Mono- and Dinuclear Aluminium Complexes Derived from Biguanide and Carbothiamide Ligands

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Abstract: Dianionic N,N-chelating ligands play a crucial role in coordination chemistry, but reports on related complexes remain limited to certain types of ligands. In here, the reactions of two diprotic ligands, i.e., a biguanide and a carbothiamide, with trimethylaluminium, are reported, which give rise to mono- and dinuclear aluminium(III) complexes. In addition, single deprotonation of the diprotic biguanide using potassium bis(trimethylsilyl)amide gives rise to a one-dimensional coordination polymer. All complexes have been fully characterized, and their solid-state structures were determined by single crystal X-ray diffraction analysis.

Keywords: aluminium; biguanides; ligand design; nitrogen ligands

1. Introduction

Diprotic N,N-chelating ligands are widely utilized in their dianionic form in the coordination chemistry of transition metals, main-group and rare-earth elements. In main-group chemistry, they have been particularly beneficial, and, thanks to the electronic and steric capabilities of diamide ligands, molecules that were formerly considered unstable such as boryllithium [1] and silylenes [2] have been isolated for the first time. While significant achievements could be realized using diamide ligands, their applicability is not universal which is why alternative dianionic N,N-chelates, Figure 1, have been used during the last decade to stabilize low-valent and electron-precise compounds of the Group 13 and 14 elements [3–14]. Furthermore, certain monoanionic ligands such as the well-established β-diketiminates, also called “NacNac”, can be transferred to their dianionic relatives [15,16]. This behavior is beneficial in terms of metal-ligand cooperativity [17,18], and the addition of hydrogen or protic substrates to gallium(III) β-diketiminate complexes generates an additional protic side within the ligand [19,20]. During our recent studies on dianionic bis(guanidine)s [21], we were able to isolate monoprotic biguanides as well as diprotic carbothiamides depending on the experimental conditions [22], and we wondered if diprotic biguanides are available as well when using a primary instead of a secondary amine. In here, we report the synthesis of the unprecedented biguanide 1 along with its reactivity towards trimethylaluminium and potassium bis(trimethylsilyl)amide. For comparison, the reactivity of the carbothiamide 2 with trimethylaluminium has been investigated as well.
2. Results and Discussion

Based on the synthetic protocol previously established for monoprotic biguanide ligands, [22] biguanide 1 could be obtained from the ethylene-bridged bis(thiourea), cyclohexylamine, and lead(II) oxide in a one-pot procedure, Scheme 1. The crystalline yield of 1 amounts to 16%, although 1 is formed in 40% based on the crude 1H NMR besides the carbothiamide 2 and the unsymmetric thiourea carrying one 2,6-diisopropylphenyl (Dipp) and one cyclohexyl substituent. Notably, such side products have also been observed in the synthesis of monoprotic biguanides [22].

The 1H NMR spectrum of 1 features four doublets and two septets for the methyl and methine resonances of the Dipp groups indicating hindered rotation about the Caryl-N bonds. The methylene resonances of the imidazoline ring appear as triplets at 3.28 and 3.98 ppm, and the NH protons resonate as a broadened singlet (3.93 ppm) and as a doublet (9.33 ppm). In order to distinguish which of the conceivable isomers, Scheme 1, prevails in solution (CDCl3), multidimensional NMR experiments have been conducted. The 1H,1H-COSY spectrum, Figure S3, shows distinct coupling between the broad NH singlet at 3.93 ppm and the triplet at 3.28 ppm, accounting for the CH2 group of the five-membered ring. The NH doublet at 9.33 ppm shows coupling with a broad singlet resonance at 2.96 ppm which is associated with the methine proton of the cyclohexyl ring. These observations are further supported by the 1H,13C-HMBC spectrum, Figure S5, and indicate that 1 is the predominant tautomer in solution at room temperature. This observation agrees well with the molecular structure in the solid state, which has been established by single-crystal X-ray diffraction, Figure 2. The amine protons reside on N1 and N5, and the C1–N3 and C4–N4 bond lengths (1.280(2) and 1.278(2) Å) are reminiscent of C=N double bonds. Hydrogen bonding, which is common for biguanides and used in
crystal engineering [23], is also observed within 1, and an intramolecular hydrogen bond, i.e., NSH1···N3, induces a pseudo-bicyclic system.

