Isolation of Cyclic Aluminium Polysulfides by Stepwise Sulfurization

Huihui Xu,[a] Catherine Weetman,[b] Franziska Hanusch,[a] and Shigeyoshi Inoue*[a]

Abstract: Despite the notable progress in aluminium chalcogenides, their sulfur congeners have rarely been isolated under mild conditions owing to limited synthetic precursors and methods. Herein, facile isolation of diverse molecular aluminium sulfides is achievable, by the reaction of *N*-heterocyclic carbene-stabilized terphenyl dihydridoaluminium (**1**) with various thiation reagents. Different to the known dihydridoaluminium **1**$^{\text{Tipp}}$, **1** features balanced stability and reactivity at the Al center. It is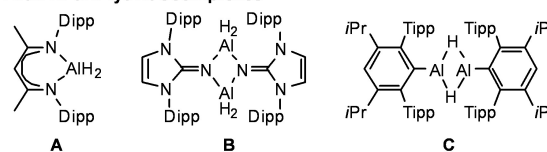 this balance that enables the first monomeric aluminium hydride hydrogensulfide **2**, the six-membered cyclic aluminium polysulfide **4** and the five-membered cyclic aluminium polysulfide **6** to be isolated, by reaction with various equivalents of elemental sulfur. Moreover, a rare aluminium heterocyclic sulfide with Al–S–P five-membered ring (**7**) was obtained in a controlled manner. All new compounds were fully characterized by multinuclear NMR spectroscopy and elemental analysis. Their structures were confirmed by single-crystal X-ray diffraction studies.
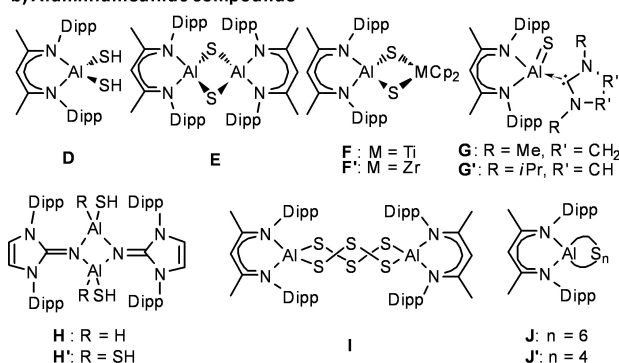
Introduction

Inorganic group 13 element chalcogenides (group 16) are omnipresent in transformations, catalysis and materials. There is ongoing interest in economical and environmentally sustainable aluminium chalcogenides, mostly because of their importance in modern industrial chemistry such as chemical vapor deposition, catalysis and electrolyte materials.[1] To understand aggregation processes that create bulk materials from single atoms, it is necessary to elucidate the bond nature between elements. In this context, synthesis and characterization of stable aluminium chalcogenides is thus an important step towards the comprehension of the basic intramolecular architecture of aluminium chemistry.[2] Among heavier aluminium chalcogenides, their sulfur analogues play a significant role in desulfurization processes of crude oil and flue-gas, which is currently receiving considerable attention.[3] However, to the best of our knowledge, only few examples of molecular aluminium sulfides are known due to synthetic challenges.

[a] H. Xu, F. Hanusch, Prof. S. Inoue
     Department of Chemistry,
     Catalysis Research Center and Institute of Silicon Chemistry
     Technische Universität München
     Lichtenbergstr. 4, 85748
     Garching bei München (Germany)
     E-mail: s.inoue@tum.de

[b] Dr. C. Weetman
     Department of Pure and Applied Chemistry
     University of Strathclyde
     295 Cathedral St, G1 1XL Glasgow (Scotland)

Aluminium hydrides have already presented themselves as viable precursors for Al–S bond formation, with β-diketiminato di-hydridoaluminium [LAlH₂] **A** (L = N(Dipp)C(Me)CHC(Me)N(Dipp), Dipp = 2,6-*i*Pr₂C₆H₃, Figure 1) being the most widely studied.[4] Transformation of compound **A** with elemental sulfur furnished
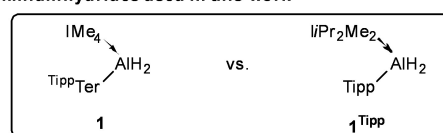

Figure 1. a) Selected aluminium hydride complexes. b) Selected aluminium sulfide compounds. c) Aluminium hydrides used in this work: IMe₄Al($^{\text{Tipp}}$Ter)H₂ **1** and I*i*Pr₂Me₂Al(Tipp)H₂ **1**$^{\text{Tipp}}$. Dipp = 2,6-*i*Pr₂C₆H₃; Tipp = 2,4,6-*i*Pr₃C₆H₂; I*i*Pr₂Me₂ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; Cp = C₅H₅; IMe₄ = 1,3,4,5-tetramethylimidazol-2-ylidene; $^{\text{Tipp}}$Ter = 2,6-(2,4,6-*i*Pr₃C₆H₂)₂C₆H₃.

