.187857	1.888639	4.474634
H	4.459617	3.035124	3.165994
C	10.349310	2.359015	7.128519
H	10.754340	2.884352	6.257149
C	10.445081	3.306625	8.330882
H	9.853013	4.213657	8.178439
H	11.484739	3.601621	8.500898
H	10.082897	2.821617	9.242982
C	11.200993	1.105354	7.361993
H	11.157224	0.436035	6.498323
H	10.848454	0.553305	8.239576

H	12.245726	1.380760	7.536358
C	11.178040	2.473376	0.994208
C	12.578111	2.569719	0.874595
C	13.188217	2.008421	-0.247426
H	14.267671	2.067945	-0.352042
C	12.440480	1.368228	-1.228513
H	12.932768	0.939261	-2.095332
C	11.063271	1.271580	-1.089721
H	10.481516	0.762060	-1.853209
C	10.408288	1.811101	0.020286
C	13.430690	3.216664	1.954694
H	12.772306	3.802186	2.604511
C	14.093780	2.135126	2.818309
H	13.345680	1.474822	3.268113
H	14.686468	2.588512	3.618987
H	14.759889	1.517284	2.206759
C	14.487222	4.167955	1.382393
H	14.045140	4.909315	0.709849
H	15.253685	3.624645	0.821352
H	14.993377	4.698899	2.193655
C	8.898754	1.660425	0.136483
H	8.578127	2.130813	1.073242
C	8.174511	2.376050	-1.009910
H	8.433390	3.438202	-1.045966
H	7.090350	2.292372	-0.886641
H	8.436722	1.934279	-1.976718
C	8.499316	0.180999	0.192648
H	8.986909	-0.323180	1.032824
H	8.787752	-0.338408	-0.726917
H	7.415825	0.079880	0.309089

2.log

SCF (M062X) = -1440.74197617

E(SCF)+ZPE(0 K)= -1440.091488

H(298 K)= -1440.053353

G(298 K)= -1440.158676

Lowest Frequency = 23.2798cm-1

Al	9.249277	1.603083	2.935899
N	8.678595	2.752133	4.312451
N	10.083714	2.895939	1.861997
C	8.539592	4.064231	4.118807
C	8.997280	4.731454	2.970686
H	8.799942	5.793274	2.920060
C	9.795530	4.192649	1.950598
C	7.878080	4.892946	5.189159
H	6.818217	4.630751	5.259473
H	7.965471	5.955353	4.965860
H	8.324185	4.687306	6.165619
C	10.377520	5.132061	0.928585
H	10.085863	4.815161	-0.077348
H	11.470098	5.100517	0.965157
H	10.041352	6.153780	1.098873
C	8.287521	2.167818	5.571336
C	6.937780	1.854544	5.803229
C	6.600038	1.294060	7.038304
H	5.563677	1.038996	7.239363
C	7.566591	1.049971	8.001778
H	7.285464	0.617569	8.956675
C	8.901738	1.335824	7.736853
H	9.649377	1.109321	8.488350

C	9.295656	1.886631	6.516819
C	5.857505	2.049684	4.750582
H	6.272870	2.645988	3.931448
C	5.440890	0.693899	4.162729
H	6.285058	0.198437	3.678812
H	4.657810	0.833868	3.411358
H	5.046383	0.043388	4.950680
C	4.631029	2.784614	5.306176
H	4.897838	3.720198	5.807132
H	4.093897	2.165043	6.030906
H	3.934254	3.015454	4.495645
C	10.765121	2.159174	6.213181
H	10.943065	1.855800	5.175672
C	11.122470	3.646562	6.340682
H	10.591212	4.266366	5.613519
H	12.195359	3.787419	6.168609
H	10.890619	4.014492	7.346362
C	11.710368	1.325440	7.080440
H	11.452928	0.263853	7.044009
H	11.696535	1.652999	8.125544
H	12.735783	1.438199	6.719546
C	11.102943	2.441607	0.951424
C	12.429354	2.388517	1.417450
C	13.409105	1.909617	0.546916
H	14.440573	1.858711	0.884699
C	13.083756	1.485953	-0.735928
H	13.858784	1.111215	-1.396745
C	11.764875	1.532854	-1.168263
H	11.514325	1.187632	-2.167301
C	10.748398	2.009891	-0.337121
C	12.816055	2.818293	2.824575

H	11.914404	3.170618	3.339106
C	13.371592	1.635027	3.626588
H	12.635786	0.828954	3.690497
H	13.629632	1.961964	4.639970
H	14.283388	1.243932	3.162835
C	13.821000	3.976588	2.801118
H	13.437378	4.837590	2.245776
H	14.762247	3.670245	2.333506
H	14.046381	4.302871	3.821001
C	9.309673	2.018884	-0.826567
H	8.697808	2.539685	-0.082575
C	9.165989	2.757014	-2.162856
H	9.576382	3.770441	-2.117249
H	8.110949	2.826612	-2.442195
H	9.684554	2.225415	-2.966856
C	8.773309	0.586033	-0.942816
H	8.802760	0.074834	0.021940
H	9.364005	0.013569	-1.666048
H	7.733562	0.597970	-1.282662
F	10.370549	0.445462	3.467000
F	7.924681	0.884152	2.152092

