Al Atom Activation of C–S Bonds: Characterization of the Aluminathietane Formed in the Reaction of Al Atoms with 1,2-Butylene Sulfide

François K. Desmarais and Helen A. Joly*

Department of Chemistry and Biochemistry, Laurentian University, 935 Ramsey Lake Road, Sudbury, ON P3E 2C6, Canada

Supporting Information

ABSTRACT: Aluminum atoms were reacted with 1,2-butylene sulfide under matrix isolation conditions in a metal atom reactor known as a "rotating cryostat". The resulting paramagnetic products were characterized using electron paramagnetic resonance (EPR) spectroscopy. The effect of isotopic substitution and temperature on the spectral lines of the paramagnetic products helped in the identification of the species formed in the reaction. The results suggest that Al atoms favor insertion into the C1–S bond, forming primarily 4-ethyl-2-aluminathietane. Support for the spectral assignments was obtained by comparing the experimental magnetic parameters with those calculated using density functional theory. As the reaction mixture was annealed in the cavity of the EPR spectrometer, the cis-methallyl radical was detected. Aluminum is thought to mediate the desulfurization of 1,2-butylene sulfide.

INTRODUCTION

There has been an increase in the number of studies involving the synthesis of non-transition-metal metallacycles because they are easily converted to carbocyclic and heterocyclic compounds. In a review article, Dzhemilev and Ibragimov1 focused on the Ti- or Zr-based metallocene-mediated preparation of alumina- and magnesacarbocycles from olefins, dienes, alkynes, and alienes. They presented many examples attesting to the fact that the highly reactive nature of the M–C bond makes the metallacycles valuable precursors for organic synthesis. In numerous studies, Rieke and co-workers showed how unligated metallacyclopentene intermediates could be used to prepare a number of different types of organic compounds. For example, γ-lactams2 were synthesized by reacting imines with substituted magnesacyclopentene intermediates in the presence of carbon dioxide, while their hydrolysis yielded secondary amines.3 The magnesacyclopentene intermediates resulting from the reaction of substituted 1,2-bis(methylene)cyclohexane with activated magnesium were found to be very versatile in that they were easily converted to substituted cyclopentanols, fused-ring cyclopentanols, β,γ-unsaturated ketones,4 and γ-lactones.4 Epoxides add to the magnesacyclopentene intermediate to give 7-methylene-2-magnesa-3-oxaspiro[5,5]undecane, which can in turn be transformed into a primary alcohol containing a quaternary center upon acid hydrolysis.5 Magnesatetrahydropyran, formed at high temperature when tetrahydropyran is treated with activated magnesium, was found to decompose to cyclobutane at 150 °C.6

A number of aluminacycles have been produced by codepositing Al atoms and organic substrates in an adamantane matrix at 77 K. Chenier et al.7 found that Al atoms produced by resistive heating of an Al wire in a tungsten basket cheletropically added to buta-1,3-diene to form aluminacyclopentene. Substituted aluminacyclopentanes8–10 result in the Al-atom-mediated cyclodimerization reaction of a number of different alkenes. Electron paramagnetic resonance (EPR) analysis of the Al hyperfine interaction (hfi) suggested that aluminacyclopentane and aluminacyclopentene have similar envelope-type structures of C2 symmetry with the Al atom assuming a position below the C4 frame. GC–MS analysis of the deuterolysis products of the intermediates formed in the Al atom + styrene and Al atom + α-methylstyrene reactions carried out at 77 K gave indirect evidence for the involvement of 3,4- and 2,4-diphenylaluminacyclopentane in the case of styrene and 3,4-dimethyl-3,4-diphenylcyclopentane in the case of α-methylstyrene.11 Insertion of Al atoms into the C1–O and C2–O bonds of 1,2-butylene oxide to form the novel aluminoxetanes CH3CH2CHCH2AlO and CH3CH2CHCH2OAl, respectively, has also been observed.12 Like the above-mentioned magnesacycles, the aluminum analogues present new potential routes for the preparation of carbocyclic and heterocyclic compounds.

In the present study, we have characterized the intermediates formed in the reaction of Al atoms with 1,2-butylene sulfide (1,2-BuS) and its deuterated analogues 1,2-butylene sulfide-1,1-d2, CH3CH2CHCD2S (1,2-BuS-1,1-d2) and 1,2-butylene sulfide-2-d1, CH3CH2CDCH2S (1,2-BuS-2-d1) at 77 K by EPR spectroscopy. We have been found that the Al atoms insert primarily into the C1–S bond, yielding 4-ethyl-2-aluminathietane. Our spectral...
assignment is supported by a comparison of the experimental nuclear hfi values to those calculated using density functional theory (DFT). This is the first report detailing the isolation of an unligated metallathietane. Finally, the detection of cis-methylallyl suggests that Al atoms mediate the desulfurization of 1,2-BS.

