

Preparation of $[\text{LAl}(\mu\text{-S})_2\text{MCp}_2]$ ($\text{M} = \text{Ti}, \text{Zr}$) from the Structurally Characterized Lithium Complexes $[\{\text{LAl}(\text{SH})[\text{SLi}(\text{thf})_2]\}_2]$ and $[\{\text{LAl}[(\text{SLi})_2(\text{thf})_3]\}_2] \cdot 2\text{THF}$ **

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

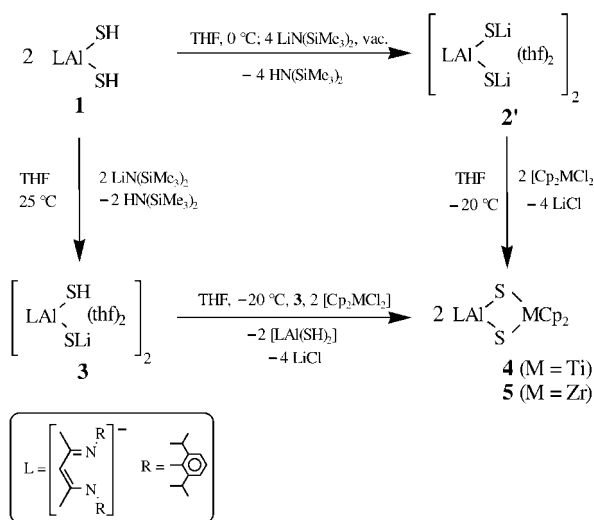
Recently, we reported the preparation of the unique monomeric $[\text{LAl}(\text{SH})_2]$ (**1**) ($\text{L} = \text{HC}(\text{CMeNAr})_2$; $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) comprising two terminal SH moieties.^[1] This unusual species led us to explore the substitution pattern of the SH protons, their exchange with transition metals would open a new route for the preparation of heterobimetallic sulfides containing aluminum. To date very few examples with aluminum bridging sulfide are known. Such species include $[(t\text{BuAl})(t\text{BuAlMe})_2(\mu_3\text{-S})_3\text{ZrCp}_2]$ ($\text{Cp} = \text{C}_5\text{H}_5$), prepared by degradation of the $[\{t\text{BuAl}(\mu_3\text{-S})\}_4]$ cage with two equivalents of $[\text{Cp}_2\text{ZrMe}_2]$.^[2] Moreover, there are known aluminum sulfides with $[\text{AlS}]_n$ core, which can be either planar ($n = 2$), cubic ($n = 4$), drum ($n = 6$), or possess more complex structures with an Al:S molar ratio different from 1:1.^[3]

Attempts to prepare heterobimetallic sulfides with **1** and ZnMe_2 or CdMe_2 through alkane elimination failed, in spite of the high affinity of these elements towards chalcogens.^[4] We observed even at low temperature only the formation of an inseparable mixture of products and the free ligand. This situation is in contrast to the successful preparation of $[\text{LAl}(\mu\text{-S})_2\text{AlL}]$ from **1** and $[\text{LAlH}_2]$.^[3] Following the protocol of Nöth et al. on the preparation of aluminum–lithium salts from LiAlH_4 and thiols,^[5] we chose the lithiation of **1** with MeLi and $n\text{BuLi}$ in diethyl ether or THF as an alternative route to the desired compounds. Unfortunately, under the given conditions the decomposition of **1** was observed. However, the difficulties encountered in the preparation of the dilithium salt $[\{\text{LAl}[(\text{SLi})_2(\text{thf})_3]\}_2] \cdot 2\text{THF}$ (**2**) were overcome by direct reaction of **1** with two equivalents of $\text{LiN}(\text{SiMe}_3)_2$ in THF at 0°C . The extremely sensitive pale yellow product **2** is a dimer solvated by eight molecules of THF as demonstrated by X-ray structural analysis. It has low solubility in THF and forms a microcrystalline precipitate within a few seconds of starting materials being mixed. The recovery of the crystals

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 $\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$; $\text{Cp} = \text{C}_5\text{H}_5$.