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202104042

Chemistry Europe
European Chemical
Societies Publishing

the first structurally characterized aluminium bis(hydrogensulfide) [LAl(SH)$_2$] **D**.[5] Subsequently, the dimeric aluminium sulfide **E**,[6] heterobimetallic sulfides [LAl(μ–S)$_2$MCp$_2$] (M=Ti, Zr) (**F** and **F'**),[7] and clusters with the Al–S–M (M=Cu and Ag) structural unit were prepared.[8] Deploying the same β-diketiminato ligand, first neutral monomeric terminally bound aluminium sulfides (**G** and **G'**) were isolated through use of an Al$^{(I)}$ compound.[9] Previous work by our group has focused on using a monodentate N-heterocylic imino ligand to support a dimeric aluminium dihydride ({μ-(NHI)AlH$_2$}$_2$ **B**, NHI=bis(2,6-diisopropylphenyl)imidazolin-2-imino).[10] This resulted in the formation of mono- and bis(hydrogensulfide) aluminium complexes ({μ-(NHI)Al(H)SH}$_2$ **H**, {μ-(NHI)Al(SH)$_2$}$_2$ **H'**) on reaction with S$_8$.[11]

Beyond these aluminium sulfides mentioned, cyclic aluminium polysulfides are of considerable interest, not only because of their structure and reactivity, but also because of their potential applications in oxidation processes and in biological or catalytic systems.[7,12] To date, however, their molecules have been rarely reported due to their elusive generation. For instance, a dimeric polysulfide LAl(μ–S$_3$)$_2$AlL (**I**) with eight-membered ring was obtained by the reaction of an Al$^{(I)}$ compound with S$_8$.[13] During the synthesis of Al–S–M clusters,[8] an aluminium hexasulfide [LAlS$_6$] **J** was formed as a side product. Whilst in the presence of [MesAg]$_4$, the reaction of **D** with excess of elemental sulfur resulted the more stable aluminium tetrasulfide [LAlS$_4$] **J'**.

Following on from the successful isolation of molecular aluminium sulfides with aluminium hydrides, we focused on expanding the scope with a view to controlling product formation. As an indispensable part of molecular aluminium chemistry, the ligand system is key to balancing stability and reactivity of the Al centre.[14] Very recently, Power and co-workers used an extremely sterically demanding terphenyl ligand Ar^{iPr8} (Ar^{iPr8}=2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$–3,5-iPr$_2$–C$_6$H) to isolate the monomeric alanediyl: AlAr^{iPr8}, which reacted with H$_2$, resulting in dimeric aluminium hydride **C**.[15] Our group recently prepared a N-heterocyclic carbene (NHC)-stabilized dihydridoaluminium (IiPr$_2$Me$_2$Al(Tipp)H$_2$ **1^{Tipp}**, IiPr$_2$Me$_2$=1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, Tipp=2,4,6-iPr$_3$C$_6$H$_2$), which was used to isolate the corresponding dialumene.[14] These results prompted us to use the relatively bulky terphenyl ligand and the prime NHC donor to stabilize the aluminium centre for preparing the dihydridoaluminium IMe$_4$Al(^{Tippp}Ter)H$_2$ **1** (IMe$_4$=1,3,4,5-tetramethylimidazol-2-ylidene, ^{Tippp}Ter=2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$). Treatment of various thiation reagents with **1** and **1^{Tipp}** aims to show the influence of the supporting ligand on the reactivity and stability, in efforts towards isolation of new aluminium sulfides.
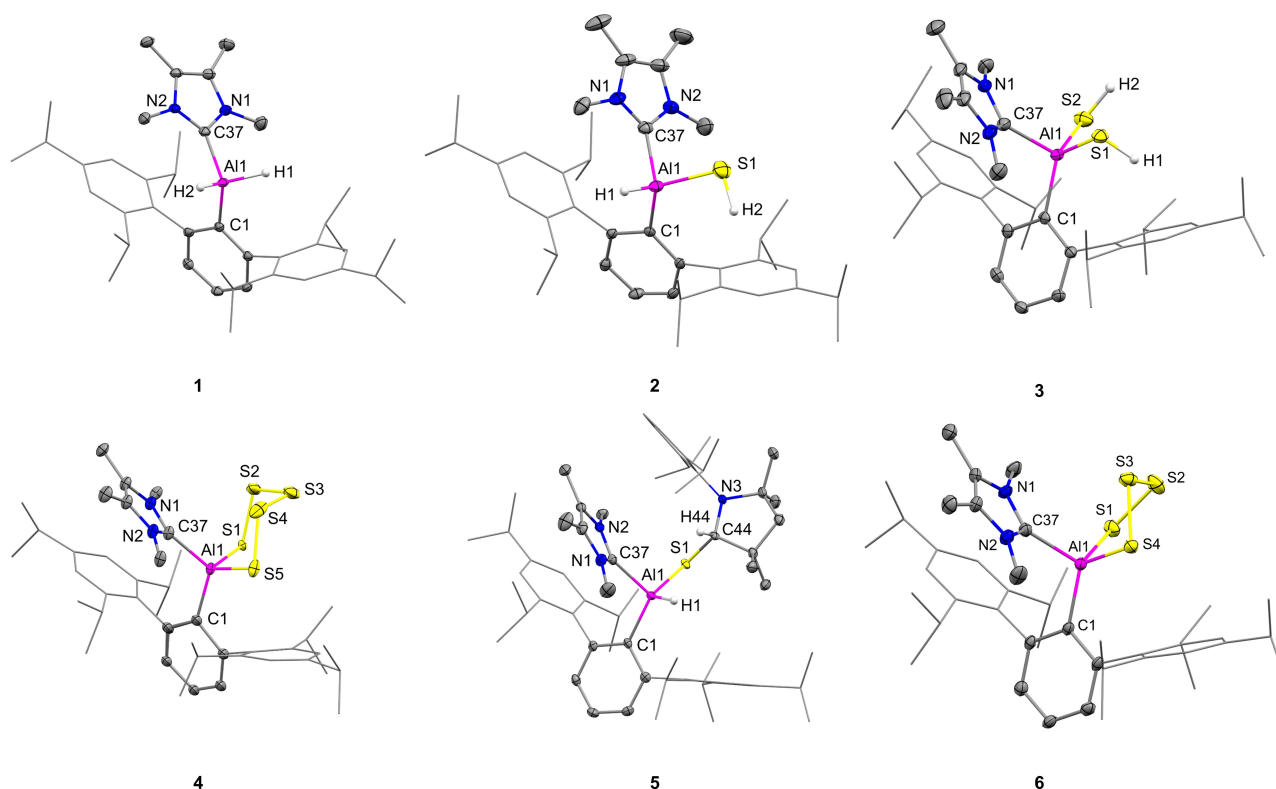
Results and Discussion