## RESULTS

### Reactions of Al Atoms with 1,2-BuS and its Isotopomers. Reaction of Al Atoms with 1,2-BuS in adamantane. The EPR spectrum of the reddish brown deposit collected from the reaction of Al atoms with 1,2-BuS was recorded at 77 K. It consists of five of the six transition lines belonging to a mononuclear Al (I = 5/2) species, BuS-1 (Figure 1). The magnetic parameters extracted from the axially symmetric spectrum are $a_{zz}(\text{Al}) = 822 \pm 3$ MHz, $a_{||}(\text{Al}) = 949 \pm 7$ MHz, $g_{||} = 2.0010 \pm 0.0015$, and $g_{\perp} = 2.0013 \pm 0.0033$. Annealing the Al atom + 1,2-BuS reaction mixture to higher temperatures in the cavity of the EPR spectrometer causes the spectrum of BuS-1 to become isotropic (Figure 2). The isotropic Al hfi and g values were found to be $859.8 \pm 0.5$ MHz and $2.0021 \pm 0.0002$, respectively. This Al hfi is consistent with the value of 864 MHz estimated from the values of $a_{\perp}(\text{Al})$ and $a_{||}(\text{Al})$ using eq 1:

$$a_{\text{iso}}(\text{Al}) = \left[ 2a_{\perp}(\text{Al}) + a_{||}(\text{Al}) \right] / 3$$

The superhyperfine interaction (superhfi) observed on the transition lines of BuS-1 at higher temperatures (Figure 3a) was simulated by assuming the unpaired electron on Al interacts with one hydrogen having $a_{\text{iso}} = 35.2$ MHz and two hydrogens having $a_{\text{iso}} = 10.5$ MHz (Figure 3b).

A second mononuclear Al species, BuS-2, with the magnetic parameters $a_{\text{iso}}(\text{Al}) = 904.1 \pm 0.3$ MHz and $g_{\text{iso}} = 1.9994 \pm 0.0001$, appeared at higher temperature (see Figure 2). The dominant features in the center of the EPR spectrum also changed as the sample was annealed. At low temperatures, at least 13 lines were observed, centered at $g = 1.9981$ and separated by $\sim 118$ MHz (Figure S1 in the Supporting Information.). These are in good agreement with the magnetic parameters reported for the well-known trimer Al$_3$, i.e., $g = 1.9939$ and $a_{\text{iso}}(\text{Al}) = 107$ MHz. As the temperature of the sample was increased, Al$_3$ decayed and a new spectrum assigned to the radical BuS-3 emerged (Figure 4a). The complex splitting pattern centered at $g_{\text{iso}} = 2.0020$ was simulated using the parameters of the cis and trans conformers of methallyl radical (Table 1). There is a great deal of overlap between the cis- and trans-methallyl radicals with the exception of the low- and high-field transition lines. trans-Methallyl produces a wider spectrum than the cis isomer. The absence of the low- and high-field lines predicted by the simulation program led us to conclude that the best simulation was obtained by assuming that only cis-methallyl formed (Figure 4d). The following H hfi values (in MHz) were used in the simulation: 39.3 (CH$_3$), 39.7 (H$_1$), 10.7 (H$_2$), 41.9 (H$_3$), and 37.9 (H$_4$).

### Reaction of Al Atoms with 1,2-BuS-2-d$_1$ in adamantane. Al atoms were reacted with 1,2-BuS-2-d$_1$ under conditions identical to those for the 1,2-BuS reaction. Analysis was conducted from 77−260 K at 10 K intervals. At low temperature, we observed an anisotropic EPR spectrum belonging to an Al-containing radical, BuS-2-d$_1$. The transition lines for BuS-1 resolved into doublets, and a new species BuS-2 appeared. The central feature is off-scale at the receiver gain used to record the spectrum of BuS-1 and BuS-2.
due to BuS-2-d₁-3 (Figure 4b). Simulation of this spectrum (Figure 4e) was carried out with the following magnetic parameters: 39.3 (CH₃), 39.7 (H₁), 1.7 (D₂), 41.9 (H₃), and 37.9 (H₄) MHz.

**Reaction of Al Atoms with 1,2-BuS-1,1-d₂ in Adamantane.**
The Al atom reaction was repeated with 1,2-BuS-1,1-d₂ under the conditions used for 1,2-BuS and 1,2-BuS-2-d₁. The EPR analysis of the paramagnetic products formed in the reaction rendered similar results. More specifically, the transition lines of BuS-1,1-d₁-1, which were anisotropic at 77 K, became isotropic as the sample was annealed to 190 K (Figure S3 in the Supporting Information). The axially symmetric g and A tensor components of the species BuS-1,1-d₁-1 were estimated to be aᵣ(Al) = 839 MHz, aₕ(Al) = 917 MHz, g∥ = 1.9997, and g⊥ = 1.9983, while the isotropic values were aᵣ(iso)(Al) = 860 ± 1 MHz and giso = 2.0020 ± 0.0004. These parameters are in agreement with those observed for BuS-1 and BuS-2-d₁-1. The fact that the superhfs of the transition lines for BuS-1,1-d₁-1 is different (i.e., a doubllet with a spacing of about 40 MHz; Figure 3e) indicates that BuS-1,1-d₁-1 is an isomer of BuS-1 and BuS-2-d₁-1 and that the deuterium nuclei at C₁ interact with the unppaired electron on the Al atom. We were able to simulate the transition lines for BuS-1,1-d₁-1 by considering the unpaired electron on Al to interact with one H nucleus having aᵣ(Al) = 35.2 MHz and two D nuclei with aᵣ(Al) = 1.6 MHz.