![Crystal engineering](image)

**Figure 2.** Solid-state structure (hydrogen atoms except the NH are omitted for the sake of clarity) with selected bond lengths (Å) and angles (deg) of 1: C1–N1 1.364(2), C4–N4 1.278(2), C1–N3 1.280(2), N2–C4–N5 124.45(11), N2–C1–N3 114.63(10).

We next explored the reactivity of 1 towards potassium bis(trimethylsilyl)amide (KHMDS) and trimethylaluminium, Scheme 2. Deprotonation of 1 using 1.2 equivalents of KHMDS affords the potassium complex 3 in 30% crystalline yield. Single crystals, suitable for an X-ray diffraction analysis, allowed establishing the molecular structure in the solid state, Figure 3.

![Reactivity scheme](image)

**Scheme 2.** Synthesis of potassium and aluminium complexes originating from 1.
Figure 3. (a) Solid-state structure (hydrogen atoms except the NH are omitted for the sake of clarity) with selected bond lengths (Å) and angles (deg) of 3: K1–N1 2.695(2), K1–N4′ 2.735(2), K1–O1 2.776(2), K1–Ph-Ring 2.857(2), N1–K1–N4′ 103.06(7), N4′–K1–O1 85.88(7); symmetry transformations used to generate equivalent atoms (marked with an ‘): −x + 3/2, y + 1/2, −z + 3/2. (b) 1D coordination polymer of 3.

Complex 3 forms a polymeric one-dimensional network [24,25], in which the monoanionic ligands provide three donor sites. Hence, each tetracoordinated potassium ion binds to the nitrogen atom N1 and the phenyl ring of the related Dipp group of one ligand in a κ^1 and η^6 mode, in κ^1 fashion to the N4 nitrogen atom of the next ligand and to one molecule of THF. The respective potassium-nitrogen bond lengths in the range of 2.695(2) to 2.735(2) Å, as well as the distance of the potassium ion to the centre of the C₆ perimeter (2.857(2) Å), are in good agreement with previously reported potassium complexes [22,26]. Hence, deprotonation occurs exclusively at N1, while the amino function at N5 remains intact, which is most likely due to the stabilization of H5 by the intramolecular N5H1···N3 hydrogen bridge. In C₆D₆ solution, 3 features well-resolved ¹H NMR resonances, and the absence of one of the NH resonances (at 3.93 ppm) and the high-field shift to 10.31 ppm of the other one agree well with only a single deprotonation. The pattern of resonances of the Dipp groups, i.e., four methyl doublets and one methine septet, indicates a plane of symmetry within the molecule. Unfortunately, repeated attempts to obtain the double deprotonation product of 1 by using higher amounts of KHMS remained without success.

The outcome of the reaction with trimethylaluminium is strongly dependent on the reaction conditions, but gives in both case dinuclear rather than mononuclear complexes. Reacting 1 with one equivalent of trimethylaluminium at room temperature affords a new species along with unreacted starting material in a 1:1 ratio. Hence, the reaction was repeated using two equivalents of trimethylaluminium which allowed isolating complex 4 in 55% crystalline yields. An X-ray diffraction analysis revealed its dinuclear nature, Figure 4a, which is reminiscent of a previously reported aluminium complex based on a monoproptic biguanide and resembles comparable Al–N and Al–C bond lengths [22]. i.e., the tetracoordinated aluminium centre is chelated by N3 and N4, forming a non-planar six-membered metallacycle. Again, the proton at N5 remains illustrating its robustness, and the donor-acceptor interaction between Al2 and N1 causes an elongation of the C1–N1 bond. The room temperature ¹H NMR spectrum of 4 shows two overlapping singlet resonances of the bridging and terminal Al-CH₃ groups, and the Dipp methyl and methine resonances appear as four doublets and two septets, respectively. Aiming to force deprotonation of the remaining NH function, the reaction with one equivalent of trimethylaluminium was repeated at 90 °C. The ¹H NMR spectrum of the crude reaction mixture reveals the formation of one main species besides several side products. Complex 5 could be isolated from this mixture in 18% crystalline yield (the crude mixture contains about 50%) and fully
characterized including an X-ray diffraction analysis. Complex 5 possesses a dinuclear structure in the solid state in which the ligand has been deconstructed by C–N bond cleavage. Two of the remaining monoanionic guanidine moieties are bridged via N1, N2, N4, and N5 forming an overall eight-membered dimetallacycle, while two protons reside on N3 and N6. The Al–N bond lengths are comparable and fall in between 1.9149(19) and 1.9306(19) Å, and the N–Al–N bite angles are more obtuse as compared to complex 4, in line with the larger ring size. The Dipp methyl and methine resonances appear as two doublets and one broad singlet in the $^1$H NMR spectrum of 5, which indicates conformational averaging on the NMR timescale at room temperature.