The dihydridoaluminium **1** was synthesized in good yields (80%) through the reaction of IMe$_4$AlH$_3$ and ^{Tippp}TerLi(THF)$_2$ at ambient temperature, following the reported procedure for preparation of compound **1^{Tipp}**.[14] The identity of compound **1** was confirmed upon inspection of the ^{1}H NMR spectrum

wherein two resonances for the iso-propyl groups were identified in a 2:1 ratio (o-^{Tippp}Ter: p-^{Tippp}Ter iso-propyl signals) as well as a characteristic broad signal for Al–H protons (^{1}H: br, δ 4.01 ppm). This is more shielded than those observed for amidinato, β-diketiminato, or 1-azaallyl aluminium dihydrides (δ 4.60–4.87 ppm),[1b,16] and the starting material IMe$_4$AlH$_3$ (^{1}H: br, 4.43 ppm), but is more deshielded than dimeric **B** (^{1}H, δ 2.60 ppm).[10] When compared with that of **1^{Tipp}** (^{1}H: br, δ 5.13 ppm) and **A** (^{1}H: br, δ 4.73 ppm),[17] the signal of Al–H protons appears at a lower chemical shift, showing that the electron density of the aluminium centre has increased and thus indicating stronger nucleophilicity. A similar trend was observed in the ^{27}Al spectrum (^{27}Al: δ 112.69 ppm (**1^{Tipp}**) vs. δ 94.72 ppm (**1**)). The solid-state structure of compound **1** was further confirmed by single-crystal X-ray crystallography (SC-XRD, Figure 2), with colourless crystals grown from a saturated pentane solution at −30 °C. The Al centre possesses pseudo-tetrahedral geometry, with the angle C1–Al1–C37 (112.61(7)°) being similar to H1–Al1–H2 (113.7(12)°), the latter being comparable to **A** (H–Al–H: 113.2 (11)°).[5,18] The NHC and terphenyl ligands are located adjacently. Al1–C37 bond length (2.0451(18) Å) indicated the dative nature of the NHC ligand, while Al1–C1 bond length (2.0087(19) Å) is close to the sum of the covalent radii (R$_{Al-C}$=2.01 Å).[19]

Sulfurization of **1^{Tipp}** and **1** by treatment with elemental sulfur were studied. **1^{Tipp}** decomposed immediately on reaction with S$_8$ (Figure S1), however, the treatment of stoichiometric amounts of S$_8$ with **1** resulted in the step-by-step dehydrogenation reaction, forming a series of molecular aluminium sulfides (Scheme 1). The aluminium hydride hydrogensulfide IMe$_4$Al-(^{Tippp}Ter)(SH)H (**2**) was isolated through the mono dehydrogenation reaction of **1** with one equivalent of sulfur ($i.e.$, 1/8 eq. S$_8$) at ambient temperature (Scheme 1, i). The structure of **2** was determined by spectroscopic and SC-XRD studies. The ^{1}H NMR spectrum of **2** showed a characteristic singlet at δ −1.77 ppm which appears at a higher chemical shift compared to the S–H proton reported for compound **H** (^{1}H: δ −2.05 ppm).[11] The ^{1}H NMR signal of Al–H proton was identified as a broad peak (δ 4.80 ppm), which appears at a higher chemical shift compared with **1** (^{1}H: br, δ 4.01 ppm), this is ascribed to the electron withdrawing capability of the SH group.