The central portion of the spectrum also underwent spectral changes during the annealing process. As the Al radical decomposed, the new radical BuS-1,1-d₁-3 emerged (Figure 4c). The spectrum of BuS-1,1-d₁-3 is described as a complex line pattern centered at g = 2.0020. A simulation was obtained by using the magnetic parameters 39.3 (CH₃), 39.7 (H₁), 10.7 (H₂), 6.3 (D₁), and 5.8 (D₂) MHz (Figure 4f).

Some noteworthy differences observed in this experiment are the following: (a) the absence of a mononuclear Al radical with magnetic parameters close to those of BuS-2 and BuS-2-d₁-2; (b) the detection of a mononuclear Al species (aᵣ(iso)(Al) = 958.0 ± 0.8 MHz, giso = 1.9994 ± 0.0003, and aᵣ = 10.8 MHz), thought to arise from the reaction of Al atoms with residual THF used in the synthesis of 1,2-butylene oxide-1,1-d₂; the magnetic parameters are close to those reported in the literature for what was thought to be an Al atom C–C insertion product of THF; and (c) the detection of HAIOH, characterized by the magnetic parameters aᵣ(iso)(Al) = 911 ± 2 MHz, giso = 2.0003 ± 0.0009, and aᵣ = 291 MHz, which are in agreement with the literature.

**Results of the Density Functional Theory Calculations.**
Al atoms were found to insert into the H–S bond of H₂S to give HAISH. The Al and H hfs values were reported as 984 and 210 MHz, respectively. We decided to use HAISH to test the ability of a number of DFT models to predict the nuclear hfs values of sulfur-containing organoaluminum radicals. The optimized geometries of the cis and trans isomers of HAISH at the B3LYP/6-31G(d,p) level of theory (Table S1 in the Supporting Information) were used to calculate H and Al hfs values with a series of different functionals (Table 2).

In general, we observed the values of aᵣ and aᵣ to be greater for the cis isomer at all levels of theory. However, the percent differences in the calculated values of the cis and trans nuclear hfs values, 100% × (aᵣ(iso)_{cis} − aᵣ(iso)_{trans})/(aᵣ(iso)_{cis}), were relatively small, i.e., 2.4% (M06)²⁸ to 4.5% (BP86)²¹,²² for aᵣ and 2.3% (BHandHLYP)²⁰,²¹,²³,²⁵ to 4.8% (M06) for aᵣ. An increase in the aᵣ values was obtained for both the cis and trans isomers as the functional was changed from BPW9¹,²² to BP86 to MPW1PW9¹,²³–²⁸ to B3LYP to BHandHLYP to M06, while

**BuS-2-d₁-1** became isotropic and the new Al-containing radical BuS-2-d₁-2 appeared (Figure S2 in the Supporting Information).

The isotropic magnetic parameters were determined to be aᵣ(iso)(Al) = 863 ± 2 MHz and giso = 2.0024 ± 0.0007 for BuS-2-d₁-1 and aᵣ(iso)(Al) = 904.2 ± 0.8 MHz and giso = 1.9991 ± 0.0003 for BuS-2-d₂-2. Two H nuclei with aᵣ(Al) = 10.5 MHz and one D nucleus with aᵣ = 5.41 MHz were responsible for the hyperfine splitting observed for the BuS-2-d₁-1 lines (Figure 3c,d). The magnetic parameters reported above are identical to those reported for BuS-1 and BuS-2 within experimental error, suggesting that the same species were formed in the different experiments. However, the transition lines for the species BuS-2-d₁-1 resolved to give a different splitting pattern than that exhibited by BuS-1 due to the interaction of the unpaired electron of Al with the deuterium nucleus bonded to C₂ of 1,2-BuS. For this reason, BuS-2-d₁-1 is believed to be an isotopomer of BuS-1.