3.log

SCF (M062X) = -3278.36924380

E(SCF)+ZPE(0 K)= -3277.071872

H(298 K)= -3276.998444

G(298 K)= -3277.173889

Lowest Frequency = 20.1815cm-1

Al	6.706209	2.674320	-0.043361

S	6.215253	4.316613	1.450237
N	8.554122	2.723199	-0.669015
N	6.818829	0.815713	0.515150
C	9.278225	3.962053	-0.829567
C	9.437833	4.509132	-2.115704
C	9.919883	4.516008	0.294588
C	9.236031	1.626361	-1.006281
C	7.683895	-0.050231	-0.018613
C	8.761111	0.323264	-0.823066
H	9.384419	-0.475157	-1.199165
C	7.558107	-1.524015	0.284342
H	7.561402	-1.710932	1.360444
H	8.372665	-2.078913	-0.178812
H	6.608734	-1.900955	-0.100804
C	6.524135	0.333687	2.885619
C	5.998860	0.290196	1.578471
C	9.757114	3.919446	1.684731
H	8.775793	3.441014	1.729761
C	10.278365	5.615853	-2.259672
H	10.413840	6.053858	-3.244222
C	4.775174	-0.341401	1.297685
C	10.769447	5.605567	0.093532
H	11.289660	6.039452	0.941162
C	2.958252	0.318562	-0.296880
H	2.160508	-0.079318	0.337366
H	2.620783	0.276816	-1.337973
H	3.119672	1.365344	-0.035146
C	8.744872	3.932788	-3.340853
H	8.358541	2.940091	-3.087511
C	10.626435	1.738946	-1.589928
H	10.584563	2.145287	-2.602705

H	11.097078	0.757432	-1.626617
H	11.248647	2.414862	-0.998832
C	10.959365	6.145831	-1.172754
H	11.625978	6.992173	-1.307454
C	4.058040	-0.886188	2.367704
H	3.099731	-1.360040	2.172960
C	7.554097	4.812843	-3.723119
H	6.838814	4.894685	-2.901329
H	7.028262	4.395807	-4.589057
H	7.899912	5.817264	-3.983449
C	5.791044	-0.261581	3.912088
H	6.185735	-0.248114	4.924698
C	7.879851	0.951781	3.197768
H	8.293262	1.361240	2.270272
C	4.236663	-0.497581	-0.115188
H	4.986856	-0.109137	-0.812463
C	4.562855	-0.862099	3.660329
H	3.999846	-1.310444	4.473350
C	9.682956	3.794822	-4.548365
H	9.939379	4.775837	-4.960294
H	9.183158	3.232313	-5.341877
H	10.620628	3.285766	-4.306743
C	3.940542	-1.965038	-0.462785
H	4.783896	-2.634377	-0.274294
H	3.668570	-2.047986	-1.519022
H	3.094128	-2.337117	0.123347
C	7.756708	2.104672	4.199626
H	7.151969	2.918891	3.787810
H	8.750622	2.496593	4.441311
H	7.297550	1.767785	5.135465
C	9.766387	4.987181	2.780561

H	10.755421	5.439585	2.907323
H	9.489102	4.537117	3.737473
H	9.040854	5.773657	2.555338
C	10.814059	2.841038	1.956329
H	10.699372	1.982105	1.286049
H	10.723262	2.473825	2.984575
H	11.824232	3.245988	1.828965
C	8.863011	-0.109692	3.708983
H	8.509761	-0.554936	4.644852
H	9.842048	0.340064	3.900468
H	8.999127	-0.916485	2.982649
Al	4.502052	4.731142	0.013406
S	4.998871	3.095812	-1.485085
N	2.758383	4.797560	0.870151
N	4.306936	6.496782	-0.794219
C	2.008680	3.600970	1.161768
C	2.096243	2.985881	2.422193
C	1.107341	3.144794	0.179018
C	2.149738	5.943549	1.184994
C	3.471013	7.422863	-0.319316
C	2.550919	7.192473	0.709066
H	1.978316	8.045183	1.044419
C	3.446860	8.810932	-0.918456
H	3.398916	8.768626	-2.009008
H	2.588212	9.365581	-0.542565
H	4.356860	9.355779	-0.658553
C	4.633800	6.562210	-3.222893
C	5.087737	6.910497	-1.936399
C	0.948453	3.840878	-1.165343
H	1.669125	4.663717	-1.214375
C	1.295166	1.864640	2.661574

H	1.364347	1.363198	3.623119
C	6.197077	7.754762	-1.747857
C	0.298749	2.049386	0.481845
H	-0.411201	1.691179	-0.259065
C	7.977420	7.333538	-0.052621
H	8.763139	7.579570	-0.772578
H	8.345224	7.572281	0.951342
H	7.791251	6.257839	-0.096876
C	2.979273	3.521156	3.537479
H	3.433552	4.457276	3.194985
C	0.921344	5.928096	2.062823
H	1.183303	5.557413	3.055893
H	0.508988	6.931470	2.158599
H	0.154495	5.259868	1.665234
C	0.394103	1.406395	1.710654
H	-0.234616	0.547522	1.925318
C	6.833040	8.267686	-2.881293
H	7.692409	8.920049	-2.756844
C	4.105783	2.538234	3.850317
H	4.682730	2.303830	2.954476
H	4.789693	2.961237	4.593830
H	3.695778	1.607301	4.252980
C	5.287958	7.121108	-4.322342
H	4.946448	6.881893	-5.324050
C	3.428091	5.657364	-3.428409
H	3.370704	4.979347	-2.573307
C	6.712070	8.132379	-0.367450
H	5.953022	7.861324	0.373618
C	6.370458	7.976898	-4.156982
H	6.863664	8.402385	-5.025615
C	2.184153	3.789970	4.824973