Reaction of **1** with two equivalents of sulfur ($i.e.$, 1/4 eq. S$_8$) yielded the aluminium bis(hydrogensulfide) complex IMe$_4$Al-(^{Tippp}Ter)(SH)$_2$ (**3**) in high yields of 90%. This was confirmed on inspection of the ^{1}H NMR spectrum, which revealed a singlet at δ −0.89 ppm that integrates to two protons from SH and is comparable to that of **D** (^{1}H: δ −0.88 ppm).[5] Notably, that is a higher chemical shift compared to the single integral of **2** (^{1}H: δ −1.77 ppm) and bisthiol **H'** (^{1}H: δ −1.86 ppm).[11] SC-XRD studies confirmed the formation of **3** (Figure 2). In addition, it is also possible to obtain **3** in a stepwise manner by addition of sulfur ($i.e.$, 1/8 eq. S$_8$) to **2** through further dehydrogenation (Figure S2–3 in Supporting Information).

Treatment of excess S$_8$ with **1** afforded the first six-membered cyclic aluminium polysulfide IMe$_4$Al(^{Tippp}Ter)S$_5$ **4** (Scheme 1, iv) in low yields (13%). This yield could be greatly increased via the reaction of bisthiol **3** and excess of S$_8$ at

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202104042

Chemistry Europe
European Chemical
Societies Publishing

Figure 2. Molecular structures of compound **1**, **2**, **3**, **4**, **5**, **6** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms (except for selected H1 and H2) and co-crystallized solvent molecules are omitted for clarity and parts of the terphenyl ligands and cAAC^{Me} are depicted in wireframe for simplicity.[20] Selected bond lengths (Å) and angles (°): **1**: Al1–C1 2.0087(19), Al1–C37 2.0451(18), Al1–H1 1.53(2), Al1–H2 1.52(2), C1–Al1–C37 112.61(7), H1–Al1–H2 113.7(12); **2**: Al1–C37 2.053(3), Al1–C1 2.000(3), Al1–S1 2.2635(12), Al1–H1 1.61(3), S1–H2 1.42(4), C1–Al1–C37 111.74(11), H1–Al1–S1 111.7(10); **3**: Al1–S1 2.2820(10), Al1–S2 2.2569(11), Al1–C37 2.054(3), Al1–C1 2.004(3), S1–H1 1.29(2), S2–H2 1.34(3), C37–Al1–C1 110.59(11), S1–Al1–S2 107.47(4); **4**: Al1–S1 2.273(4), Al1–S5 2.300(4), Al1–C37 2.017(9), Al1–C1 1.950(18), S1–S2 2.082(4), S2–S3 2.041(4), S3–S4 2.058(5), S4–S5 2.049(4), C37–Al1–C1 118.7(6), S1–Al1–S5 106.13(15); **5**: Al1–S1 2.2607(10), Al1–C37 2.069(3), Al–C1 2.013(2), S1–C44 1.882(2), Al1–H1 1.49(3), C37–Al1–C1 111.49(10), S1–Al1–H1 107.4(10), Al1–S1–C44 100.22(8); **6**: Al1–S1 2.300(2), Al1–S4 2.302(2), Al1–C37 2.062(6), Al1–C1 1.987(6), S1–S2 2.093(2), S2–S3 2.048(2), S3–S4 2.086(2), C37–Al1–C1 113.1(2), S1–Al1–S4 101.93(9).
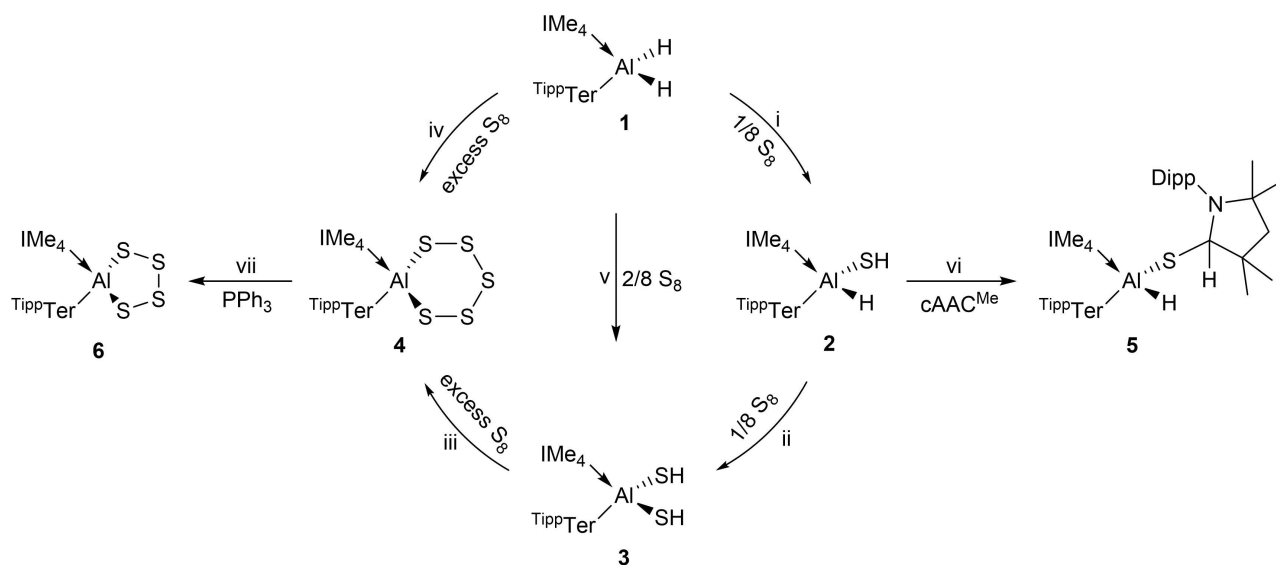
Scheme 1. Formation of aluminium sulfide compounds IMe$_4$Al(^{TippTer})(SH)H **2**, IMe$_4$Al(^{TippTer})(SH)$_2$ **3**, IMe$_4$Al(^{TippTer})S$_5$ **4**, IMe$_4$Al(^{TippTer})(H)S(H-cAAC^{Me}) **5**, IMe$_4$Al(^{TippTer})S$_4$ **6**. (i) Pentane, (1) −78°C, 15 min, (2) rt, 16 h; (ii) C$_6$D$_6$, rt, 2 h; (iii) Et$_2$O, (1) −30°C, 5 min, (2) rt, 72 h; (iv) Et$_2$O, (1) −78°C, 30 min, (2) rt, 16 h; (v) Et$_2$O, (1) −78°C, 1 h, (2) rt, 48 h; (vi) Toluene, (1) −30°C, 5 min, (2) rt, 16 h; (vii) THF, 65°C, 2 h. ^{Tipp}Ter = 2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$, IMe$_4$ = 1,3,4,5-tetramethylimidazol-2-ylidene, Dipp = 2,6-iPr$_2$C$_6$H$_3$.