Figure 4. (a) Solid-state structure (hydrogen atoms except the NH are omitted for the sake of clarity) with selected bond lengths (Å) and angles (deg) of: (a) 4: Al1–N4 1.9325(17), Al1–N3 1.9255(17), C1–N1 1.318(2), C1–N3 1.330(2), Al2–N1 2.0160(17), N4–Al1–N3 124.89(7), C35–Al1–C36 121.04(11); (b) 5: Al1–N1 1.9282(19), Al1–N5 1.9188(19), Al2–N2 1.9149(19), Al2–N4 1.9306(19), C13–N1 1.338(3), C13–N2 1.349(3), C16–N4 1.334(3), C16–N5 1.350(3), N1–Al1–N5 114.59(8), C31–Al1–C32 113.80(11), N2–Al2–N4 113.42(8), C33–Al2–C34 115.16(11); (c) 6: Al1–N4 1.9245(17), Al1–N3 1.9165(18), C1–N1 1.318(3), C1–N3 1.318(3), S1–C4 1.682(2), N3–Al1–N4 92.75(7), C29–Al1–C30 113.82(11).

As double deprotonation of 1 did not work out, we considered the carbothiamide 2 as a suitable dianionic ligand and allowed it to react with two equivalents of trimethylaluminium either at room temperature or at 90 °C, Scheme 3. However, in both cases, only the mononuclear complex 6 could be isolated, although in different yields of 36% and 23%, respectively. Notably, the crude $^1$H NMR spectrum of the reaction performed at room temperature evidences a yield of about 70%. The $^1$H NMR spectrum of 6 features sharp, well-resolved resonances including one singlet at −0.53 ppm for the Al(CH$_3$)$_2$ and four doublets as well as two septets accounting for the iso-propyl groups of the Dipp residues, indicating hindered rotation about the C$_{aryl}$–N bonds. However, only one of the NH functions has been deprotonated, as evidenced by a broad resonance at 3.48 ppm. This finding agrees well with the solid-state structure of 6, Figure 4c. The complex features comparable Al–N bond lengths within in the six-membered metallacycle that are in good agreement with those reported for thioacetamide heteroscorpionate ligands [27]. Finally, the residual proton could be located at N1.

Scheme 3. Reaction of the carbothiamide 2 with trimethylaluminium.
3. Materials and Methods

3.1. General Considerations

The solvents and starting materials were purchased from ABCR, Sigma Aldrich, or VWR and used as delivered. 1,1′-(ethane-1,2-diyl)bis(3-(2,6-diisopropylphenyl)thiourea) and 2 were prepared as described elsewhere [22]. All preparations were performed under an inert atmosphere of dinitrogen by means of standard Schlenk-line techniques, while the samples for analytics were handled in a glovebox (GS-Systemtechnik and MBraun). Traces of oxygen and moisture were successively removed from the inert gas by passing it over a BASF R 3-11 (CuO/MgSiO₃) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally P₂O₁₀. Toluene, n-pentane, and tetrahydrofuran were used as p.a. grade and distilled from Na/benzophenone prior to use. C₆D₆ was dried by distillation from potassium.