H	1.843422	2.850091	5.271031
H	2.824271	4.287287	5.559396
H	1.299459	4.411965	4.665997
C	7.011388	9.631960	-0.230397
H	6.185733	10.266673	-0.565260
H	7.224618	9.871862	0.815010
H	7.895477	9.910257	-0.812450
C	3.567535	4.773835	-4.669753
H	4.520980	4.238666	-4.654995
H	2.764845	4.031886	-4.687046
H	3.497487	5.351914	-5.597070
C	1.247600	2.892465	-2.330998
H	0.589973	2.016636	-2.307800
H	1.079122	3.406866	-3.283275
H	2.286597	2.549349	-2.299586
C	-0.453170	4.449792	-1.304552
H	-0.661317	5.168329	-0.506123
H	-0.547650	4.972351	-2.261349
H	-1.224432	3.673387	-1.268545
C	2.124890	6.465923	-3.472332
H	2.169269	7.231525	-4.255023
H	1.278295	5.805946	-3.691558
H	1.920899	6.960522	-2.516357

int3.log

SCF (M062X) = -1838.85273531

E(SCF)+ZPE(0 K)= -1838.201793

H(298 K)= -1838.161392

G(298 K)= -1838.272813

Lowest Frequency = 21.5551cm-1

Al	9.080853	1.644828	2.791200
N	8.701512	2.735363	4.282891
N	10.057394	2.912819	1.815491
C	8.616925	4.057299	4.131701
C	9.048524	4.745235	2.979557
H	8.866322	5.811034	2.960575
C	9.798422	4.216163	1.921615
C	8.033328	4.881136	5.250251
H	6.960048	4.683700	5.330290
H	8.185050	5.944234	5.068454
H	8.481336	4.605595	6.207981
C	10.314535	5.146938	0.856183
H	9.752029	4.963683	-0.066648
H	11.365029	4.952549	0.632205
H	10.189197	6.189818	1.145622
C	8.305266	2.128927	5.532363
C	6.946518	1.874883	5.781652
C	6.606040	1.296504	7.007804
H	5.562415	1.085787	7.222357
C	7.577449	0.976012	7.943742
H	7.293140	0.529399	8.891104
C	8.919884	1.200184	7.657924
H	9.672381	0.910754	8.382847
C	9.314009	1.766419	6.446169
C	5.857329	2.140496	4.754188
H	6.285899	2.717270	3.927988
C	5.355592	0.812559	4.169663
H	6.169548	0.256450	3.700545
H	4.594529	0.999132	3.406347
H	4.910904	0.194566	4.956982

C	4.683530	2.935626	5.339777
H	5.008040	3.858831	5.829442
H	4.137186	2.345054	6.081657
H	3.977175	3.198131	4.547338
C	10.785955	1.969075	6.115031
H	10.911656	1.751035	5.049103
C	11.233905	3.418382	6.347894
H	10.722257	4.119863	5.681791
H	12.309415	3.515528	6.163023
H	11.040666	3.720068	7.383240
C	11.701446	0.999673	6.864180
H	11.357695	-0.031402	6.747218
H	11.757061	1.234376	7.932531
H	12.716041	1.069873	6.462650
C	11.105072	2.427113	0.961405
C	12.413407	2.384503	1.488511
C	13.426530	1.883199	0.670441
H	14.445298	1.848252	1.044032
C	13.149803	1.416043	-0.610312
H	13.951517	1.023998	-1.227818
C	11.848336	1.436635	-1.093779
H	11.637404	1.050595	-2.086932
C	10.799822	1.941802	-0.320448
C	12.727562	2.882285	2.893165
H	11.783879	2.932721	3.447509
C	13.656647	1.933009	3.655175
H	13.247414	0.919496	3.682569
H	13.776922	2.286012	4.684642
H	14.655463	1.897589	3.208756
C	13.324230	4.296230	2.864277
H	12.630487	5.024887	2.436285

H	14.244453	4.313749	2.270569
H	13.567841	4.624012	3.879725
C	9.377484	1.921383	-0.853315
H	8.739581	2.468758	-0.151453
C	9.271841	2.605784	-2.220866
H	9.672746	3.623642	-2.195371
H	8.226212	2.654702	-2.537164
H	9.822090	2.050478	-2.986955
C	8.852851	0.481015	-0.924183
H	8.884210	-0.005093	0.054939
H	9.452228	-0.111816	-1.623522
H	7.814196	0.472392	-1.266061
F	7.615573	1.216317	2.034082
S	10.495800	-0.112491	3.089844
F	9.739499	-0.649160	4.498979

int4.log

SCF (M062X) = -3079.93131295

E(SCF)+ZPE(0 K)= -3078.631174

H(298 K)= -3078.556492

G(298 K)= -3078.735960

Lowest Frequency = 12.6596cm-1

Al	6.749357	2.040821	-0.894619
N	8.580337	2.514136	-0.733403
N	6.855446	0.476789	0.222567
C	9.140762	3.836951	-0.788611
C	9.426324	4.412200	-2.039293
C	9.492060	4.463440	0.417527
C	9.444059	1.493898	-0.834597

