Aluminum Complexes

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Oxidative Cleavage of C=S and P=S Bonds at an $\mathrm{Al^I}$ Center: Preparation of Terminally Bound Aluminum Sulfides

*Terry Chu, Sergei F. Vyboishchikov, Bulat Gabidullin, and Georgii I. Nikonov**

Dedicated to Professor Herbert W. Roesky

Abstract: *The treatment of cyclic thioureas with the aluminum(I) compound NacNacAl (**1**; NacNac = [ArNC(Me)CHC(Me)NAr]$^-$, Ar = 2,6-$\mathrm{Pr^i_2C_6H_3}$) resulted in oxidative cleavage of the C=S bond and the formation of **3** and **5**, the first monomeric aluminum complexes with an Al=S double bond stabilized by N-heterocyclic carbenes. Compound **1** also reacted with triphenylphosphine sulfide in a similar manner, which resulted in cleavage of the P=S bond and production of the adduct [NacNacAl=S(S=$\mathrm{PPh_3}$)] (**8**). The Al=S double bond in **3** can react with phenyl isothiocyanate to furnish the cycloaddition product **9** and zwitterion **10** as a result of coupling between the liberated carbene and PhN=C=S. All novel complexes were characterized by multinuclear NMR spectroscopy, and the structures of **5**, **9**, and **10** were confirmed by X-ray diffraction analysis. The nature of the Al=S bond in **5** was also probed by DFT calculations.*

The activation of robust bonds on metal centers is at the heart of many catalytic processes.[1] Although there are different methods of bond activation, oxidative addition is one of the most important and challenging.[2] Earlier studies were concerned with the activation of stable, but relatively reactive, bonds, such as H−H,[3] H−$\mathrm{SiR_3}$,[4] and C−X (X = Cl–I).[5] Later, focus was shifted towards the oxidative addition of C−H,[6] C−C,[7] and even more robust C−O[8] and C−F bonds.[9] More recently, oxidative addition to main-group elements has received increased attention[10] in the context of developing cheaper and more benign main-group surrogates for the traditional transition-metal catalysts,[11] and examples of H−H,[12] Si−H,[13] and C−X[14] (X = Cl–I) addition reactions have been reported. This research has culminated in observations of the oxidative addition of C−O and C−F bonds to low-valent main-group compounds.[15] Given this success, a logical question arises: What about the activation of multiple bonds? Transformations of unsaturated bonds by metathetical reactions with transition-metal complexes are well-known,[16] but formal oxidative addition reactions are limited. Examples include activation of the weak N=N bond in diazenes, RN=NR, by low-valent metals, such as aluminum,[17] chromium,[18] and vanadium,[19] the cleavage of destabilized C=C bonds in electron-rich tetraamino-substituted olefins, $\mathrm{(R_2N)_2C{=}C(NR_2)_2}$,[20] and activation of the C=S bond in carbon disulfide.[21,22] Rare examples of the oxidative addition of a robust multiple bond include the activation of the C=C bond of quinoxaline by a tungsten complex, as reported by Sattler and Parkin,[23] carbon–carbon bond cleavage of benzene by a trinuclear titanium hydride, as demonstrated by Hou and co-workers,[24] and silylene insertion into the aromatic carbon-carbon bond of benzene upon photoirradiation, as documented by Kira et al.[25] Closely related to the current study is the report by Okazaki and co-workers on the cleavage of the C=S bond of $\mathrm{CS_2}$ at a silylene center to give a sulfide-bridged $\mathrm{Si^{IV}}$ derivative[26,27] as well as the reaction of a diarylborinium cation with carbon disulfide, which was shown by Shoji et al. to yield a thioaroyl cation as a result of C=S bond cleavage.[28] Herein we report the oxidative addition of stable C=S and P=S bonds to an $\mathrm{Al^I}$ compound, which led to the first aluminum sulfide with a terminal Al=S bond.

Following the recent finding that compound **1** can oxidatively add very strong σ C−O (86 kcal mol^{-1}) and C−F bonds (116 kcal mol^{-1}),[15d–f] we became curious as to whether the oxidative cleavage of multiple bonds at the same metal atom was possible. Complete oxidative addition of $\mathrm{R}_n\mathrm{X{=}YR}_m$ to $\mathrm{Al^I}$ is not possible because the reaction would be a four-electron process and $\mathrm{Al^I}$ can only be oxidized to $\mathrm{Al^{III}}$. However, we supposed that if either the $\mathrm{R}_n\mathrm{X}$ or $\mathrm{R}_m\mathrm{Y}$ fragment could act as a two-electron donor to the resulting metal center, the oxidative cleavage of this multiple bond would be an allowed, two-electron process. Our attention was drawn to thioureas, $\mathrm{(R_2N)_2C{=}S}$, owing to the well-established ability of amino groups to stabilize diaminocarbenes[29] and because the C=S bond (137 kcal mol^{-1}) is the weakest type of C=X bond (X = C, N, O, S). We were further motivated by the fact that no terminal aluminum sulfide compound has been reported previously;[30] however, the first terminal aluminum telluride was reported recently by Inoue et al.[31]