was performed within 15 min of the addition of the solvent to avoid decomposition caused by free $\text{HN}(\text{SiMe}_3)_2$. However, compound **2** loses THF upon drying in vacuo, leading to a dimeric product $[\{\text{LAl}[(\text{SLi})_2(\text{thf})_2]\}_2]$ (**2'**) containing only four molecules of THF as determined by ^1H NMR spectroscopy. This final product proved to be stable upon storage for several months under an inert atmosphere. After the successful isolation of **2'**, we became interested in the preparation of the monolithium salt $[\{\text{LAl}(\text{SH})[\text{SLi}(\text{thf})_2]\}_2]$ (**3**). To our knowledge such systems are not known for any kind of metal and, could be precursors for substitution reactions. For the preparation of **3** a similar method was used as for **2'**. After removal of all volatiles in vacuo compound **3** was isolated in 84 % yield. Moreover, no decomposition was detected in the presence of $\text{HN}(\text{SiMe}_3)_2$ or during the removal of the solvent, thus demonstrating a higher stability of **3** compared to that of **2**. As expected, **3** has a dimeric arrangement in the solid state, with each lithium coordinated to two molecules of THF and two sulfur atoms. The amount of THF in **3** remains unchanged even after keeping **3** for several hours in vacuo (Scheme 1).



Scheme 1. Synthesis of compounds **2'**–**5**.

We focused on reactivity studies of **2'** and **3** towards the transition-metal halides, namely $[\text{Cp}_2\text{TiCl}_2]$ and $[\text{Cp}_2\text{ZrCl}_2]$. When a solution of $[\text{Cp}_2\text{MCl}_2]$ ($\text{M} = \text{Ti}, \text{Zr}$) in THF was added dropwise to the solution of **2'** in THF at -20°C , the color of the resulting mixture became brownish-green, $\text{M} = \text{Ti}$, and deep yellow for $\text{M} = \text{Zr}$. After removal of the THF, extraction of the crude product with toluene and several purification steps, compounds $[\text{LAl}(\mu\text{-S})_2\text{MCp}_2]$ ($\text{M} = \text{Ti}$ (**4**), $\text{M} = \text{Zr}$ (**5**)) were isolated in 89 % and 85 % yield, respectively.

Surprisingly the reaction of **3** with $[\text{Cp}_2\text{TiCl}_2]$ or $[\text{Cp}_2\text{ZrCl}_2]$ in a molar ratio 2:1 does not yield the expected $[\{\text{LAl}(\text{SH})\text{S}\}_2\text{MCp}_2]$ but rather a mixture of **1** and **4** (or **5**) is formed. This result suggests that the formation of the four-membered ring $[\text{LAl}(\mu\text{-S})_2\text{MCp}_2]$ is preferred over a $\text{LAl}(\text{SH})\text{-S-M}(\text{Cp})_2\text{-S-Al}(\text{SH})\text{L}$ chain arrangement containing free SH groups. One pathway for the formation of **1** and **4** (or **5**) in the above reaction may involve the intermediate

$[\text{LAl}(\text{SH})(\mu\text{-S})\text{M}(\text{Cl})\text{Cp}_2]$, followed by a translithiation with a second molecule of **3**, yielding **1** and $[\text{LAl}(\text{SLi})(\mu\text{-S})\text{M}(\text{Cl})\text{Cp}_2]$. Subsequently, $[\text{LAl}(\text{SLi})(\mu\text{-S})\text{M}(\text{Cl})\text{Cp}_2]$ undergoes an intramolecular elimination of LiCl to yield $[\text{LAl}(\mu\text{-S})_2\text{MCp}_2]$. A second possible mechanism is an in situ formation of $[\{\text{LAl}(\text{SH})(\mu\text{-S})\}_2\text{MCp}_2]$ followed by its rapid rearrangement to yield **1** and **4** (or **5**) (Scheme 1).

X-ray quality crystals of **2** and **3** were obtained by slow cooling their THF solutions.^[6] Both derivatives crystallize in the monoclinic space group $P2_1/n$ as pale yellow crystals. Compound **3** shows a simple coordination environment for the Li atoms $[\text{LAl}(\text{SH})(\mu_3\text{-S})(\mu\text{-Li-2 THF})_2(\mu_3\text{-S})\text{Al}(\text{SH})\text{L}]$, while the structure of **2** is more complex and none of the four lithium atoms are equivalent. As depicted in Figure 1, the lithium atoms Li(1), Li(2) and Li(4) are coordinated by two, one, and three THF molecules, respectively, whereas Li(3) is not coordinated to THF. This diversity is due to the steric bulk of the ligand L.