C	7.911791	-0.302725	-0.003441
C	9.085747	0.157471	-0.623240
H	9.851118	-0.585383	-0.806085
C	7.929478	-1.747198	0.436451
H	8.663395	-1.886298	1.234675
H	8.248058	-2.359709	-0.411421
H	6.956123	-2.093316	0.782496
C	6.161252	-0.028155	2.526001
C	5.848553	0.058351	1.155871
C	9.118789	3.851889	1.757759
H	8.255839	3.195102	1.587790
C	10.166336	5.595382	-2.058540
H	10.414662	6.054712	-3.010275
C	4.557492	-0.252218	0.674564
C	10.252532	5.633110	0.348702
H	10.565101	6.123042	1.265601
C	2.759491	-0.278928	-1.123624
H	2.289445	-1.232690	-0.857772
H	2.605793	-0.122584	-2.195022
H	2.252087	0.524234	-0.581912
C	8.922235	3.775760	-3.322857
H	8.754081	2.708698	-3.143689
C	10.886002	1.771203	-1.186985
H	10.948770	2.182415	-2.199644
H	11.472751	0.854814	-1.138599
H	11.320602	2.515013	-0.514486
C	10.609766	6.179755	-0.877413
H	11.208243	7.085210	-0.912139
C	3.579338	-0.602245	1.603693
H	2.575497	-0.826867	1.262946
C	7.568560	4.397621	-3.690144

H	6.831276	4.280730	-2.887557
H	7.159735	3.928546	-4.590850
H	7.687078	5.470142	-3.873034
C	5.142417	-0.392444	3.413421
H	5.365636	-0.459286	4.475082
C	7.552008	0.213308	3.101745
H	8.250222	0.425126	2.284877
C	4.256632	-0.288523	-0.817727
H	4.671279	0.607365	-1.288190
C	3.861627	-0.665489	2.964113
H	3.081035	-0.938241	3.668225
C	9.903032	3.909923	-4.490813
H	9.984695	4.947021	-4.831633
H	9.550289	3.316738	-5.338654
H	10.906941	3.563766	-4.224323
C	4.922001	-1.497797	-1.489250
H	6.011052	-1.441065	-1.438667
H	4.647745	-1.532239	-2.547297
H	4.592028	-2.428719	-1.014462
C	7.574493	1.422756	4.042206
H	7.349361	2.347416	3.506419
H	8.558854	1.520630	4.510684
H	6.836814	1.309183	4.843329
C	8.698206	4.907025	2.784520
H	9.532229	5.562564	3.056123
H	8.370126	4.412077	3.704698
H	7.868469	5.511903	2.407109
C	10.271465	2.987942	2.288015
H	10.462471	2.126042	1.640012
H	10.043025	2.612071	3.289100
H	11.191824	3.579397	2.350666

C	8.053427	-1.025475	3.861725
H	7.503455	-1.150851	4.799924
H	9.112158	-0.913414	4.114478
H	7.927508	-1.944374	3.284351
Al	4.603046	5.260853	0.325463
S	4.939536	3.300544	-0.640300
N	2.879830	5.201440	1.132140
N	4.197670	6.739716	-0.820840
C	2.283051	3.960349	1.545623
C	2.586279	3.422515	2.804407
C	1.391586	3.329024	0.660611
C	2.182818	6.321263	1.336661
C	3.309203	7.661187	-0.444922
C	2.448753	7.513394	0.656602
H	1.831194	8.365338	0.905178
C	3.186940	8.945520	-1.228960
H	3.134492	8.745752	-2.301669
H	2.300226	9.497025	-0.919214
H	4.067977	9.572349	-1.063304
C	4.575558	6.409784	-3.222280
C	4.966067	7.008692	-2.011229
C	1.055991	3.913976	-0.703955
H	1.721618	4.765895	-0.879999
C	1.971748	2.225162	3.173572
H	2.205522	1.780607	4.136691
C	6.048242	7.903064	-1.937603
C	0.783856	2.144129	1.081610
H	0.078278	1.644531	0.422430
C	7.765993	7.679655	-0.159882
H	8.588767	7.848347	-0.860299
H	8.088052	7.993016	0.838738