To our delight, addition of the cyclic thiourea **2** at −30 °C to a solution of **1** in [$\mathrm{D_8}$]toluene resulted in clean formation of the carbene-stabilized sulfide **3** (Scheme 1), which was subsequently characterized by multinuclear NMR spectroscopy at low temperature. In particular, the ^{1}H NMR spectrum of **3**

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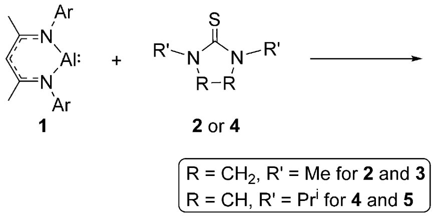
[*] T. Chu, Dr. G. I. Nikonov
Department of Chemistry, Brock University
1812 Sir Isaac Brock Way, St. Catharines, Ontario, L2S 3A1 (Canada)
E-mail: gnikonov@brocku.ca

Dr. S. F. Vyboishchikov
Institut de Química Computacional i Catàlisi and
Departament de Química
Carrer Maria Aurèlia Capmany 69, 17003 Girona (Spain)

Dr. B. Gabidullin
X-Ray Core Facility, Faculty of Science, University of Ottawa
150 Louis Pasteur, Ottawa, Ontario, K1N 6N5 (Canada)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201607735.



Scheme 1. Reaction of thioureas **2** and **4** with **1** to give aluminum sulfides **3** and **5**.

is consistent with the expected C_s symmetry in solution: Two septets at 3.87 and 2.80 ppm for the isopropyl methine protons are coupled to four doublets at 1.85, 1.29, 1.22, and 1.07 ppm for the isopropyl methyl protons. The resulting carbene ligand has restricted rotation about the Al–C bond because of the *N*-aromatic groups on the NacNac ligand. Two singlets are therefore observed at 4.11 and 3.08 ppm for the *N*-methyl protons, whereas the methylene units in the backbone appear as broad multiplets at 3.52 and 3.08 ppm (overlapped with the *N*-methyl singlet). In the ^{13}C NMR spectrum, the central carbon atom of the NHC is found at 186.1 ppm. While complex **3** remains soluble in toluene at low temperatures, warming of the solution above 0 °C results in the precipitation of **3** as a bright-yellow solid. Upon precipitation, **3** became insoluble in common organic solvents; however, its constitution was unchanged, as confirmed by elemental analysis of the isolated solid and subsequent reactivity studies (see below). Despite numerous attempts, we were unable to obtain crystals of **3** suitable for X-ray crystallographic analysis.

Changing the reagent to the unsaturated cyclic thiourea **4** resulted in a related, but more crystalline complex **5** (Scheme 1), which was cleanly generated in solution at 0 °C and isolated by crystallization from toluene at −30 °C. Akin to complex **3**, crystals of **5** are insoluble in most common organic solvents. However, complex **5** is sparingly soluble in bromobenzene, and NMR spectra were recorded in [D$_5$]bromobenzene. The ^{1}H NMR spectrum of **5** shows two septets at 3.76 and 2.38 ppm coupled to four doublets at 1.54, 1.00, 0.86, and 0.44 ppm arising from the isopropyl groups on the aromatic rings, a pattern consistent with C_s symmetry in solution. Analogous to the carbene ligand in **3**, the unsaturated NHC in **5** also has restricted rotation about the Al–C bond, thus giving rise to two septets at 8.39 and 4.81 ppm coupled to two doublets at 1.09 and 0.75 ppm. Interestingly, the two methine proton signals appear at significantly different chemical shifts, the disparity probably due to the difference in proximity between the two hydrogen atoms relative to the terminal sulfide ligand. The C–H hydrogen atoms in the backbone of the imidazole framework give rise to two singlets at 6.57 and 6.42 ppm. Owing to the poor solubility of **5** in bromobenzene, the expected signal for the central carbon atom in the NHC ligand was not observed.

The molecular structure of **5** was determined by X-ray diffraction analysis (Figure 1, top). The aluminum atom lies in a four-coordinate environment formed by the bidentate NacNac ligand, NHC, and a terminal sulfido ligand. The Al=S bond length of 2.104(1) Å is significantly shorter than the lowest value for a Al–S single bond (ranging from 2.150–2.739 Å, with the average being 2.289 Å for 118 structures from the CCDC), consistent with the multiple-bond character. The closest relative of compound **5** is the deprotonated alumothiol [NacNacAl(S)X]$^-$ reported by Roesky et al.[32] Four derivatives of this anion differing in the identity of the countercation and the nature of the X group (X = SH or OP(OEt)$_2$) have been structurally characterized, with the Al–S distances falling in the range of 2.115–2.124 Å. Another closely related compound, also reported by the Roesky group, is the NHC-stabilized aluminum hydride complex **6** with a deprotonated NacNac ligand.[33] Analogous to other complexes of the type [NacNacAlX(Y)], the aluminum atom in **5** deviates from the plane defined by the NacNac ligand by 0.458 Å and from the N$_2$S plane by 0.663 Å, such that the geometry around the aluminum atom can be described as a distorted tetrahedron. A similar coordination mode was observed by Driess and co-workers for the NHC-stabilized silanone compound **7** featuring a Si=O double bond.[34] The Al–C bond length of 2.107(2) Å in **5** is longer than the average Al–C distance in four-coordinate NHC complexes of aluminum (2.065 Å, average for 25 structures from the CCDC). However, this parameter falls within a wide range of lengths (2.008–2.162 Å) with only four structures containing longer Al–C distances (ranging from 2.118(2)[35] to 2.162(2) Å[36]). The Al–N distances of 1.927(1) and 1.952(2) Å are slightly elongated as compared to the average Al–N