As the reaction mixture was annealed, a change in the appearance of the central features of the spectrum was also observed, notably the decay of the transition lines due to Al₁ and the emergence of a seven-line spectrum centered at giso = 2.0020

**Figure 3.** (a) Superhyperfine structure of the M₁ = 3/2 transition line recorded at 220 K (ν = 9126 MHz, mp = 20 mW) of BuS-1. (b) Simulation of the BuS-1 M₁ = 3/2 transition line assuming that the unpaired electron on Al interacts with one hydrogen having aᵣ = 35.2 MHz and two hydrogens having aᵣ = 10.5 MHz. (c) Superhyperfine structure of the M₁ = 1/2 transition line recorded at 130 K (ν = 9125 MHz, mp = 20 mW) of species BuS-2-d₁-1. (d) Simulation of the BuS-2-d₁-1 M₁ = 1/2 transition line assuming that the unpaired electron on Al interacts with one deuterium having aᵣ = 5.41 MHz and two hydrogens having aᵣ = 10.5 MHz. (e) Superhyperfine structure of the M₁ = 1/2 transition line of BuS-1,1-d₁-1 recorded at 220 K (ν = 9130 MHz, mp = 20 mW). (f) Simulation of the M₁ = 1/2 transition line of BuS-1,1-d₁-1 assuming that the unpaired electron on Al interacts with one hydrogen having aᵣ = 35.2 MHz and two deuteriums with aᵣ = 1.6 MHz.

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1266
the H values increased as the functional was changed from BPW91 to MPW1PW91 to BP86 to M06 to B3LYP to BHandHLYP.

In comparing the experimental nuclear hf values of HAlSH to those calculated using DFT, we find that aAl is underestimated by all of the functionals with the exception of the calculations involving BHandHLYP and M06 for the cis isomer. The percent differences between the experimental and calculated aAl values, \(100\% \times \frac{a_{\text{Al,exptl}} - a_{\text{Al,calcd}}}{a_{\text{Al,exptl}}}\), range from 0.1% (BHandHLYP) to 7.3% (BPW91) in the case of the cis isomer and 0.5% (M06) to 11.4% (BPW91) for the trans isomer. The values of aH predicted for the cis isomer vary from 188 MHz (BPW91) to 222 MHz (BHandHLYP), with the closest agreement between theory and experiment (210 MHz) occurring at the M06 level (208 MHz). For the trans isomer, the predicted aH values vary from 182 MHz (BPW91) to 217 MHz (BHandHLYP), with the closest agreement between theory and experiment occurring at the B3LYP level (213 MHz).

![Figure 4](image)

Table 1. Hydrogen Hyperfine Interaction Parameters of cis- and trans-Methallyl Radical\(^a\) Used in the Spectral Simulation of the BuS-3 Radical

<table>
<thead>
<tr>
<th></th>
<th>cis (MHz)</th>
<th>trans (MHz)</th>
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<td>Me</td>
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<td>H3</td>
<td>41.9</td>
<td>41.4</td>
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<tr>
<td>H4</td>
<td>37.9</td>
<td>38.8</td>
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</tbody>
</table>

\(^a\)From ref 15.

Table 2. Al hfi values (aAl), H hfi values (aH), and Potential Energies (E) Calculated for the Cis and Trans Isomers of HAlSH Using Different DFT Models with the 6-311+G(d,p) Basis Set: The Experimental hfi Values are aAl = 984 MHz and aH = 210 MHz

<table>
<thead>
<tr>
<th>isomer</th>
<th>parameter</th>
<th>B3LYP(^a)</th>
<th>BPW91(^a)</th>
<th>MPW1PW91(^a)</th>
<th>BP86(^a)</th>
<th>BHandHLYP(^a)</th>
<th>M06(^a)</th>
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<tr>
<td>cis</td>
<td>aAl(^b)</td>
<td>962 (2.2%)</td>
<td>912 (7.3%)</td>
<td>936 (4.9%)</td>
<td>917 (6.8%)</td>
<td>985 (0.1%)</td>
<td>1003 (1.9%)</td>
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<td></td>
<td>aH(^b)</td>
<td>219 (4.3%)</td>
<td>188 (10.5%)</td>
<td>189 (10.0%)</td>
<td>193 (8.1%)</td>
<td>222 (5.7%)</td>
<td>208 (1.0%)</td>
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<td>(E)(^d)</td>
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<td>−641.8524867</td>
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<td>−641.8988232</td>
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<tr>
<td>trans</td>
<td>aAl(^b)</td>
<td>926 (5.9%)</td>
<td>872 (11.4%)</td>
<td>900 (8.5%)</td>
<td>876 (11.0%)</td>
<td>955 (2.9%)</td>
<td>979 (0.5%)</td>
</tr>
<tr>
<td></td>
<td>aH(^b)</td>
<td>213 (1.4%)</td>
<td>182 (13.3%)</td>
<td>184 (12.4%)</td>
<td>187 (11.0%)</td>
<td>217 (3.3%)</td>
<td>198 (5.7%)</td>
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<td></td>
<td>(E)(^d)</td>
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</table>

\(^a\)B3LYP, refs 18–20; BPW91, refs 21 and 22; MPW1PW91, refs 23–25; BP86, refs 21 and 26; BHandHLYP, refs 20, 21, 26, and 27; M06, ref 28.