The NMR-spectra were recorded on Bruker Avance 300 and 400 spectrometers (T = 300 K) with δ (given in ppm) referenced to external tetramethylsilane (1H and 13C). 1H and 13C NMR spectra were calibrated by using the solvent residual peak (δ 1H (CDCl₃) = 7.26), and the solvent peak (δ 13C (CDCl₃) = 77.16), respectively. The coupling constants J are given in Hz. High-resolution mass spectra were measured by using a Waters LCT Micromass spectrometer. Infrared spectra were measured by using a Bruker ALPHA spectrometer equipped with a diamond ATR unit; the results were as follows: 1.65 g, 3.1 mmol, 16%. Elemental analysis was performed on a Vario micro cube (Elementar Analysensysteme GmbH); however, a few samples were consistently low on carbon content, while providing satisfactory H and N values.

3.2. Synthesis of the Protio-Ligand 1

A mixture of 9.75 g (19.5 mmol) 1,1′-(ethane-1,2-diyl)bis(3-(2,6-diisopropylphenyl)thiourea), 38.65 g (390.0 mmol) cyclohexylamine, and 8.73 g (39.0 mmol) PbO in 250 mL of toluene was stirred at 100 °C for 16 h. After cooling to room temperature, the solids were filtered off, washed with toluene (30 mL), and the combined filtrates were concentrated en vacuo. The residue was dissolved in boiling acetonitrile (50 mL), and the desired product 1 crystallized in the form of colourless blocks upon standing at r.t.

The results were as follows: 1.65 g, 3.1 mmol, 16%. 1H NMR (400 MHz, CDCl₃): δ = 0.85 (br, 2H, (NCH(CH₂)₂(CH₂)₂(CH₂)), 0.92 (br, 2H, (NCH(CH₂)₂(CH₂)₂(CH₂)), 0.99 (br, 2H, (NCH(CH₂)₂(CH₂)₂(CH₂))), 1.16 (d, 3J_HH = 6.8 Hz, 6H, CHCH₃), 1.24 (d, 3J_HH = 6.8 Hz, 6H, CHCH₃), 1.26 (d, 3J_HH = 6.8 Hz, 6H, CHCH₃), 1.32 (br, 2H, (NCH(CH₂)₂(CH₂)₂(CH₂)), 1.38 (br, 2H, (NCH(CH₂)₂(CH₂)₂(CH₂)), 2.96 (br, 1H, CH₂CH₂CHNHN), 3.09 (sept, 3J_HH = 6.8 Hz, 2H, CHCH₃), 3.20 (sept, 3J_HH = 6.8 Hz, 2H, CHCH₃), 3.28 (t, 3J_HH = 7.8 Hz, 2H, NCH₂CH₂NHC), 3.93 (br, 1H, NCH₂CH₂NHC), 3.98 (t, 3J_HH = 7.8 Hz, 2H, NCH₂CH₂NHC), 6.90 (t, 3J_HH = 7.3 Hz, 1H, p-CH₃), 7.02 (d, 3J_HH = 7.2 Hz, 2H, m-CH₃), 7.04 (t, 3J_HH = 7.8 Hz, 1H, p-CH₃), 7.02 (d, 3J_HH = 7.2 Hz, 2H, m-CH₃), 7.13 (d, 3J_HH = 7.2 Hz, 2H, m-CH₃), 9.33 (d, 3J_HH = 9.2 Hz, 1H, (HN cyclohexylamineCNdipp), 13C[1H] NMR (101 MHz, CDCl₃): δ = 22.3 (CH₃), 23.1 (CH₃), 23.9 (CH₃), 24.8 (NCH(CH₂)₂(CH₂)₂(CH₂)), 25.7 (NCH(CH₂)₂(CH₂)₂(CH₂)), 28.5 (CH₂CH₃), 28.7 (CH₃CH₂NHC), 34.4 (NCH(CH₂)₂(CH₂)₂(CH₂)), 38.9 (NCH₂CH₂NHC), 46.0 (NCH₂CH₂NHC), 49.8 (CNHC=N), 121.0 (p-CH₃), 122.3 (m-CH₃), 132.4 (m-CH₃), 138.5 (o-CH₃), 140.6 (o-CH₃), 142.9 (HN cyclohexylamineCNdipp), 143.2 (i-CH₃), 145.3 (i-CH₃), 151.5 (NH), IR [cm⁻¹]: ν(NH) = 3378, ν(NH) = 3143, ν(CH₃) = 2959, ν(CN) = 1541. HR-ESI-MS: calcd. for C₃₄H₅₁N₅ [M + H]⁺ 530.4222; found 530.4180.