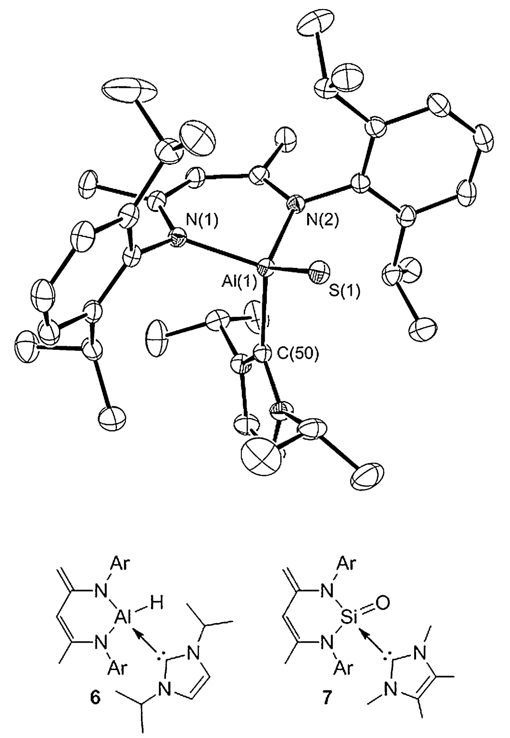


Figure 1. Top: Molecular structure of **5** (thermal ellipsoids are shown at 30%; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Al(1)–S(1) 2.104(1), Al(1)–C(50) 2.109(2), Al(1)–N(1) 1.952(2), Al(1)–N(2) 1.927(1); S(1)-Al(1)-C(50) 114.0(5), N(1)-Al(1)-N(2) 94.9(6). Bottom: Related, structurally characterized aluminum and silicon complexes **6** and **7**.

distance (1.912 Å) in other four-coordinate NacNac-ligated aluminum complexes reported by us previously.[15e,37]

To elucidate the bonding situation in compound **5**, we performed density-functional calculations. According to the calculations, the reaction $[L_2Al] + NHC{=}S \rightarrow [L_2Al{=}S(NHC)]$ is exothermic, with a calculated ΔE_e value of $-61.4\ \text{kcal mol}^{-1}$ and ΔG°_{298} value of $-41.1\ \text{kcal mol}^{-1}$. The carbene dissociation energy corresponding to the process $[L_2Al{=}S(NHC)] \rightarrow [L_2Al{=}S] + NHC$ is relatively low ($\Delta E_e = 47.7\ \text{kcal mol}^{-1}$ and $\Delta G^{\circ}_{298} = 28.1\ \text{kcal mol}^{-1}$). The optimized metal–ligand bond lengths are given in Table 1. Very good agreement between the calculated and experimental distances for **5** was observed, with a maximum deviation of 0.014 Å for one of the Al–N bonds. The optimized structure of the monomeric sulfide $[L_2Al{=}S]$ exhibits a typical trigonal-planar geometry around the aluminum center. Coordination of the NHC to this species to give **5** results in elongation of all metal–ligand bonds, probably owing to increased steric congestion. Interestingly, the parent Al^I complex **1** also exhibits substantially longer Al–N bonds than $[L_2Al{=}S]$, presumably a reflection of the larger size of the Al^I ion.

Table 1: Experimental and calculated aluminum–ligand distances [Å].

	5	$[L_2Al(S)]$	**1**[38]
$Al–C^{NHC}$ (exptl)	2.107(2)	–	–
$Al–C^{NHC}$ (calcd)	2.094	–	–
$Al–N^1$ (exptl)	1.953(1)	–	1.957(2)
$Al–N^1$ (calcd)	1.962	1.879	2.004
$Al–N^2$ (exptl)	1.927(1)	–	1.957(2)
$Al–N^2$ (calcd)	1.941	1.879	2.004
Al–S (exptl)	2.104(6)	–	–
Al–S (calcd)	2.111	2.034	–