\(^b\)hfi values in MHz. The values in parentheses are the percent differences between the calculated and experimental hfi values, 100% × \((a_{N,\text{exptl}} - a_{N,\text{calcd}})/a_{N,\text{exptl}}\) (where N = Al, H). \(^d\)Energies in hartrees.
The trans isomer is approximately 1 kcal/mol more stable than the cis isomer. On the basis of a Boltzmann population analysis at the temperatures that the HAISH was observed (77–170 K), $N_{\text{cis}}/N_{\text{trans}}$ ranges from 0.001 to 0.05. This approximation indicates that the contribution of the cis isomer to the observed hfi is negligible. If we assume that the major isomer formed is trans-HAISH, the best agreement between experiment and theory is found at the M06 level for $a_{h}$ and the B3LYP level for $a_{Al}$. It should be noted that all of the methods tested predict nuclear hfi values that are within the accepted error limits. To date no one method has been used exclusively to predict nuclear hfi values. The comparison of the nuclear hfi values obtained using several methods strengthens the use of DFT calculations in predicting the structure of organoaluminum radicals.

In a similar fashion, the H and Al hfi values were calculated for CH$_3$CH$_2$CH$_2$AlS (the C–C insertion product of 1,2-BuS), CH$_3$CH$_2$CH$_2$AlS (the C–S insertion product of 1,2-BuS), and CH$_3$CH$_2$CH$_2$SAl (the C–S insertion product of 1,2-BuS) using the functionals mentioned above. The optimized geometries of the radicals determined at the B3LYP/6-31G(d,p) level of theory can be found in Table S2 in the Supporting Information, while the calculated Al and H hfi values and potential energies are presented in Table 3.

The $a_{Al}$ values for the insertion products increase in the following order: $a_{B3LYP} \approx a_{BP86} < a_{BHandHLYP} < a_{MPW1PW91} < a_{M06}$. For all of the calculations conducted, the calculated values follow the order $a_{Al}(C_1-S) > a_{Al}(C_2-S) > a_{Al}(C_1-C_2)$. In general, the DFT calculations indicated that $a_{H} \approx a_{H} \approx a_{H}$ for the C$_1$–S insertion product, $a_{H} < a_{H} < a_{H}$ for the C$_2$–S insertion product, and $a_{H} \approx a_{H}$ for the C$_1$–C$_2$ insertion product. In terms of stability, the C$_1$–S insertion product is 2–3 kcal/mol more stable than the C$_2$–S insertion product and 24–27 kcal/mol more stable than the C–C insertion product.

### DISCUSSION

**Al Atom C–S Insertion Product.** In the reaction of Al atoms with 1,2-BuS, the species BuS-1 has a large Al hfi typical of divalent Al-containing radicals. These include Al atom insertion products, some of which are presented in Table 4 for the purpose of comparison. In addition, the superhyperfine structure of the spectrum labeled BuS-1 changed upon substitution of the hydrogens at C$_1$ and C$_2$ of the 1,2-BuS molecule with deuterium. This suggests that the unpaired electron that resides on Al is situated in such a way that it can interact with nuclei attached to both the C$_1$ and C$_2$ atoms. Insertion of the Al atom into the 1,2-BuS ring could account for the spectral changes observed.
Table 4. Comparison of the Magnetic Parameters of the Al Insertion Species Reported in the Study of 1,2-Butylene Oxide12 1,2-Butylene Oxide-2-d$_1$21 and 1,2-Butylene Oxide-1,1-d$_2$23 with those for BuS-1, BuS-2-d$_1$-1, and BuS-1,1-d$_2$-1

<table>
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<th>Species</th>
<th>$a_\text{Al}$</th>
<th>$a_\text{H(1)b}$</th>
<th>$a_\text{H(2)b}$</th>
<th>$g_{so}$</th>
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<td>37.5</td>
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<td>1.6</td>
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$^*$From ref 12. $^\dagger$The number in parentheses represents the number of hydrogen nuclei.

upon isotopic substitution. There are three different possible ring insertion products, resulting from C$_1$−S (1), C$_2$−S (2), and C$_1$−C$_2$ (3) insertion.