H	7.567186	6.604041	-0.124551
C	3.584693	4.099507	3.724278
H	3.742400	5.122599	3.366980
C	1.035615	6.304469	2.315443
H	1.404308	6.007894	3.303088
H	0.570425	7.287045	2.385306
H	0.282623	5.567601	2.026907
C	1.070073	1.594024	2.325559
H	0.592963	0.667840	2.632707
C	6.706566	8.234260	-3.124027
H	7.545459	8.923120	-3.092466
C	4.927637	3.368254	3.647190
H	5.307995	3.333711	2.619622
H	5.675658	3.866142	4.273100
H	4.811064	2.333661	3.988726
C	5.251259	6.789553	-4.383890
H	4.961517	6.355756	-5.335227
C	3.419614	5.423466	-3.281992
H	3.362468	4.922865	-2.311329
C	6.531976	8.464934	-0.610920
H	5.751969	8.312733	0.141163
C	6.296971	7.704261	-4.340714
H	6.808470	7.985637	-5.256065
C	3.094397	4.176160	5.173541
H	3.029241	3.182223	5.627225
H	3.793335	4.764422	5.774712
H	2.105709	4.640437	5.243128
C	6.852208	9.962693	-0.672528
H	6.023267	10.551301	-1.077741
H	7.077807	10.335538	0.330423
H	7.730817	10.156536	-1.295604

C	3.640026	4.323895	-4.322292
H	4.595841	3.818791	-4.154847
H	2.847225	3.575503	-4.241636
H	3.617092	4.712647	-5.345615
C	1.295050	2.903042	-1.829174
H	0.665874	2.014458	-1.710356
H	1.043285	3.352820	-2.795041
H	2.342909	2.587497	-1.852510
C	-0.386730	4.434559	-0.747387
H	-0.560046	5.214589	-0.000394
H	-0.607457	4.858159	-1.732233
H	-1.099036	3.623848	-0.560609
C	2.092444	6.157897	-3.513566
H	2.136844	6.757846	-4.429335
H	1.269805	5.442728	-3.617265
H	1.850127	6.823823	-2.678120
F	5.789460	5.768515	1.453104
F	6.641199	1.414392	-2.496878

SF2.log

SCF (M062X) = -597.793504381

E(SCF)+ZPE(0 K)= -597.788962

H(298 K)= -597.784677

G(298 K)= -597.813987

Lowest Frequency = 347.4353cm-1

S	-1.740008	0.902842	-0.373533
F	-1.845601	0.902842	-1.984223
F	-0.129318	0.902842	-0.267940

SF4.log

SCF (M062X) = -797.446212815

E(SCF)+ZPE(0 K)= -797.434574

H(298 K)= -797.428819

G(298 K)= -797.463025

Lowest Frequency = 216.4082cm-1

S	-1.770059	0.902842	-0.343661
F	-1.677515	-0.763805	-0.436152
F	-1.677515	2.569489	-0.436152
F	-1.925991	0.902842	-1.907505
F	-0.206304	0.902842	-0.186851

SF6.log

SCF (M062X) = -997.091208135

E(SCF)+ZPE(0 K)= -997.070211

H(298 K)= -997.063652

G(298 K)= -997.096969

Lowest Frequency = 339.2113cm-1

S	-1.771229	0.902842	-0.342312
F	-1.771229	-0.679290	-0.342312
F	-1.771229	0.902842	1.239820
F	-3.353361	0.902842	-0.342312
F	-1.771229	2.484974	-0.342312
F	-1.771229	0.902842	-1.924444
F	-0.189097	0.902842	-0.342312

TS1.log

SCF (M062X) = -2237.93906378

E(SCF)+ZPE(0 K)= -2237.277453

H(298 K)= -2237.233553

G(298 K)= -2237.353460

Lowest Frequency = -433.0549cm-1

Al	0.905325	0.412608	-0.087925
N	-0.394989	1.529514	0.890027
N	1.029408	1.770242	-1.519136
C	-0.603840	2.835261	0.711616
C	-0.120230	3.551398	-0.390840
H	-0.375283	4.601488	-0.437688
C	0.578520	3.022816	-1.483280
C	-1.436507	3.595619	1.716453
H	-2.489143	3.304534	1.644521
H	-1.357657	4.669159	1.547127
H	-1.112060	3.361018	2.733576
C	0.824331	3.928822	-2.664291
H	0.430560	3.471392	-3.576605
H	1.897885	4.070732	-2.821002
H	0.353968	4.900138	-2.515901
C	-1.139681	0.862315	1.927354
C	-2.495310	0.553928	1.683243
C	-3.215188	-0.092552	2.685134
H	-4.260214	-0.335008	2.523690
C	-2.608439	-0.457599	3.883361
H	-3.181510	-0.974208	4.646337
C	-1.269768	-0.169257	4.094480
H	-0.798181	-0.461561	5.028537
C	-0.511701	0.505729	3.130773

C	-3.136391	0.852562	0.335122
H	-2.669714	1.750427	-0.084296
C	-2.856780	-0.301491	-0.636787
H	-1.783337	-0.503025	-0.724627
H	-3.244248	-0.069730	-1.635368
H	-3.328289	-1.223872	-0.283346
C	-4.640028	1.123768	0.421130
H	-4.870756	1.887396	1.170234
H	-5.198976	0.218490	0.676189
H	-5.010824	1.469833	-0.547556
C	0.936498	0.849515	3.439233
H	1.337812	1.426382	2.598583
C	1.045137	1.731547	4.689673
H	0.447145	2.642496	4.592333
H	2.086080	2.021369	4.860111
H	0.698406	1.197672	5.579865
C	1.785797	-0.417918	3.592780
H	1.745223	-1.031577	2.689081
H	1.425783	-1.028473	4.427546
H	2.829844	-0.155567	3.790447
C	1.715417	1.307634	-2.696772
C	3.093052	1.559868	-2.843531
C	3.741577	1.047642	-3.967606
H	4.805488	1.225160	-4.094540
C	3.053108	0.306061	-4.920182
H	3.575818	-0.085451	-5.786796
C	1.697785	0.059547	-4.753914
H	1.164559	-0.531214	-5.493575
C	1.004846	0.548321	-3.643514
C	3.889894	2.320874	-1.795529
H	3.184671	2.824396	-1.126030