The bonding situation in complex **5** was examined by means of Mayer bond orders[39] and Wiberg bond indices[40] (in the natural atomic basis;[41] Table 2). The Mayer bond orders are clearly indicative of multiple-bond character in the Al–S bond in compounds **5** and $[L_2Al{=}S]$. In the trigonal-planar complex $[L_2Al{=}S]$, the Al–S bond order is the largest, which correlates well with the shortest calculated Al–S bond length. Only a minor decrease in the Mayer bond order was observed on going from $[L_2Al{=}S]$ to **5**, which suggests that the transfer of electron density from the carbene to aluminum is rather minor. Further corroborating this hypothesis is the observation that the corresponding molecular orbital in **5** has primarily carbon lone-pair character, with only a minor contribution of aluminum, thus leading to the conclusion that the Al–C interaction is mainly electrostatic in nature. The two highest occupied molecular orbitals of **5** are nearly degenerate at an orbital energy of approximately −4.5 eV (Figure 2). These orbitals mostly correspond to the sulfur lone pairs, but the HOMO also has a significant contribution from an aluminum p_π orbital, thus providing further evidence of the multiple-bond character in the Al–S bond. The lower-lying HOMO-2 with an orbital energy of about −5.9 eV is the Al–S σ-bonding orbital. The Wiberg bond indices follow the same trend as the Mayer bond orders, but have lower absolute values.

Table 2: Mayer bond orders and Wiberg bond indices for complexes **5**, $[L_2Al{=}S]$, and **1**.

	5	$[L_2Al(S)]$	**1**
Mayer bond orders			
$Al–C^{NHC}$	0.48	–	–
$Al–N^{L1}$	0.45	0.64	0.51
$Al–N^{L2}$	0.46	0.64	0.51
Al–S	1.49	1.75	–
Wiberg bond indices			
$Al–N^{L1}$	0.24	0.30	0.15
$Al–N^{L2}$	0.25	0.30	0.15
Al–S	1.20	1.50	–

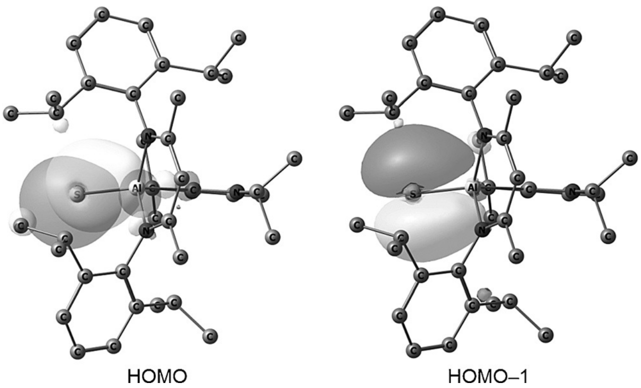
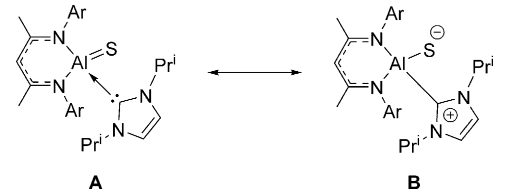

HOMO HOMO–1

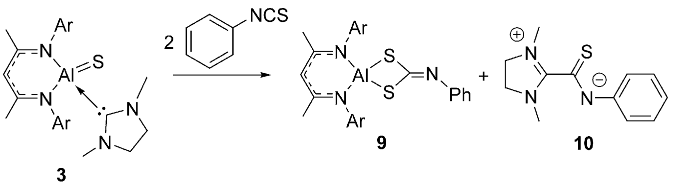
Figure 2. Two highest occupied molecular orbitals of $[L_2Al{=}S(NHC)]$. Hydrogen atoms are omitted for clarity.

The multiple-bond character in sulfides $[L_2Al{=}S]$ and **5** was further elaborated by splitting the Mayer bond orders into the σ and π components by using the method outlined by Bridgeman et al.[42] The calculated σ and π components of the Mayer bond order in both compounds are quite comparable, for example, 0.89 and 0.86 for $[L_2Al{=}S]$, respectively. Coordination of the carbene to give **5** does not strongly alter the σ-bond order (0.81) and results in a moderate decrease in the π-bond-order component to 0.68. Therefore, on the basis of the combination of X-ray crystallographic and DFT data, we believe that the canonical form **A** is a better representation of the bonding situation in compound **5** than the zwitterionic form **B** (Scheme 2).