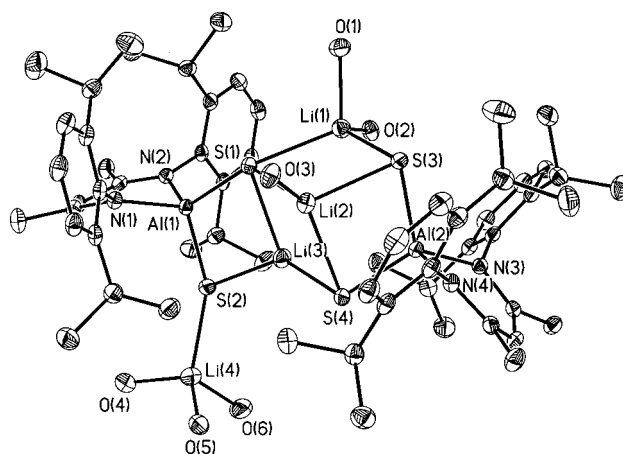


Figure 1. Molecular structure of $[\{\text{LAl}[(\text{SLi})_2(\text{thf})_3]\}_2] \cdot 2\text{THF}$ (**2**); thermal ellipsoids set at 50% probability. All hydrogen atoms, noncoordinated THF molecules and carbon atoms of the coordinating THF molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–S(1) 2.186(1), Al(1)–S(2) 2.182(1), Al(2)–S(3) 2.173(1), Al(2)–S(4) 2.181(1), Li(1)–S(1) 2.482(2), Li(1)–S(3) 2.414(2), Li(2)–S(1) 2.544(2), Li(2)–S(3) 2.449(2), Li(2)–S(4) 2.565(2), Li(3)–S(1) 2.502(2), Li(3)–S(2) 2.345(2), Li(3)–S(4) 2.323(2), Li(4)–S(2) 2.343(3); S(1)–Al(1)–S(2) 111.6(1), S(3)–Al(2)–S(4) 113.0(1), Al(1)–S(1)–Li(1) 149.6(1), Al(1)–S(1)–Li(2) 126.3(1), Al(1)–S(1)–Li(3) 74.3(1), Al(1)–S(2)–Li(3) 77.7(1), Al(1)–S(2)–Li(4) 152.1(1), Al(2)–S(3)–Li(1) 114.8(1), Al(2)–S(3)–Li(2) 76.3(1), Al(2)–S(4)–Li(2) 73.7(1), Al(2)–S(4)–Li(3) 118.0(1), Li(1)–S(1)–Li(2) 68.2(1), Li(1)–S(1)–Li(3) 92.5(1), Li(1)–S(3)–Li(2) 70.8(1), Li(2)–S(1)–Li(3) 66.0(1), Li(2)–S(4)–Li(3) 68.2(1), Li(3)–S(2)–Li(4) 116.8(1), S(1)–Li(1)–S(3) 112.1(1), S(1)–Li(2)–S(3) 108.9(1), S(1)–Li(2)–S(4) 107.8(1), S(1)–Li(3)–S(2) 96.4(1), S(1)–Li(3)–S(4) 117.6(1), S(2)–Li(3)–S(4) 134.6(1), S(3)–Li(2)–S(4) 92.8(1).

The two THF molecules coordinated to Li(1) require there to be more space between the 2,6-*i*-Pr₂C₆H₃ moieties of L and thus force the substituents on the opposite side closer together. This steric pressure results in Li(4) being pushed out of the central area of the dimer. Subsequently the coordination of three THF molecules covers the unsaturated sites on Li(4). For the two remaining Li atoms, the situation is similar.

Li(2) can still be coordinated by one THF molecule whereas Li(3) is coordinated only to three sulfur atoms. These different coordination sites of lithium atoms are compensated by the variation of the Li–S bond lengths (2.323–2.565 Å). The $\text{Al}_2\text{S}_4\text{Li}_4$ core can also be described as being a six-membered AlS_3Li_2 ring with alternating sulphur and metal atoms, which is capped by another lithium atom and a bent Al–S–Li unit is joined to one of the S–Li edges of this hexagonal pyramid to form a condensed four-membered AlS_2Li ring. The shortness of the S(4)–Li(3) bond (2.323 Å) is caused by the unsaturated coordination sphere of Li(3) which contains only three sulfur atoms and is one of the shortest S–Li bonds observed to date.^[7a–c] All the other S–Li bonds of **2** (2.343–2.565 Å) and **3** (2.424 and 2.478 Å) are in the range observed for similar species (2.327–2.964 Å).^[5,7] Figure 2 shows the molecular structure of **3** in which the S_2Li_2 core is essentially planar owing to the crystal symmetry.