C	4.716419	1.342401	-0.949802
H	4.076532	0.594461	-0.470830
H	5.270565	1.876541	-0.171779
H	5.437192	0.810826	-1.579898
C	4.795482	3.393965	-2.410248
H	4.239064	4.068940	-3.067545
H	5.602369	2.947060	-2.998768
H	5.260369	3.990318	-1.620171
C	-0.472346	0.223075	-3.485439
H	-0.847819	0.753445	-2.602868
C	-1.293104	0.701049	-4.688687
H	-1.159206	1.772262	-4.865608
H	-2.357273	0.511735	-4.518625
H	-1.004486	0.171659	-5.602108
C	-0.668363	-1.281517	-3.255716
H	-0.123063	-1.624447	-2.370382
H	-0.302967	-1.853566	-4.114896
H	-1.727308	-1.519321	-3.114800
S	-0.629385	-3.249422	0.960188
F	-1.889209	-2.441789	1.585193
F	0.122836	-3.194347	2.397000
F	0.125590	-1.745989	0.489246
F	0.617079	-4.077873	0.335021
F	-1.396675	-3.324616	-0.475544
F	-1.313412	-4.621305	1.381263

TS2.log

SCF (M062X) = -2038.30024359

E(SCF)+ZPE(0 K)= -2037.646086

H(298 K)= -2037.603698

G(298 K)= -2037.719676

Lowest Frequency = -402.4344cm-1

Al	10.303808	1.503627	3.623757
N	9.102787	2.768459	4.580233
N	10.611060	2.863895	2.207040
C	9.007155	4.083920	4.377466
C	9.574999	4.744419	3.282268
H	9.407730	5.810990	3.217870
C	10.270460	4.149612	2.220924
C	8.222682	4.919213	5.360859
H	7.165866	4.634936	5.353142
H	8.305886	5.979633	5.125296
H	8.590013	4.744017	6.376362
C	10.645389	5.025512	1.050793
H	10.254797	4.599899	0.121936
H	11.733295	5.072079	0.942713
H	10.255953	6.035068	1.176967
C	8.307072	2.180032	5.622364
C	6.969374	1.839653	5.328439
C	6.237566	1.153938	6.298476
H	5.208738	0.875299	6.095407
C	6.807962	0.817299	7.524733
H	6.226151	0.274640	8.262980
C	8.118458	1.181723	7.801514
H	8.559442	0.916643	8.758099
C	8.889565	1.876446	6.863181
C	6.347322	2.203048	3.986647
H	6.841185	3.110976	3.623519
C	6.593441	1.105052	2.945434
H	7.656095	0.849668	2.868973

H	6.245430	1.431098	1.958724
H	6.073155	0.183908	3.220665
C	4.851570	2.513519	4.086675
H	4.642811	3.249694	4.868883
H	4.267010	1.613865	4.301038
H	4.491524	2.912174	3.134237
C	10.310636	2.285879	7.213867
H	10.691426	2.910128	6.397714
C	10.345865	3.129331	8.494831
H	9.682825	3.997217	8.428322
H	11.362191	3.487291	8.682670
H	10.037680	2.539984	9.363885
C	11.229650	1.065446	7.347986
H	11.240093	0.468612	6.431864
H	10.887110	0.408976	8.154021
H	12.251432	1.386228	7.574325
C	11.309702	2.339288	1.063538
C	12.710901	2.459304	0.990794
C	13.367137	1.884283	-0.097954
H	14.448378	1.959619	-0.167284
C	12.663393	1.208529	-1.087598
H	13.192184	0.766245	-1.925650
C	11.283637	1.093714	-0.995238
H	10.736682	0.555556	-1.764518
C	10.581976	1.649379	0.077523
C	13.518963	3.146882	2.080180
H	12.828882	3.714969	2.712789
C	14.208531	2.100214	2.965937
H	13.480031	1.414269	3.409977
H	14.767685	2.584485	3.772441
H	14.909972	1.503729	2.373188

C	14.548831	4.131095	1.514231
H	14.089934	4.853476	0.832433
H	15.339058	3.610674	0.964738
H	15.027230	4.683308	2.328017
C	9.073131	1.474742	0.151018
H	8.705986	2.030123	1.021341
C	8.374254	2.049387	-1.086711
H	8.626510	3.103136	-1.237375
H	7.288418	1.968796	-0.978648
H	8.658940	1.504117	-1.992050
C	8.708298	-0.003211	0.342554
H	9.161526	-0.411009	1.252472
H	9.061496	-0.601115	-0.503946
H	7.623650	-0.127421	0.416440
S	8.371914	-1.494018	5.605723
F	9.323656	-0.333164	4.672294
F	9.050553	-2.792928	4.992904
F	9.636087	-1.478393	6.734032
F	7.309575	-1.542451	4.275413