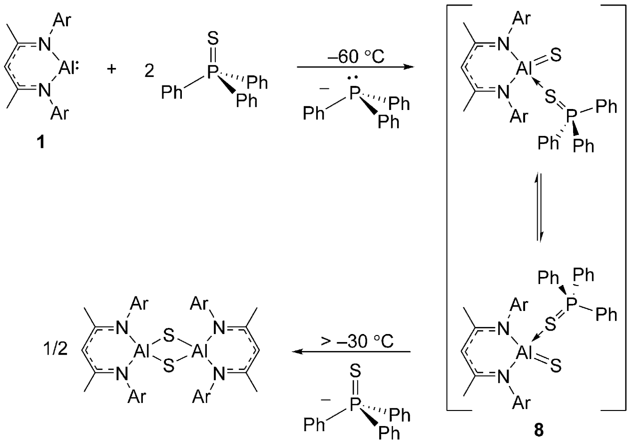
Wishing to extend this oxidative-cleavage reactivity to other multiple bonds, we treated compound **1** with triphenylphosphine sulfide (P=S bond energy: 80 kcal mol^{-1}). Mixing of reagents in a 1:1 ratio did not afford the expected product, $[NacNacAl{=}S(PPh_3)]$, but resulted in a mixture of the terminal sulfide $NacNacAl{=}S(S{=}PPh_3)$ (**8**), unreacted **1**, and free triphenylphosphine. The difference in the outcome of the reaction is probably due to the large steric profile of triphenylphosphine, making it incompatible with the bulky 2,6-diisopropylphenyl substituents of the NacNac ligand. Complex **8** could be cleanly generated in solution by treating **1** with two equivalents of $Ph_3P{=}S$ (Scheme 3). The ^1H NMR spectrum acquired at −60 °C is in accord with the expected C_s



Scheme 2. Valence-bond representation of bonding in compound **5**.



Scheme 4. Cycloaddition of phenyl isothiocyanate with **3** to give **9** and **10**.



Scheme 3. Generation of **8** at low temperature from the reaction between **1** and triphenylphosphine sulfide, followed by decomposition at higher temperatures.

symmetry in solution. Two broad singlets were observed at 3.51 and 3.14 ppm, assigned to the isopropyl methine protons, which are coupled to three broad singlets (two signals overlap) at 1.67, 1.11, and 0.70 ppm from the isopropyl methyl protons. Interestingly, upon warming to −30 °C, the signals in the ^{1}H NMR spectrum merged to a more symmetric C_{2v} averaged pattern for the NacNac ligand, thus suggesting a fast exchange process. Variable-temperature NMR studies in the temperature range of −80 to −30 °C revealed a $\Delta^{\ddagger}G^{\circ}$ value of 10.2 kcal mol^{-1} as the barrier for this exchange process, probably due to the phosphine sulfide coordinating from either the top or bottom face of [NacNacAl=S], at a coalescence temperature of −50 °C. Even at −80 °C, no signal in the ^{31}P NMR spectrum was observed for the coordinated phosphine sulfide. In contrast to compounds **3** and **5**, warming of solutions of **8** above −30 °C resulted in the precipitation of a white crystalline material, the identity of which was determined, by X-ray diffraction analysis to be the known sulfide-bridged dimer [{NacNacAl(μ-S)}$_2$] reported previously by Roesky and co-workers.[43]

To underpin the multiple-bond character in **3**, we tested its activity towards cycloaddition with phenyl isothiocyanate. Thus, the reaction of **3** with two equivalents of PhN=C=S yielded the cycloaddition product [NacNacAl(S$_2$CNPh)] (**9**), with the concomitant production of zwitterion **10** resulting from the reaction of the liberated carbene with phenyl isothiocyanate (Scheme 4). Similar coupling between carbenes and phenyl isothiocyanate has been reported previously by Cheng and co-workers.[44]

Compounds **9** and **10** were fully characterized by multinuclear NMR spectroscopy and X-ray diffraction analysis. The ^{1}H NMR spectrum of **9** is consistent with C_s symmetry in solution, as evidenced by the pattern of signals observed for the isopropyl moieties, with two multiplets at 2.94 and 2.87 ppm coupled to four doublets at 1.19, 1.02, 0.92, and 0.75 ppm. For **10**, the ^{1}H NMR spectrum revealed a simple pattern of signals with two singlets at 3.85 and 3.20 ppm correlated to the methylene protons in the imidazolidine ring and *N*-methyl protons, respectively, whereas signals for the hydrogen atoms on the phenyl ring are found between 7.40 and 7.00 ppm. In the ^{13}C NMR spectrum, signals for the thioamide and central imidazolidine carbon atom are found downfield at 167.6 and 164.4 ppm.

The structure of **9** revealed a four-coordinate aluminum center in a distorted tetrahedral geometry (Figure 3). The Al−S bond lengths are essentially equidistant at 2.226(1) and 2.227(1) Å and fall within the wide range of Al−S single-bond lengths discussed above. The aluminum atom sits much closer to the N$_2$C$_3$ plane, deviating by only 0.228 Å as a result of the reduced steric bulk around the aluminum center in **9**. The AlS$_2$C fragment adopts a planar, kite-shaped configuration with the sum of the angles equal to 359.9°. The plane defined by the AlS$_2$C fragment was found to be nearly perpendicular