Chem. Eur. J. **2021**, e202104042 (3 of 6)

© 2021 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202104042

Chemistry Europe
European Chemical
Societies Publishing

ambient temperature (85%, Scheme 1, iii). In this instance, **4** was isolated as the sole product, offering a selective and controlled activation of elemental sulfur. Pale yellow single crystals suitable for SC-XRD analysis were grown by slow evaporation of a saturated benzene solution. The single-crystal structure revealed the aluminium centre to have pseudo-tetrahedral geometry (C37–Al1–C1 118.7(0)°, S1–Al1–S5 106.13(15)°), and confirmed the six-membered ring. The S–S bond length (av. 2.058 Å) is longer than in **J** (av. 2.01 Å) and shorter than in **J′** (av. 2.07 Å).[8] The Al1–S1 (2.273(4) Å) and Al1–S5 (2.300(4) Å) bond lengths are longer than in bisthiol **D** (av. 2.22 Å)[5] and dimer **E** (av. 2.24 Å).[6]

When it comes to the reactivity of **2**, **3**, and **4**, dehydrogenation or desulfurization are of considerable interest. Cyclic (alkyl)(amino) carbenes (cAAC^{Me}) have been used in hydrogen or sulfur transfer, due to its relatively strong σ-donating and π-accepting nature.[21] Here, the reaction of **2** with one equivalent of cAAC^{Me} resulted in oxidative addition of the S–H bond at the carbene carbon, yielding compound **5** (Scheme 1, vi). The structure of **5** was determined by ^{1}H and ^{13}C NMR spectroscopy and SC-XRD. The signal for H44 of H–cAAC^{Me} (Figure 2, δ 4.56 ppm) is diagnostic, while the signal for H2 of **2** (δ −1.77 ppm) disappeared. In comparison to that of compound **2** (^{1}H: δ 4.80 ppm) and **1** (^{1}H: δ 4.01 ppm), the Al–H proton signal of **5** (^{1}H: δ 4.25 ppm) resonates in between. The crystal structure of **5** revealed that the Al–S bond length (Al1–S1 2.2607(10) Å) was comparable to **2** (Al1–S1 2.2635(12) Å). The Al1–C37 bond length (2.069(3) Å) and the Al1–C1 bond length (2.013(2) Å) were elongated, compared to other Al compounds (Al1–C37 2.0451(18) Å (**1**), Al1–C37 2.053(3) Å (**2**), Al1–C37 2.054(3) Å (**3**), Al1–C37 2.017(9) Å (**4**); Al1–C1 2.0087(19) Å (**1**), Al1–C1 2.000(3) Å (**2**), Al1–C1 2.004(3) Å (**3**), Al1–C1 1.950(18) Å (**4**)), indicating that the interactions of NHC and terphenyl ligands with the Al center were weakened. Attempts to form analogous products on reaction of **3** or **4** with cAAC^{Me} did not form isolable products.