3.3. Synthesis of the Complexes 3–6

For 3: A mixture of 0.53 g (1.0 mmol) of 1 and 0.23 g (1.2 mmol) potassium bis(trimethylsilyl)amide in 20 mL of toluene and 1 mL of tetrahydrofuran was stirred at 90 °C for 16 h. Solids were filtered off, and the filtrate was concentrated to dryness en vacuo. The thus obtained residue was dissolved in a boiling toluene/pentane mixture (2:1, 7 mL),
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and 3 crystallized as colourless blocks upon standing at room temperature; 0.19 g, 0.3 mmol, 30%. 1H NMR (400 MHz, C6D6): δ = 0.99–1.02 (m, 3H, (N(CH2CH2)=CH2)2(CH3)), 1.13–1.44 (m, 7H, (N(CH2CH2)=CH2)2(CH3)), 1.08–1.18 (d, 3JHH = 6.8 Hz, 6H, CH3(CH3)), 1.27 (d, 3JHH = 6.8 Hz, 6H, CH3(CH3)), 1.30 (d, 3JHH = 6.8 Hz, 6H, CH3(CH3)). 13C{1H} NMR (101 MHz, C6D6): δ = 22.5 (CH2(C6H5)), 23.1 (CH2(C6H5)), 24.2 (CH2(C6H5)), 25.1 (N(CH2CH2)=CH2(CH3)), 25.8 (O(CH2CH2)=CH2(CH3)), 25.9 (N(CH2CH2)=CH2(CH3)), 28.7 (CH3(CH3)), 29.1 (CH3(CH3)), 35.0 (N(CH2CH2)=CH2(CH3)), 40.0 (N(CH2CH2)N), 46.6 (N(CH2CH2)N), 50.2 (N(CH2CH2)=CH2(CH3)), 67.8 (O(CH2CH2)=CH2(CH3)), 121.7 (CHarom), 122.8 (CHarom), 123.6 (CHarom), 137.6 (CHarom), 138.8 (CHarom), 141.3 (N(C6hexasubstituted-1naphthalenyl)CNDipp), 144.0 (CHarom), 145.9 (N=CNDipp). IR (cm⁻¹): v(NH) = 3428, v(CH2) = 2958, v(CH3) = 2927, v(CH3) = 2864, v(CN) = 1570. Anal. Calcd for C39H48N2O: C, 71.31; H, 9.13; N, 10.94. Found: C, 69.41; H, 8.67; N, 10.44.