In a study carried out with the oxygen analogue, 1,2-butylene oxide, two cyclic Al atom insertion products were detected, i.e., the C$_1$−O and the C$_2$−O insertion products.12 A comparison of the experimental nuclear $hfi$ values for BuS-1, BuS-2-d$_1$-1, and BuS-1,1-d$_2$-1 with the Al atom C$_1$−O and C$_2$−O insertion products of 1,2-butylene oxide is shown in Table 4. In all cases, the $a_\text{Al}$ of species BuS-1 and its isotopomers is nearly identical to the reported value for the C$_1$−O insertion product of 1,2-butylene oxide. More importantly, however, the $hfi$ values observed for species BuS-1 follow the same trend as those reported for the C$_1$−O insertion product of 1,2-butylene oxide, i.e., two C$_1$ hydrogens with identical $a_\text{H}$ values of ~14 MHz and one C$_2$ hydrogen with $a_\text{H} \approx 30$ MHz, accounting for the superhyperfine pattern. In contrast, the C$_1$−O insertion product of 1,2-butylene oxide yields a superhyperfine pattern demonstrating the contribution of two C$_1$ hydrogens with $a_\text{H} = 18.5$ MHz, a C$_2$ hydrogen with $a_\text{H} = 15.5$ MHz, and a C$_3$ hydrogen with $a_\text{H} = 37.8$ MHz.12 We therefore assign BuS-1 as the Al atom C$_1$−S insertion product of 1,2-BuS (1). As well, we are able to attribute the values of the $hfi$ to the respective hydrogens by monitoring the effect of isotopic substitution. The $a_\text{H}$ of the two C$_1$−H is 10.5 MHz, while that of C$_2$−H is 35.2 MHz.

The results of the DFT calculations of the nuclear $hfi$ values of the C$_1$−S, C$_2$−S, and C$_1$−C$_2$ insertion products also support this assignment. We found that (a) the C$_1$−S insertion product is the more stable product by at least 2 kcal/mol; (b) the calculated values of $a_\text{H}$ are all smaller than the experimental value of 860 MHz; and (c) $a_\text{H}(C_1−S) > a_\text{H}(C_2−S) > a_\text{H}(C_1−C_2)$ for all of the calculations carried out. Therefore, the theoretical Al $hfi$ value for the C$_1$−S Al atom insertion product of 1,2-BuS is in closer agreement with the experimental results at all levels of theory, with the best agreement occurring at the M06 level of theory, as was observed for trans-HAISH. The percent difference of ~1% between the experimental and calculated Al $hfi$’s obtained for the C$_1$−S insertion product is small compared with that observed for the C$_2$−S (13%) and C$_1$−C$_2$ (25%) insertion products determined at the M06 level of theory. The discrepancy between the theoretical Al $hfi$ obtained for the C$_1$−S Al insertion product and the experimental value is in line with previous DFT calculations of the nuclear $hfi$ values of known Al atom insertion products.29

DFT calculations of the H $hfi$ also support the assignment of BuS-1 to the C$_1$−S insertion product. It is known from the isotopic labeling studies that only the three ring hydrogens (labeled H$_p$, H$_q$, and H$_i$; see Table 3) contribute to the superhyperfine structure of the spectrum labeled BuS-1. Although the magnitudes of the calculated H $hfi$ values differ from the experimental values, the DFT calculations at all levels of theory predict the superfi for the C$_1$−S insertion product to be dependent strictly on the ring hydrogens (the hydrogens present on C$_1$ and C$_2$), which is consistent with BuS-1. However, this was not the case for the H $hfi$ values calculated for the C$_2$−S and C$_1$−C$_2$ insertion products. In the case of the C$_2$−S insertion product, H$_p$, H$_q$, and H$_i$ (methylene hydrogen) are expected to contribute to the superhyperfine structure while H$_i$ has a relatively small contribution. The calculations on the C$_1$−C$_2$ insertion product suggest that the C$_2$ hydrogen interaction is insignificant. This is inconsistent with the results, as deuteration of the hydrogen of C$_2$ caused a collapse of the superhyperfine structure of the transition lines of BuS-1 in the Al atom + 1,2-BuS-2-d$_1$ experiment. The findings presented suggest that BuS-1 and its isotopomers are in fact the C$_1$−S Al atom insertion products.

At low temperature, BuS-1 displayed axial symmetry. The anisotropic magnetic parameters $g_{\perp} = 2.0005$, $g_{\parallel} = 2.0013$, $a_{\parallel}(Al) = 822$ MHz, and $a_{\perp}(Al) = 949$ MHz were extracted from the EPR spectrum. We can estimate the isotropic $a_{iso}(Al)$ and $g_{iso}$ values using eq 1 (see the Results) and eq 2.53

$$g_{iso} = \frac{g_{\perp} + 2g_{\parallel}}{3}$$

The calculated $g_{iso}$ is 2.0008, which can be compared to the experimental value of 2.0021 ± 0.0002. With respect to $a_{iso}(Al)$, a value of 864 MHz is obtained if we assume that $a_{\parallel}(Al)$ and $a_{\perp}(Al)$ have the same sign. This result is reasonably close to the experimental value of 859.8 ± 0.5 MHz.