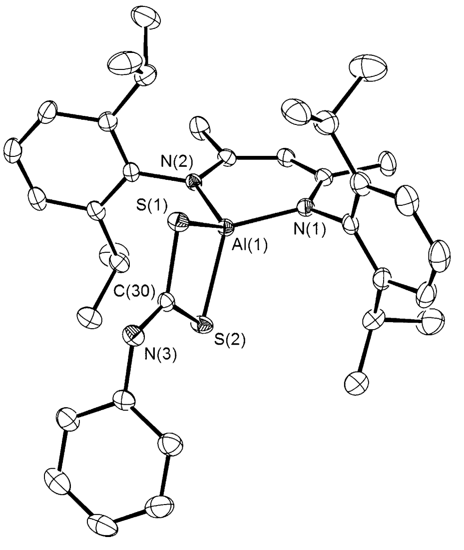


Figure 3. Molecular structure of **9** (thermal ellipsoids are shown at 30%; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Al(1)–S(1) 2.226(7), Al(1)–S(2) 2.227(1), Al(1)–N(1) 1.859(3), Al(1)–N(2) 1.859(3); N(1)-Al(1)-N(2) 99.5(1), S(1)-Al(1)-S(2) 82.9(4), S(1)-C(30)-S(2) 112.2(2), Al(1)-S(1)-C(30) 82.6(1), Al(1)-S(2)-C(30) 82.1(1).

to the plane defined by the NacNac ligand, with an angle of 87.4° between them. In accord with the zwitterionic nature of the compound, the structure of **10** (see Figure SI7) revealed a C–S distance of 1.693(2) Å, which is intermediary between the average length for a carbon–sulfur single bond, 1.76 Å, and the average length for a C=S bond of 1.62 Å. Similarly, the C–N distances of 1.313(2) and 1.313(3) in the imidazolidine ring are essentially identical and intermediate between the average lengths for a single and double carbon–nitrogen bond, whereas the C–N$^{\text{phenyl}}$ bond length of 1.282(2) Å is closer to a double bond. The same cycloaddition product was also observed upon the reaction of aluminum sulfides **5** and **8** with phenyl isothiocyanate.

In conclusion, facile C=S and P=S bond cleavage was observed upon the reaction of cyclic thioureas or triphenylphosphine sulfide with **1** to give the first examples of neutral aluminum sulfides with terminal Al=S bond. The new products were characterized by multinuclear NMR spectroscopy and an X-ray crystal structure in the case of **5**. DFT calculations were performed, and the results support the existence of multiple-bond character in **5**. The reactivity of the Al=S bond was demonstrated by the facile cycloaddition of phenyl isothiocyanate to give a novel aluminum heterocycle. Future studies will focus on expanding the oxidative chemistry to ureas and guanidines to access novel aluminum oxo and imido species.

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[1] J. F. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books, Sausalito, California, **2010**.

[2] J. A. Labinger, *Organometallics* **2015**, *34*, 4784–4795.

[3] R. Mas-Ballesté, A. Lledós in *Comprehensive Inorganic Chemistry II*, *Vol. 9*, 2nd ed. (Ed.: K. Poeppelmeier), Elsevier, Amsterdam, **2013**, pp. 727–766.

[4] J. Y. Corey, *Chem. Rev.* **2011**, *111*, 863–1071.

[5] S. Komiya, M. Hirano in *Current Methods in Inorganic Chemistry*, *Vol. 3* (Eds.: K. Hideo, Y. Akio), Elsevier, Amsterdam, **2003**, pp. 115–186.

[6] a) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507–514; b) K. I. Goldberg, A. S. Goldman, *Activation and Functionalization of C−H Bonds*, *Vol. 885*, American Chemical Society, Washington, **2004**.

[7] a) C.-H. Jun, *Chem. Soc. Rev.* **2004**, *33*, 610–618; b) K. Ruhland, *Eur. J. Org. Chem.* **2012**, 2683–2706.

[8] a) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* **2010**, *110*, 3552–3599; b) D.-G. Yu, S. Luo, F. Zhao, Z.-J. Shi in *Homogeneous Catalysis for Unreactive Bond Activation* (Ed.: Z.-J. Shi), Wiley, Hoboken, **2014**, pp. 347–439.

[9] a) L. Keyes, J. A. Love in *C−H and C−X Bond Functionalization: Transition Metal Mediation* (Ed.: X. Ribas), The Royal Society of Chemistry, Cambridge, **2013**, pp. 159–192; b) M. F. Kuehnel, D. Lentz, T. Braun, *Angew. Chem. Int. Ed.* **2013**, *52*, 3328–3348; *Angew. Chem.* **2013**, *125*, 3412–3433; c) M. K. Whittlesey, E. Peris, *ACS Catal.* **2014**, *4*, 3152–3159.

[10] S. Yadav, S. Saha, S. S. Sen, *ChemCatChem* **2016**, *8*, 486–501.

[11] P. P. Power, *Nature* **2010**, *463*, 171–177.

[12] a) G. H. Spikes, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233; b) G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439–441; c) Z. Zhu, X. Wang, Y. Peng, H. Lei, J. C. Fettinger, E. Rivard, P. P. Power, *Angew. Chem. Int. Ed.* **2009**, *48*, 2031–2034; *Angew. Chem.* **2009**, *121*, 2065–2068; d) C. Fan, L. G. Mercier, W. E. Piers, H. M. Tuononen, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 9604–9606; e) J. Li, C. Schenk, C. Goedecke, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 18622–18625.