For 4: 0.53 g (1.0 mmol) of 1 were dissolved in 20 mL of toluene. Then, 1 mL of a trimethylaluminium solution (2 mmol, 2 M in toluene) was added at room temperature, and the solution was stirred for 16 h. The mixture was filtered, and the filtrate was concentrated to dryness en vacuo. The residue was dissolved in a boiling toluene/pentane mixture (2:1, 7 mL), and 4 crystallized as colourless blocks upon standing at room temperature; 0.19 g, 0.3 mmol, 30%. 1H NMR (400 MHz, C6D6): δ = −0.57 (s, 9H, Al(CH3)3), −0.56 (s, 6H, Al(CH3)2), 0.40–0.50 (m, 2H, (N(CH2CH2)=CH2)2(CH3)), 0.53–0.62 (m, 1H, (N(CH2CH2)=CH2)2(CH3)), 0.75–0.84 (m, 2H, (N(CH2CH2)=CH2)2(CH3)). 11B (δ, 3JHH = 6.8 Hz, 6H, CH3(CH3)), 1.13 (d, 3JHH = 6.8 Hz, 6H, CH3(CH3)), 1.18–1.29 (m, 3H, (N(CH2CH2)=CH2)2(CH3)), 1.33 (d, 3JHH = 6.8 Hz, 6H, CH3(CH3)), 1.40–1.44 (m, 2H, (N(CH2CH2)=CH2)2(CH3)), 1.60 (d, 3JHH = 6.8 Hz, 6H, CH3(CH3)), 2.85 (br, 1H, CH2CH2(CH3N)), 3.04 (sept, 3JHH = 6.8 Hz, 2H, CH3(CH3)), 3.23 (t, 3JHH = 7.3 Hz, 2H, NCH2CH2NHC), 3.29 (sept, 3JHH = 6.8 Hz, 2H, CH3(CH3)), 3.72 (t, 3JHH = 7.3 Hz, 2H, NCH2CH2NHC), 4.02 (d, 3JHH = 9.2 Hz, 1H, (HNcyclohexylamine-CNDipp), 6.99–7.09 (m, 3H, CHarom), 7.24 (br, 3H, CHarom). 13C{1H} NMR (101 MHz, C6D6): δ = −9.7 (Al(CH3)2), −6.1 (Al(CH3)3), 24.7 (N(CH2CH2)=CH2)2(CH3)), 24.8 (CH3(CH3)), 24.9 (CH3(CH3)), 25.1 (N(CH2CH2)=CH2)2(CH3)), 25.3 (CH3(CH3)), 25.4 (CH3(CH3)), 28.3 (CH3(CH3)), 29.9 (CH3(CH3)), 33.7 (N(CH2CH2)=CH2)2(CH3)), 47.9 (N(CH2CH2)N), 50.0 (N(CH2CH2)N), 55.5 (CNHC=N), 125.5 (m-CHarom), 125.8 (m-CHarom), 127.3 (p-CHarom), 129.0 (p-CHarom), 134.1 (N-CHarom), 138.8 (o-CHarom), 143.6 (o-CHarom), 154.7 (N(C6hexasubstituted-1naphthalenyl)CNDipp), 160.5 (N=CNDipp). 27Al NMR (104 MHz, C6D6): δ = no signal. IR (cm⁻¹): v(NH) = 3360, v(CH3) = 2959, v(CH3) = 2863, v(CN) = 1606. Anal. Calcd for C39H48N2Al2N5: C, 71.20; H, 9.96; N, 10.64. Found: C, 70.90; H, 9.71; N, 10.62.

For 5: 0.53 g (1.0 mmol) of 1 were dissolved in 20 mL of toluene, and the solution was heated to 90 °C, before 0.5 mL of a trimethylaluminium solution (1 mmol, 2 M in toluene) were added. After stirring for 16 h at 160 °C, the mixture was filtered at room temperature, and the filtrate was concentrated to dryness en vacuo. The residue was dissolved in a boiling toluene/pentane mixture (2:1, 7 mL), and 5 crystallized as colourless blocks upon standing at room temperature; 0.11 g, 0.2 mmol, 18%. 1H NMR (400 MHz, C6D6): δ = −0.51 (br, 12H, Al(CH3)2), 1.19 (d, 3JHH = 6.8 Hz, 12H, CH3(CH3)), 1.42 (d, 3JHH = 6.8 Hz, 12H, CH3(CH3)). 1H NMR (400 MHz, C6D6): δ = −0.51 (br, 12H, Al(CH3)2), 1.19 (d, 3JHH = 6.8 Hz, 12H, CH3(CH3)), 1.42 (d, 3JHH = 6.8 Hz, 12H, CH3(CH3)). 13C{1H} NMR (101 MHz, C6D6): δ = −7.0 (Al(CH3)2), 24.3 (CH3(CH3)), 26.0 (CH3(CH3)), 28.0 (CH3(CH3)), 42.8 (N(CH2CH2)N), 51.1 (N(CH2CH2)N), 124.7 (m-CHarom), 127.2 (p-CHarom), 141.5 (o-CHarom), 146.0 (N-CHarom), 168.9 (N=CNDipp). 27Al NMR (104 MHz, C6D6): δ = no signal. IR (cm⁻¹): v(NH) = 3396, v(CH2) = 2962, v(CH2) = 2945, v(CH2) = 2925, v(CH2) = 2886, v(CN) = 1593. Anal. Calcd for C34H38Al2N6: 0.65 C2H8: C, 69.87; H, 9.31; N, 12.68. Found: C, 65.83; H, 9.01; N, 12.93.