As the first example of a cyclic six-membered aluminium polysulfide ring, further understanding of the stability and reactivity of **4** is attractive.[12c] As such, the reaction of **4** with triphenylphosphine PPh$_3$, tris(dimethylamino)phosphine P-(NMe$_2$)$_3$ and IMe$_4$ as well as the thermal stability of **4** were studied. Reaction of **4** with P(NMe$_2$)$_3$, or IMe$_4$ was unsuccessful, however, treatment of PPh$_3$ with **4** at 65 °C furnished the five-membered cyclic aluminium polysulfide IMe$_4$Al(^{Tipp}Ter)S$_4$ **6** within 2 h through desulfurization (Scheme 1, vii). However, it is of note that compound **4** is somewhat unstable in solution, it is slowly converted to **6** at room temperature over 30 days (15% conversion, Figure S5) or at 80 °C over 24 h (30% conversion, Figure S6). These results indicate that the desulfurization of **4** is accelerated significantly by PPh$_3$. The solid-state structure of compound **6** was confirmed by SC-XRD (Figure 2), with yellow crystals grown from a saturated THF solution. In contrast to **4** (Al1–C37 2.017(9) Å, Al1–C1 1.950(18) Å), the interaction of NHC and aryl ligand with the Al centre in **6** was weakened while the bond lengths were elongated (**6**: Al1–C37 2.062(6) Å, Al1–C1 1.987(6) Å). Whilst the overall ring size decreased from six (**4**) to five (**6**), longer Al–S bonds (**4**: Al1–S1 2.273(4) Å, Al1–S5
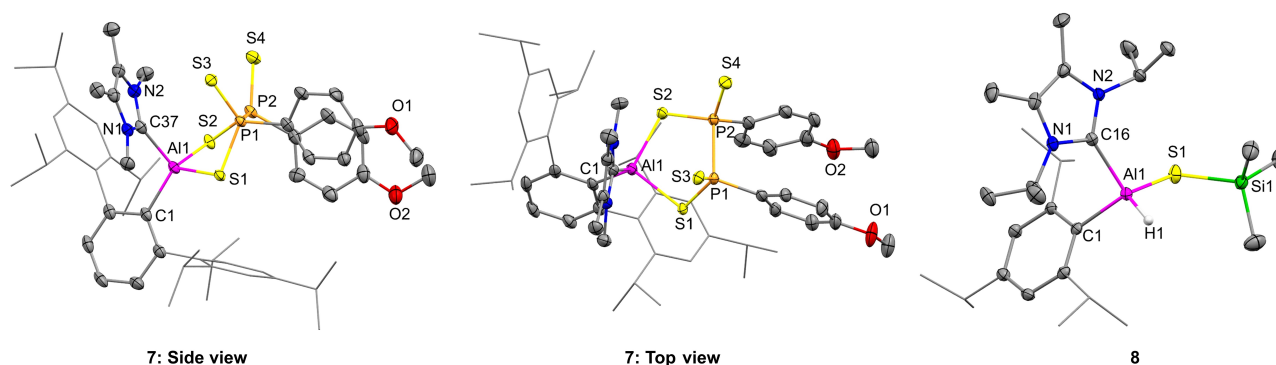
2.300(4) Å; **6**: Al1–S1 2.300(2) Å, Al1–S4 2.302(2) Å) and longer S–S bonds (**4**: S–S av. 2.0575 Å; **6**: S–S av. 2.0757 Å) were observed. Further desulfurization attempts with PPh$_3$ and elevated temperatures, were unsuccessful.

In addition to elemental sulfur, Lawesson's reagent (2,4-bis-(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide, LR) has received attention in reactions with group 13 compounds. It is an effective thiation reagent, for example in the transformation of aldehydes and ketones to their thio derivatives. Reported by Cowley and co-workers in 1998, unusual reactions of LR with germylenes and stannylenes were described, affording unusual Ge–S and Sn–S compounds.[22] Here, the reaction of **1**^{Tipp} with LR occurred, but the product decomposed immediately. However, the treatment of **1** with 1.5 equivalents of LR gave the first example of a five-membered Al–S–P–P–S ring containing complex **7** (Scheme 2, i). According to the single-crystal structure (Figure 3), the geometry of the Al centre is pseudo-tetrahedral, with an S1–Al1–S2 angle of 99.60(6)°. The distances of Al1–C1 (1.997(3) Å), Al1–C37 (2.032(3) Å) and Al1–S1 (2.2904(18) Å) and Al1–S2 (2.2848(13) Å) were located within the range of all Al compounds mentioned above. In contrast to the afore mentioned Ge–S compound ([Ge(S–P–C$_6$H$_4$OMe)$_4$], P–P: 2.220(2) Å),[22] the P1–P2 bond length of **7** (2.2694(11) Å) was slightly longer, indicating covalent bond character. Moreover, compared with the mentioned Sn–S compound ([(Me$_3$Si)$_2$Sn–(S–S)–P(=S)C$_6$H$_4$OMe)], P=S 1.9315(9) Å), the P1=S3 (1.9495(14) Å) and P2=S4 (1.9580(16) Å) bond lengths of **7** were slightly longer, which showed double bond features. Compound **7** shows an interesting puckered heterocyclic five-membered Al–S–P ring. It is thermally stable at 75 °C for at least 24 h.