Knowing that the signs of $a_{\parallel}(Al)$ and $a_{\perp}(Al)$ are the same, we can calculate the dipolar Al $hfi$ ($A_{iso}(Al)$) using eq 3:13

$$A_{iso}(Al) = \left[ a_{\parallel}(Al) - a_{\perp}(Al) \right]/3$$

Since the value of $A_{iso}(Al)$ must be positive, $a_{\parallel}(Al)$ and $a_{\perp}(Al)$ must be positive. Substitution of $a_{\parallel}(Al) = 822$ MHz and $a_{\perp}(Al) = 949$ MHz into eq 3 gives $A_{iso}(Al) = 42.3$ MHz. The $s$ and $p$ characters of the semioccupied molecular orbital (SOMO) can be estimated by dividing $a_{iso}(Al)$ and $A_{iso}(Al)$ by the one-electron atomic parameter for an Al 3s orbital ($A = 3911$ MHz)13 and 3p orbital ($P = 83.4$ MHz), respectively. Hence, $\rho_{3s}(Al) = a_{iso}(Al)/A = 0.22$ and $\rho_{3p}(Al) = A_{iso}(Al)/P = 0.51$. The total spin density on Al, $\rho_{total}(Al)$, in the C$_1$−S insertion product equals 0.73. Ideally, $\rho_{total}(Al)$ is equal to 1, and deviations from this value result from delocalization of the spin density onto the ligands. It is also important to note that $A$ and $P$ are theoretical values, which could also partially account for the deviation from unit spin density. The ratio of the $s$ and $p$ spin densities is 1.2:3.

We can compare our results to those obtained for alumina-cyclpentane,23 aluminacyclopentene,12 and aluminaoxetane12
Table 5. Al 3s and 3p Spin Populations ($\rho$) for a Number of Cyclic Organoauminum Radicals

<table>
<thead>
<tr>
<th>Radical</th>
<th>$\rho_{\text{s}}$(Al)</th>
<th>$\rho_{\text{p}}$(Al)</th>
<th>$\rho_{\text{un}}$(Al)</th>
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<tbody>
<tr>
<td>$\text{Al}^*$</td>
<td>0.18</td>
<td>0.65</td>
<td>0.83</td>
<td>1:3.6</td>
</tr>
<tr>
<td>$\text{H}_2\text{H}$</td>
<td>0.16</td>
<td>0.16</td>
<td>0.32</td>
<td>1:1</td>
</tr>
<tr>
<td>$\text{H}_2\text{H}$</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>0.19</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{H}_2\text{S}$</td>
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(Table 5). We see that the nature of the bonding in the C1-S insertion product is closer to that reported for alumina- and pentane, with the two displaying similar sp$^3$ hybridization. The alumina- and pentane both has less 3s and less 3p spin density on Al. The anisotropic parameters were not available for the alumina- and pentane. We can therefore only comment on the similarity in the $\rho_{\text{s}}$(Al) values of the C-O and C=S insertion products.

Central Radical. Two additional radicals, centered at a g value of ~2.0, were observed upon EPR analysis of the Al + 1,2-BuS reaction mixture. As mentioned previously, the features observed at 77 K are undoubtedly due to the Al radical. As the reaction mixture was annealed in the cavity of the EPR spectrometer, the signal due to the Al radical weakened and a second radical was detected.

The formation of a mixture of cis- and trans-methallyl radicals was reported in the Al atom + 1,2-butylene oxide study. The spectra that developed upon annealing of the Al atom + 1,2-BuS, 1,2-BuS-2-d1, and 1,2-BuS-1,1-d2 reaction mixtures closely resemble those in the Al atom + 1,2-butylene oxide study. However, spectral simulation suggests that mainly cis-methallyl, cis-methallyl-2-d1, and cis-methallyl-1,1-d2, respectively, form. The cis-methallyl radical arises from desulfurization of 1,2-BuS.

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**CONCLUSION**

Al atoms react with 1,2-BuS under matrix isolation conditions to produce a novel unligated alumina-thietane. We were able to extract both the anisotropic ($\alpha_{\text{a}}$(Al) = 822 ± 3 MHz, $\alpha_{\text{a}}$(Al) = 949 ± 7 MHz, $g_{\parallel}$ = 2.0005 ± 0.0015, and $g_{\perp}$ = 2.0013 ± 0.0033) and isotropic ($\alpha_{\text{iso}}$(Al) = 859.8 ± 0.5 MHz and $g_{\text{iso}}$ = 2.0021 ± 0.0002) magnetic parameters from EPR spectra recorded at low and high temperature, respectively. These values are consistent with those reported for cyclic organoauminum radicals. Good agreement was also found between the experimental isotropic hfi and those predicted using DFT calculations for the Al atom C1-S insertion product of 1,2-BuS. Finally, the presence of cis-methallyl suggests that Al atoms are capable of desulfurization of 1,2-BuS.

### EXPERIMENTAL SECTION

**Materials.** The purest commercially available adamantane (99+%) and 1,2-butylene oxide were purchased from Sigma-Aldrich. Al wire (Fisher, Certified ACS) was used to generate the Al atoms. Tungsten baskets were obtained from Ernest F. Fullam (Schenectady, NY).