For 6: 0.46 g (1.0 mmol) of 2 were dissolved in 20 mL of toluene, and 0.5 mL of a trimethylaluminium solution (1 mmol, 2 M in toluene) were added at room temperature.
The mixture was stirred for 16 h, filtered, and the filtrate was concentrated to dryness en vacuo. The residue was dissolved in a boiling toluene/pentane mixture (2:1, 7 mL), and 6 crystallized as colourless blocks upon standing at room temperature; 0.22 g, 0.4 mmol, 36%. 1H NMR (400 MHz, CD2D2): δ = −0.53 (br, 6H, Al(CH3)2), 0.98 (d, 3JHH = 6.8 Hz, 6H, CHCH3), 1.27 (d, 3JHH = 6.8 Hz, 6H, CHCH3), 1.46 (d, 3JHH = 6.8 Hz, 6H, CHCH3), 1.68 (d, 3JHH = 6.8 Hz, 6H, CHCH3), 1.92 (t, 3JHH = 8.4 Hz, 2H, NCH2CH2N), 3.36 (sept, 3JHH = 6.8 Hz, 2H, CHCH3), 3.48 (br, 1H, CH2CH2CNH), 3.62 (sept, 3JHH = 6.8 Hz, 2H, CHCH3), 4.23 (t, 3JHH = 8.4 Hz, 2H, NCH2CH2N), 7.00–7.14 (m, 3H, CHarom), 7.29 (br, 3H, CHarom). 13C([1H] NMR (101 MHz, CD2D2): δ = −9.2 (Al(CH3)2), 24.3 (CHCH3), 25.1 (CHCH3), 25.3 (CHCH3), 26.7 (CHCH3), 28.4 (CHCH3), 29.3 (CHCH3), 38.4 (NCH2CH2N), 52.0 (NCH2CH2N), 124.7 (m-CHarom), 125.5 (m-CHarom), 127.2 (p-CHarom), 136.0 (o-CHarom), 141.5 (o-CHarom), 144.9 (p-CHarom), 156.2 (HNCNDipp), 184.3 (S=CNDipp). 27Al NMR (104 MHz, CD6D6): δ = no signal. IR [cm⁻¹]: ν(NH) = 3420, ν(CH3) = 2966, ν(CH3) = 2927, ν(CH3) = 2867, ν(CN) = 1617. Anal. Calcd for C30H45AlN4S · 1.05 C2H6; C, 72.65; H, 8.72; N, 9.07. Found: C, 73.14; H, 8.64; N, 9.51.

### 3.4. Crystallographic Details

The single crystal X-ray diffraction data for 1 were recorded on a GV-50 diffractometer with a TitanS2 detector from Rigaku Oxford Diffraction (formerly Agilent Technologies) applying a Cu Kα radiation (λ = 1.54184 Å). Analytical absorption corrections were applied to the data [28]. The intensity data for the compounds 3, 4, 5, and 6 were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account with a TitanS2 detector from Rigaku Oxford Diffraction (formerly Agilent Technologies)

Potentials of related complexes to be used for metal-ligand cooperativity, which we will investigate in the future.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/1424-8220/10/3/3390/inorganics9070052/s1: Table S1: Crystal data and refinement details for the X-ray structure.
3. Liew, S.K.; Al-Rafia, S.M.I.; Goettel, J.T.; Lummis, P.A.; McDonald, S.M.; Miedema, L.J.; Ferguson, M.J.; McDonald, R.; Rivard, Driess, M.; Yao, S.; Brym, M.; van Wüllen, C. A Heterofulvene-Like Germylene with a Betain Reactivity.

10. Driess, M.; Yao, S.; Brym, M.; van Wüllen, C. A New Type of N-Heterocyclic Silylene with Ambivalent Reactivity.

13. Schwamm, R.J.; Anker, M.D.; Lein, M.; Coles, M.P.; Fitchett, C.M. Indyllithium and the Indyl Anion InL⁻: Heavy Analogues of Reduction vs. Addition: The Reaction of an Aluminyl Anion with 1,3,5,7-

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