Compared with the effective S$_8$ and LR thiation reagents, bis(trimethylsilyl) sulfide S(TMS)$_2$ is considered a modest thiation reagent. Whereas no reaction between compound **1** and S(TMS)$_2$ occurred, the treatment of S(TMS)$_2$ with **1**^{Tipp} at high temperature yielded the IiPr$_2$Me$_2$Al(Tipp)(H)STMS complex **8** (Scheme 2, ii) via a mono dehydrogenation reaction. This finding is consistent with previous results that **1** features less reactive than **1**^{Tipp}. The ^{1}H NMR spectrum revealed the Al–H
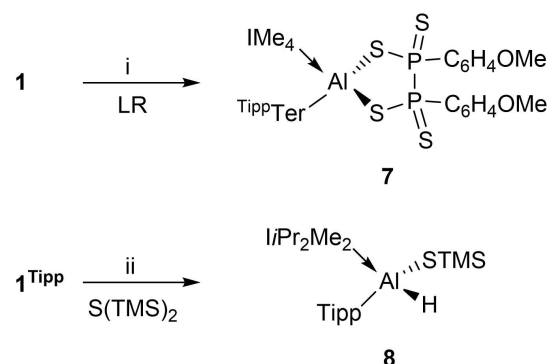
Scheme 2. Formation of compounds **7** and **8**. (i) Toluene, (1) 0 °C, 15 min, (2) rt, 16 h. (ii) Toluene, (1) −78 °C, 15 min, (2) 75 °C, 48 h. LR = Lawesson's reagent; ^{Tipp}Ter = 2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$; IMe$_4$ = 1,3,4,5-tetramethylimidazol-2-ylidene; TMS = trimethylsilyl; IiPr$_2$Me$_2$ = 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene.

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202104042

Chemistry Europe
European Chemical
Societies Publishing

7: Side view   **7: Top view**   **8**

Figure 3. Molecular structure of compound **7** and **8** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms (except for selected H1) and co-crystallized solvent molecules are omitted for clarity and parts of the terphenyl ligands are depicted in wireframe for simplicity.[20] Selected bond lengths (Å) and angles (°): **7** Al1–C37 2.032(3), Al1–C1 1.997(3), Al1–S2 2.2848(13), Al1–S1 2.2904(18), S1–P1 2.0584(18), S2–P2 2.0712(14), P1–P2 2.2694(11), P1–S3 1.9495(14), P2–S4 1.9580(16), C37–Al1–C1 112.85(12), S1–Al1–S2 99.60(6). **8** Al1–H1 1.4499(12), Al1–C16 2.086(3), Al1–C1 2.013(3), Al1–S1 2.2738(11), S1–Si1 2.1236(11), C1–Al1–C16 102.09(11), Si1–S1–Al1 107.71(5), S1–Al1–H1 111.35(6).

proton as a broad peak (δ 5.43 ppm), which appears at a slightly higher chemical shift compared to **1**^{Tipp} (^{1}H: br, δ 5.13 ppm). The singlet at δ 0.72 ppm is assigned to TMS methyl protons. The SC-XRD revealed (Figure 3) that the Al centre is in a pseudo-tetrahedral coordination environment with C1–Al1–C16 (102.09(11)°) and H1–Al1–S1 (111.35(6)°) angles. Compound **8** is thermally stable, as attempts to force the elimination of TMSH at high temperatures was unsuccessful.

Conclusion

Herein, the monomeric dihydridoaluminium **1**, stabilized by NHC and sterically demanding terphenyl ligand has been isolated. **1** shows comparatively more balanced stability and reactivity at the Al centre in contrast to the known dihydridoa-luminium **1**^{Tipp}. It is implicated that **1** could react with conventional thiation reagents such as elemental sulfur and Lawesson's reagent under mild reaction conditions, while elevated temperature only initiated the reaction of modest thiation reagent S(TMS)$_2$ with **1**^{Tipp}. In this regard, the first aluminium hydride hydrogensulfide **2**, an aluminium bis(hydrogensulfide) complex **3**, the first six-membered cyclic aluminium polysulfide **4** and a five-membered cyclic aluminium polysulfide **6** as well as the first five-membered heterocyclic Al–S–P complex **8** were isolated in a controlled manner. These results offer experimental insight into the nature of Al–S containing compounds, which is significant for molecular aluminium chemistry. The relatively increased stability and reactivity enables commendable prospect on bimetallic catalytic reactions and in addition is able to access novel aluminium species through organic transformations. Especially, the further reactivity and the application in preparation of bimetallic aluminium-sulfur clusters as well as biological or catalytic systems of compound **2–8** will be studied in the future.

Experimental Section

Experimental details are discussed in the Supporting Information.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

[1] a) D. Franz, T. Szilvasi, E. Irran, S. Inoue, *Nat. Commun.* **2015**, *6*, 10037; b) C. Cui, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Organometallics* **1999**, *18*, 5120–5123; c) A. H. Cowley, R. A. Jones, P. R. Harris, D. A. Atwood, L. Contreras, C. J. Burek, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1143–1145; d) N. Kambe, K. Kondo, N. Sonoda, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 1009–1010; e) W. Lee, S.-J. Park, *Chem. Rev.* **2014**, *114*, 7487–7556; f) Y. Ding, X. Ma, Y. Liu, W. Liu, C. Ni, B. Yan, L. Yan, Z. Yang, *Inorg. Chim. Acta* **2019**, *497*, 119091; g) H. Senoh, T. Takeuchi, H. Kageyama, H. Sakaebe, M. Yao, K. Nakanishi, T. Ohta, T. Sakai, K. Yasuda, *J. Power Sources* **2010**, *195*, 8327–8330.