[13] G. D. Frey, J. D. Masuda, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 9444–9447; *Angew. Chem.* **2010**, *122*, 9634–9637.

[14] a) M. S. Hill, P. B. Hitchcock, R. Pongtavornpinyo, *Inorg. Chem.* **2007**, *46*, 3783–3788; b) A. Kempter, C. Gemel, R. A. Fischer, *Inorg. Chem.* **2008**, *47*, 7279–7285; c) Y. Xiong, S. Yao, M. Driess, *Organometallics* **2009**, *28*, 1927–1933.

[15] a) A. Jana, P. P. Samuel, G. Tavčar, H. W. Roesky, C. Schulzke, *J. Am. Chem. Soc.* **2010**, *132*, 10164–10170; b) R. Azhakar, H. W. Roesky, H. Wolf, D. Stalke, *Chem. Commun.* **2013**, *49*, 1841–1843; c) G. Tan, T. Szilvási, S. Inoue, B. Blom, M. Driess, *J. Am. Chem. Soc.* **2014**, *136*, 9732–9742; d) M. R. Crimmin, M. J. Butler, A. J. P. White, *Chem. Commun.* **2015**, *51*, 15994–15996; e) T. Chu, Y. Boyko, I. Korobkov, G. I. Nikonov, *Organometallics* **2015**, *34*, 5363–5365; f) L. Kong, R. Ganguly, Y. Li, R. Kinjo, *Chem. Eur. J.* **2016**, *22*, 1922–1925.

[16] a) A. P. Duncan, R. G. Bergman, *Chem. Rec.* **2002**, *2*, 431–445; b) N. Hazari, P. Mountford, *Acc. Chem. Res.* **2005**, *38*, 839–849; c) Y. Chauvin, *Angew. Chem. Int. Ed.* **2006**, *45*, 3740–3747; *Angew. Chem.* **2006**, *118*, 3824–3831; d) R. H. Grubbs, *Angew. Chem. Int. Ed.* **2006**, *45*, 3760–3765; *Angew. Chem.* **2006**, *118*, 3845–3850; e) R. R. Schrock, *Angew. Chem. Int. Ed.* **2006**, *45*, 3748–3759; *Angew. Chem.* **2006**, *118*, 3832–3844.

[17] a) H. Zhu, J. Chai, H. Fan, H. W. Roesky, U. N. Nehete, H.-G. Schmidt, M. Noltemeyer, *Eur. J. Inorg. Chem.* **2005**, 2147–2150; b) Y. Zhao, Y. Liu, L. Yang, J.-G. Yu, S. Li, B. Wu, X.-J. Yang, *Chem. Eur. J.* **2012**, *18*, 6022–6030.

[18] W. H. Monillas, G. P. A. Yap, L. A. MacAdams, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 8090–8091.

[19] Y.-C. Tsai, P.-Y. Wang, K.-M. Lin, S.-A. Chen, J.-M. Chen, *Chem. Commun.* **2008**, 205–207.

[20] M. F. Lappert, *J. Organomet. Chem.* **1988**, *358*, 185–213.

[21] a) I. S. Butler, A. E. Fenster, *J. Organomet. Chem.* **1974**, *66*, 161–194; for more recent examples, see: b) A. M. Bradford, M. C. Jennings, R. J. Puddephatt, *Organometallics* **1989**, *8*, 2367–2371; c) J. S. Qi, P. W. Schrier, P. E. Fanwick, R. A. Walton, *Inorg. Chem.* **1992**, *31*, 258–262; d) A. Martín, M. J. Mays, P. R. Raithby, G. A. Solan, *J. Chem. Soc. Dalton Trans.* **1993**, 1789–1796; e) A. R. Johnson, W. M. Davis, C. C. Cummins, S. Serron, S. P. Nolan, D. G. Musaev, K. Morokuma, *J. Am. Chem. Soc.* **1998**, *120*, 2071–2085; f) L. J. J. Wang, S.-J. You, S.-L. Huang, Y.-L. Yang, Y.-C. Lin, G.-H. Lee, S.-M. Peng, *J. Chem. Soc. Dalton Trans.* **1999**, 2243–2248; g) D. S. A. George, R. W. Hilts, R. McDonald, M. Cowie, *Inorg. Chim. Acta* **2000**, *300–302*, 353–368; h) G. Hogarth, M. H. Lavender, K. Shukri, *J. Organomet. Chem.* **2000**, *595*, 134–139; i) S.-H. Hsu, J.-C. Chang, C.-L. Lai,

C.-H. Hu, H. M. Lee, G.-H. Lee, S.-M. Peng, J.-H. Huang, *Inorg. Chem.* **2004**, *43*, 6786 – 6792; j) J. Ballmann, A. Yeo, B. A. MacKay, S. V. Rijt, B. O. Patrick, M. D. Fryzuk, *Chem. Commun.* **2010**, *46*, 8794 – 8796; k) S. I. Kalläne, T. Braun, M. Teltewskoi, B. Braun, R. Herrmann, R. Laubenstein, *Chem. Commun.* **2015**, *51*, 14613 – 14616.