TS3.log

SCF (M062X) = -1838.64872188

E(SCF)+ZPE(0 K)= -1838.000523

H(298 K)= -1837.960088

G(298 K)= -1838.071515

Lowest Frequency = -378.6808cm-1

Al	10.833324	1.681103	3.954227
N	9.315513	2.740453	4.736406
N	10.693327	2.800812	2.291024

C	9.156144	4.043735	4.511106
C	9.706696	4.696398	3.402168
H	9.526459	5.759885	3.322154
C	10.328369	4.077123	2.300663
C	8.359163	4.872489	5.491737
H	8.178372	5.875241	5.104850
H	8.926074	4.953670	6.426060
H	7.405000	4.401870	5.736973
C	10.581660	4.936999	1.084929
H	10.254058	4.427381	0.175452
H	11.654147	5.124923	0.977870
H	10.065924	5.892893	1.171272
C	8.430905	2.074123	5.635772
C	7.250275	1.516749	5.088262
C	6.404613	0.796862	5.936844
H	5.491879	0.363565	5.539898
C	6.724459	0.609850	7.278444
H	6.061144	0.038821	7.919981
C	7.892124	1.158563	7.794106
H	8.139093	1.002971	8.840582
C	8.763762	1.896944	6.990051
C	6.885205	1.736623	3.625972
H	7.815506	1.948451	3.089360
C	6.234821	0.514415	2.973636
H	6.869737	-0.372201	3.056316
H	6.061563	0.714803	1.911992
H	5.260295	0.284498	3.416265
C	5.973477	2.962108	3.467924
H	6.466914	3.881245	3.793581
H	5.056487	2.838000	4.054200
H	5.692999	3.089810	2.417628

C	10.048570	2.445777	7.584545
H	10.534380	3.065033	6.822260
C	9.777481	3.323683	8.812287
H	9.063198	4.122304	8.591324
H	10.707369	3.779493	9.164024
H	9.368449	2.732271	9.637595
C	11.007262	1.302406	7.941604
H	11.229395	0.687206	7.064907
H	10.566528	0.656539	8.708718
H	11.948859	1.700481	8.331860
C	11.298242	2.248898	1.110982
C	12.660970	2.478617	0.844148
C	13.214499	1.905648	-0.303977
H	14.265671	2.068891	-0.523890
C	12.450129	1.125045	-1.157620
H	12.896993	0.690795	-2.046158
C	11.114359	0.879900	-0.860446
H	10.533661	0.244948	-1.520146
C	10.516909	1.420357	0.278737
C	13.560639	3.273306	1.778816
H	12.932411	3.779156	2.520033
C	14.501790	2.327419	2.537939
H	13.937259	1.586557	3.110670
H	15.134780	2.891530	3.230112
H	15.152835	1.794757	1.836566
C	14.376870	4.341348	1.039330
H	13.748818	4.987338	0.418853
H	15.125313	3.883822	0.385146
H	14.912109	4.969044	1.757408
C	9.059356	1.130452	0.612331
H	9.004716	0.957130	1.693739

C	8.155276	2.325326	0.275616
H	8.367666	3.194226	0.904865
H	7.102836	2.060446	0.423220
H	8.283618	2.615155	-0.773190
C	8.526905	-0.132444	-0.067121
H	9.185341	-0.988054	0.104952
H	8.413974	0.006650	-1.147641
H	7.539849	-0.376628	0.334503
S	8.781175	-1.105702	5.031449
F	9.599133	-0.010633	3.841028
F	9.828347	-2.312984	4.731657

TS4.log

SCF (M062X) = -3079.73054308

E(SCF)+ZPE(0 K)= -3078.432911

H(298 K)= -3078.358289

G(298 K)= -3078.537474

Lowest Frequency = -308.1656cm-1

Al	6.305703	3.098785	-0.686534
N	8.250944	3.035880	-0.968946
N	6.235684	1.320612	0.052499
C	9.016172	4.244177	-1.118296
C	9.180470	4.807180	-2.395813
C	9.608240	4.811018	0.026833
C	8.863714	1.891746	-1.249577
C	7.105888	0.379018	-0.330801
C	8.274709	0.634502	-1.050289
H	8.862926	-0.226424	-1.336877
C	6.905988	-1.058587	0.095084

H	7.410181	-1.720899	-0.609850
H	5.854472	-1.334103	0.167236
H	7.356500	-1.209160	1.081011
C	5.615277	0.720260	2.345831
C	5.241281	0.905635	1.002376
C	9.455317	4.163457	1.397484
H	8.502143	3.619913	1.411988
C	9.954348	5.966397	-2.504861
H	10.086836	6.424651	-3.480935
C	3.942850	0.618473	0.539957
C	10.382689	5.960672	-0.136053
H	10.851486	6.417096	0.729853
C	2.083427	0.847953	-1.167988
H	1.580283	-0.103160	-0.957909
H	1.896875	1.092778	-2.217005
H	1.629020	1.622315	-0.544140
C	8.541651	4.198568	-3.634443
H	8.140768	3.215273	-3.373194
C	10.270753	1.894317	-1.800154
H	10.713971	0.902394	-1.716362
H	10.905038	2.620299	-1.288843
H	10.244669	2.174224	-2.857492
C	10.556406	6.535796	-1.390817
H	11.156878	7.433923	-1.496236
C	3.011729	0.151359	1.470086
H	1.995308	-0.055876	1.154728
C	7.363271	5.055121	-4.100308
H	6.629173	5.200925	-3.301793
H	6.850639	4.577052	-4.941371
H	7.719923	6.036233	-4.426459
C	4.653851	0.224547	3.229644