[2] a) C. Weetman, H. Xu, S. Inoue, in *Encyclopedia of Inorganic and Bioinorganic Chemistry* (Ed.: R. A. Scott), **2020**, pp. 1–20; b) P. Bag, C. Weetman, S. Inoue, *Angew. Chem. Int. Ed.* **2018**, *57*, 14394–14413;

Angew. Chem. **2018**, *130*, 14594–14613; c) D. Franz, S. Inoue, *Dalton Trans.* **2016**, *45*, 9385–9397.

[3] a) C. Schnitter, A. Klemp, H. W. Roesky, H.-G. Schmidt, C. Röpken, R. Herbst-Irmer, M. Noltemeyer, *Eur. J. Inorg. Chem.* **1998**, *1998*, 2033–2039; b) R. J. Wehmschulte, P. P. Power, *Chem. Commun.* **1998**, 335–336; c) R. J. Wehmschulte, P. P. Power, *J. Am. Chem. Soc.* **1997**, *119*, 9566–9567; d) M. Taghiof, M. J. Heeg, M. Bailey, D. G. Dick, R. Kumar, D. G. Hendershot, H. Rahbarnoohi, J. P. Oliver, *Organometallics* **1995**, *14*, 2903–2917; e) W. Uhl, A. Vester, W. Hiller, *J. Organomet. Chem.* **1993**, *443*, 9–17.

[4] C. Cui, H. W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem. Int. Ed.* **2000**, *39*, 1815–1817; *Angew. Chem.* **2000**, *112*, 1885–1887.

[5] V. Jancik, Y. Peng, H. W. Roesky, J. Li, D. Neculai, A. M. Neculai, R. Herbst-Irmer, *J. Am. Chem. Soc.* **2003**, *125*, 1452–1453.

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

[7] 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.

[8] B. Li, J. Li, H. W. Roesky, H. Zhu, *J. Am. Chem. Soc.* **2015**, *137*, 162–164.

[9] T. Chu, S. F. Vyboishchikov, B. Gabidullin, G. I. Nikonov, *Angew. Chem. Int. Ed.* **2016**, *55*, 13306–13311; *Angew. Chem.* **2016**, *128*, 13500–13505.

[10] D. Franz, E. Irran, S. Inoue, *Dalton Trans.* **2014**, *43*, 4451–4461.

[11] D. Franz, S. Inoue, *Chem. Eur. J.* **2014**, *20*, 10645–10649.

[12] a) N. Takeda, N. Tokitoh, R. Okazaki, in *Elemental Sulfur und Sulfur-Rich Compounds II* (Ed.: R. Steudel), Springer Berlin Heidelberg, Berlin, Heidelberg, **2003**, pp. 153–202; b) R. Okazaki, *Phosphorus Sulfur Silicon Relat. Elem.* **2001**, *168*, 41–50; c) P. Chen, C. Cui, *Chemistry* **2016**, *22*, 2902–2905.

[13] Y. Peng, H. Fan, V. Jancik, H. W. Roesky, R. Herbst-Irmer, *Angew. Chem. Int. Ed.* **2004**, *43*, 6190–6192; *Angew. Chem.* **2004**, *116*, 6316–6318.

[14] C. Weetman, A. Porzelt, P. Bag, F. Hanusch, S. Inoue, *Chem. Sci.* **2020**, *11*, 4817–4827.

[15] J. D. Queen, A. Lehmann, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2020**, *142*, 20554–20559.

[16] a) M. L. Cole, C. Jones, P. C. Junk, M. Kloth, A. Stasch, *Chem. Eur. J.* **2005**, *11*, 4482–4491; b) N. Kuhn, S. Fuchs, M. Steimann, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1387–1392.

[17] S. Ito, K. Tanaka, Y. Chujo, *Inorganics* **2019**, *7*, 100.

[18] B. Twamley, N. J. Hardman, P. P. Power, *Acta Crystallogr. Sect. E* **2001**, *57*, m227–m228.

[19] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186–197.

[20] Deposition Numbers 2118428–2118435 (Compound **1**–**8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

[21] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851–5855.

[22] C. J. Claire, J. A. C. Clyburne, A. H. Cowley, V. Lomeli, B. G. McBurnett, *Chem. Commun.* **1998**, 243–244.

RESEARCH ARTICLE

The NHC stabilized terphenyl dihydridoaluminium, the first monomeric aluminium hydride hydrogensulfide, the aluminium bis(hydrogensulfide), the six- or five-membered cyclic aluminium polysulfide as well as a rare five-membered heterocyclic aluminium sulfide were synthesized controllably in mild manners. Reactions of the known dihydridoaluminium and the terphenyl dihydridoaluminium with various thiation reagents formed a series of aluminium-sulfur species. This provided insights into the influence of the supporting ligands on the reactivity and stability.
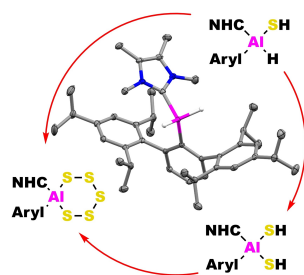
*H. Xu, Dr. C. Weetman, F. Hanusch, Prof. S. Inoue**

1 – 7

Isolation of Cyclic Aluminium Polysulfides by Stepwise Sulfurization