[22] For examples of related reactions with CO_2, see: a) C. C. Lu, C. T. Saouma, M. W. Day, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 4 – 5; b) C. T. Saouma, C. C. Lu, M. W. Day, J. C. Peters, *Chem. Sci.* **2013**, *4*, 4042 – 4051; c) C. H. Lee, D. S. Laitar, P. Mueller, J. P. Sadighi, *J. Am. Chem. Soc.* **2007**, *129*, 13802 – 13803; d) B. Horn, C. Limberg, C. Herwig, B. Braun, *Chem. Commun.* **2013**, *49*, 10923 – 10925; e) A.-C. Schmidt, A. V. Nizovtsev, A. Scheurer, F. W. Heinemann, K. Meyer, *Chem. Commun.* **2012**, *48*, 8634 – 8636; f) N. Tsoureas, L. Castro, A. F. R. Kilpatrick, F. G. N. Cloke, L. Maron, *Chem. Sci.* **2014**, *5*, 3777 – 3788.

[23] A. Sattler, G. Parkin, *Nature* **2010**, *463*, 523 – 526.

[24] S. Hu, T. Shima, Z. Hou, *Nature* **2014**, *512*, 413 – 415.

[25] M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **2002**, *124*, 3830 – 3831.

[26] N. Tokitoh, H. Suzuki, R. Okazaki, *Chem. Commun.* **1996**, 125 – 126.

[27] For related stannylenes, oxidative coupling of CS_2 takes place: a) M. Saito, N. Tokitoh, R. Okazaki, *Organometallics* **1995**, *14*, 3620 – 3622; b) C. Yan, Z. Xu, X.-Q. Xiao, Z. Li, Q. Lu, G. Lai, M. Kira, *Organometallics* **2016**, *35*, 1323 – 1328.

[28] Y. Shoji, N. Tanaka, D. Hashizume, T. Fukushima, *Chem. Commun.* **2015**, *51*, 13342 – 13345.

[29] W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162 – 2187; *Angew. Chem.* **1997**, *109*, 2256 – 2282.

[30] D. Franz, S. Inoue, *Dalton Trans.* **2016**, *45*, 9385 – 9397.

[31] D. Franz, T. Szilvasi, E. Irran, S. Inoue, *Nat. Commun.* **2015**, *6*, 10037.

[32] a) V. Jancik, H. W. Roesky, D. Neculai, A. M. Neculai, R. Herbst-Irmer, *Angew. Chem. Int. Ed.* **2004**, *43*, 6192 – 6196; *Angew. Chem.* **2004**, *116*, 6318 – 6322; b) V. Jancik, H. W. Roesky, *Inorg. Chem.* **2005**, *44*, 5556 – 5558; c) A. P. Gómora-Figueroa, V. Jancik, R. Cea-Olivares, R. A. Toscano, *Inorg. Chem.* **2007**, *46*, 10749 – 10753.

[33] H. Zhu, J. Chai, A. Stasch, H. W. Roesky, T. Blunck, D. Vidovic, J. Magull, H.-G. Schmidt, M. Noltemeyer, *Eur. J. Inorg. Chem.* **2004**, 4046 – 4051.

[34] a) Y. Xiong, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2009**, *131*, 7562 – 7563; the germanium analogue has also been reported: b) S. Yao, Y. Xiong, M. Driess, *Chem. Commun.* **2009**, 6466 – 6468.

[35] A. R. Kennedy, R. E. Mulvey, S. D. Robertson, *Dalton Trans.* **2010**, *39*, 9091 – 9099.

[36] A.-L. Schmitt, G. Schnee, R. Welter, S. Dagorne, *Chem. Commun.* **2010**, *46*, 2480 – 2482.

[37] T. Chu, I. Korobkov, G. I. Nikonov, *J. Am. Chem. Soc.* **2014**, *136*, 9195 – 9202.

[38] C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, *Angew. Chem. Int. Ed.* **2000**, *39*, 4274 – 4276; *Angew. Chem.* **2000**, *112*, 4444 – 4446.

[39] a) I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270 – 274; b) I. Mayer, *Int. J. Quantum Chem.* **1984**, *26*, 151 – 154.

[40] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083 – 1096.

[41] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735 – 746.

[42] A. J. Bridgeman, G. Cavigliasso, L. R. Ireland, J. Rothery, *J. Chem. Soc. Dalton Trans.* **2001**, 2095 – 2108.

[43] V. Jancik, M. M. Moya Cabrera, H. W. Roesky, R. Herbst-Irmer, D. Neculai, A. M. Neculai, M. Noltemeyer, H.-G. Schmidt, *Eur. J. Inorg. Chem.* **2004**, 3508 – 3512.

[44] M.-F. Liu, B. Wang, Y. Cheng, *Chem. Commun.* **2006**, 1215 – 1217.

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