**Synthesis of 1,2-BuS.** 1,2-BuS was synthesized by reacting 1,2-butylene oxide with a solution of aqueous potassium thiocyanate according to a method found in the literature. More specifically, 1 mL (11.5 mmol) of 1,2-butylene oxide was added dropwise to a stirred aqueous potassium thiocyanate solution (3 mL, 7 M). The mixture was allowed to react for a 16 h period. The organic layer was then separated from the aqueous layer and stirred for 5 h with another 2 mL portion of the potassium thiocyanate solution. This procedure was repeated, and the percent conversion of epoxide to thiirane was monitored by $^1$H NMR spectroscopy. Once the reaction was complete, the organic layer was dried using calcium chloride and transferred to a clean Pasteur pipet. The yield of 1,2-BuS was 0.78 g (77%). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ in ppm: 1.1 (t, 3H), 1.7 (m, 2H), 2.2 (dd, 1H), 2.5 (dd, 1H), 2.9 (m, 1H). The NMR parameters are in agreement with those found in the literature.

**Synthesis of Deuterated 1,2-BuS.** 1,2-BuS-1,1-d$_2$, and 1,2-BuS-2-d$_1$ were synthesized from the corresponding oxides, i.e., 1,2-butylene oxide-1,1-d$_2$, and 1,2-butylene oxide-2-d$_1$. The deuterated 1,2-butylene oxides were treated with potassium thiocyanate and the reaction progress was monitored as outlined above. Details of the synthesis of 1,2-butylene oxide-1,1-d$_2$, and 1,2-butylene oxide-2-d$_1$ are described elsewhere.

**Reactions of the 1,2-BuS Isotopomers with Al Atoms.** The 1,2-BuS isotopomers were subjected to several freeze–thaw cycles on a vacuum line prior to use in the metal atom reactions. A rotating cryostat, described elsewhere, was used to react Al atoms with the 1,2-BuS isotopomers. The reactions took place at 77 K on the surface of a liquid-nitrogen-filled stainless steel drum housed in a reaction vessel maintained at approximately 10 Torr. Al atoms produced by resistive heating of Al metal placed in a tungsten basket were co-condensed with the 1,2-BuS isotopomers and adamantane vapor onto the surface of the spinning drum (ca. 2000 rpm). The amounts of adamantane and organic substrate were controlled using a bath at the appropriate temperature. An Al/1,2-BuS/adamantane ratio of about 1:10:1000 was conserved throughout the reaction. After completion of the experiment, the reaction products were scraped off the reactor drum into a quartz glass tube, which was sealed under vacuum at 77 K.

**Identification of the Reaction Products.** EPR spectra of the paramagnetic reaction products prepared on the rotating cryostat were recorded at 77 K immediately after synthesis using a Varian E-109 spectrometer operating in the X band. Spectra were calibrated using a Varian gaussmeter and a Systron-Donner 6016 frequency counter. At a later date, the samples were annealed from 100 to 260 K in the cavity of the spectrometer, with spectra being collected at 10 K intervals. The EPR magnetic parameters of the paramagnetic species were determined with the aid of computer programs that solve the spin Hamiltonian for the isotropic and anisotropic magnetic parameters. The isotropic magnetic parameters of the radical species ($\alpha_{\text{iso}}$ and $g_{\text{iso}}$) were obtained from the EPR spectral data and the FORTRAN computer program ESRLSQ, while ANISO was used to determine the anisotropic magnetic parameters ($\alpha_{\text{a}}$, $\alpha_{\text{g}}$, and $g_{\text{g}}$). The spectral simulations that appear in the paper were carried out using ISOPLOT.

**Computational Methods.** DFT calculations of the nuclear hfi values were carried out for a test system, namely HAISH, using the suite of programs included in Gaussian 09. The molecular geometries of the...
cis and trans isomers were optimized with the B3LYP functional18–20 and the split-valence basis set 6-31G(d,p). The species were characterized by frequency analysis. Theoretical values for the Al and H hfi were obtained from single-point calculations using the B3LYP, BPW91,1,21,22 MPW1PW91,23 BHandHLYP,24 and M0628 functionals with the 6-311+G(2df,p) basis set. Subsequently, the geometries and the nuclear hfi values of the C1−S, C2−S, and C1−C2 Al atom insertion products (1−3, respectively) were determined as outlined above for HAISH.

ASSOCIATED CONTENT

# Supporting Information
EPR spectra of Al3, BuS-2-d1-1, BuS-2-d1-2, BuS-1,1-d1-1, and BuS-1,1-d1-2 (Figures S1−S3) and the DFT geometries of HaI5SH and the C1−S, C2−S, and C1−C2 Al atom insertion products of 1,2-BuS (Tables S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Tel.: 705-675-1151 ext. 2333. E-mail: hjoly@laurentian.ca.

Notes
The authors declare no competing financial interest.

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REFERENCES