H	4.917842	0.070945	4.272460
C	7.010291	1.045281	2.863412
H	7.671061	1.212926	2.004783
C	3.587954	0.754982	-0.935694
H	4.026066	1.689060	-1.306480
C	3.364744	-0.055859	2.799528
H	2.626418	-0.431573	3.501970
C	9.546111	4.036298	-4.783424
H	9.847333	5.009696	-5.183861
H	9.087624	3.475504	-5.602857
H	10.456879	3.513534	-4.476347
C	4.158135	-0.386924	-1.790911
H	5.247105	-0.359232	-1.853984
H	3.774449	-0.301276	-2.811762
H	3.849187	-1.360801	-1.393522
C	6.992532	2.337313	3.691349
H	6.646032	3.186753	3.096619
H	7.998005	2.558109	4.068105
H	6.324865	2.227437	4.553722
C	9.422213	5.185478	2.536233
H	10.408321	5.629800	2.707104
H	9.119341	4.694445	3.465471
H	8.709115	5.988391	2.327740
C	10.548931	3.115780	1.647453
H	10.480407	2.284511	0.939892
H	10.451729	2.703133	2.657378
H	11.543001	3.567093	1.555898
C	7.602706	-0.093909	3.703897
H	7.078724	-0.192687	4.659785
H	8.652840	0.114618	3.928743
H	7.546015	-1.060697	3.196061

Al	3.510081	4.921963	-0.458280
S	6.357856	4.805074	0.860822
N	1.734735	5.237200	0.356986
N	3.437311	6.685243	-1.382453
C	1.029189	4.101921	0.886450
C	1.374026	3.586012	2.146371
C	-0.018933	3.547345	0.121759
C	1.154656	6.431098	0.513961
C	2.548693	7.650028	-1.153432
C	1.562421	7.581471	-0.156876
H	0.973864	8.473680	0.006630
C	2.493003	8.872422	-2.046279
H	2.064368	8.576263	-3.010550
H	1.851137	9.634245	-1.604065
H	3.474555	9.297471	-2.254676
C	4.017209	6.595640	-3.771396
C	4.357974	6.963107	-2.458550
C	-0.437457	4.170704	-1.203761
H	-0.171681	5.232588	-1.177294
C	0.720399	2.430144	2.584535
H	0.995620	1.999426	3.543840
C	5.512889	7.715342	-2.175560
C	-0.658906	2.409163	0.611456
H	-1.461960	1.956788	0.037983
C	7.442439	7.838443	-0.562740
H	8.021089	8.621446	-1.065947
H	7.693523	7.873322	0.502481
H	7.763209	6.868206	-0.950855
C	2.372182	4.289176	3.050630
H	2.675171	5.218570	2.560656
C	-0.060350	6.551855	1.402932

H	0.132726	6.096702	2.377368
H	-0.332097	7.598000	1.540031
H	-0.911622	6.019595	0.966472
C	-0.276991	1.837681	1.822434
H	-0.775685	0.941862	2.179864
C	6.254002	8.203362	-3.253864
H	7.134203	8.810064	-3.061835
C	3.632680	3.451767	3.270069
H	4.061324	3.115183	2.321204
H	4.392260	4.042682	3.792392
H	3.408982	2.564896	3.871653
C	4.801052	7.090757	-4.815777
H	4.551341	6.829675	-5.840102
C	2.853600	5.663545	-4.061624
H	2.228902	5.614262	-3.162064
C	5.935072	8.031915	-0.748494
H	5.431604	7.321174	-0.088047
C	5.884542	7.922873	-4.563906
H	6.467212	8.319769	-5.389764
C	1.740454	4.647645	4.402859
H	1.474188	3.746403	4.964493
H	2.451954	5.217044	5.008000
H	0.832512	5.247534	4.290274
C	5.517454	9.444245	-0.316355
H	4.431064	9.548134	-0.247309
H	5.933815	9.671597	0.669671
H	5.891239	10.193649	-1.023546
C	3.389515	4.253143	-4.351162
H	4.028997	3.882347	-3.542038
H	2.560701	3.551894	-4.501148
H	3.991627	4.265033	-5.267255

C	0.328449	3.546013	-2.375528
H	0.047238	2.494653	-2.495735
H	0.101624	4.072908	-3.309167
H	1.412027	3.583063	-2.212938
C	-1.946485	4.087094	-1.449949
H	-2.515656	4.471834	-0.598333
H	-2.212249	4.672990	-2.334283
H	-2.269805	3.058111	-1.634922
C	1.963522	6.152430	-5.208120
H	2.494674	6.133625	-6.164780
H	1.091917	5.498452	-5.309604
H	1.607851	7.173599	-5.040587
F	4.601781	5.410755	1.062279
F	5.801067	3.044432	-2.333527

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