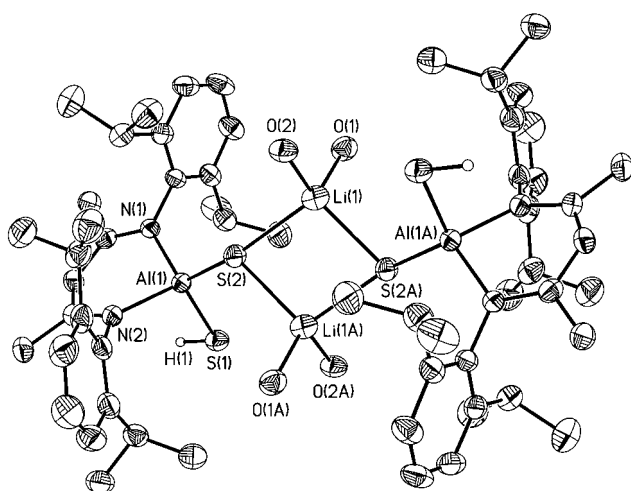


Figure 2. Molecular structure of $[\{\text{LAL}(\text{SH})[\text{SLi}(\text{thf})_2]\}_2]$ (**3**); thermal ellipsoids set at 50% probability. All hydrogen atoms (except those of the S–H moieties), and the carbon atoms of the THF molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.928(2), Al(1)–N(2) 1.935(2), Al(1)–S(1) 2.268(1), Al(1)–S(2) 2.123(1), H(1)–S(1) 1.28(5), Li(1)–S(2) 2.478(5), Li(1)–S(2A) 2.424(5); S(1)–Al(1)–S(2) 115.7(1), Al(1)–S(2)–Li(1) 151.6(1), Al(1)–S(2)–Li(1A) 111.7(1), Li(1)–S(2)–Li(1A) 78.0(2), S(2)–Li(1)–S(2A) 102.0(2).

This S_2Li_2 motif can be found in many substances containing these two elements including **2**.^[5,7] The free SH groups are not involved in any kind of hydrogen bonding and are orientated *trans* to each other.

Crystals of **4** were obtained by slow cooling of its toluene/hexane solution.^[6] **4** crystallizes in the monoclinic space group $P2_1$ and its molecular structure is shown in Figure 3.

The AlS_2Ti ring is essentially planar with the sum of inner angles of 360°. The widest angle (102.5°) corresponds to that at the aluminum center, while the one at the titanium center is almost a right angle (89.3°). The Ti– X_{Cp} separations (X_{Cp} is the centroid of the Cp group) are 2.091 and 2.090 Å and the $\text{X}_{\text{Cp1}}\text{–Ti–X}_{\text{Cp2}}$ angle is 130°. All these data are in good agreement with those reported for $[\text{Cp}_2\text{Ti}(\mu\text{-S})\text{ML}'\text{L}']$ (e.g. M = Si, Ti, Ru, L' = Cp, L'' = Cl) species (2.425–2.458 Å for

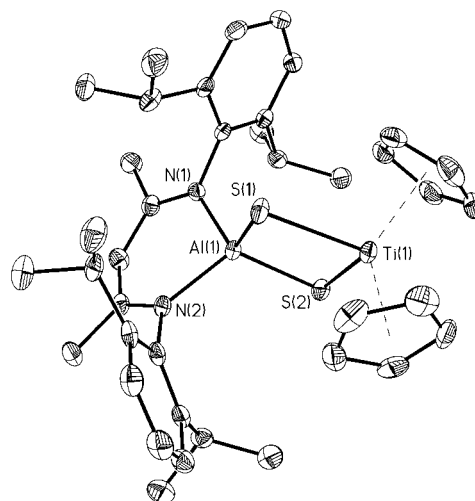


Figure 3. Molecular structure of $[\text{LAL}(\mu\text{-S})_2\text{TiCp}_2]$ (**4**); thermal ellipsoids set at 50% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.918(2), Al(1)–N(2) 1.921(2), Al(1)–S(1) 2.208(1), Al(1)–S(2) 2.197(1), Ti(1)–S(1) 2.416(1), Ti(1)–S(2) 2.473(1), Ti(1)– X_{Cp1} 2.091(3), Ti(1)– X_{Cp2} 2.090(3); S(1)–Al(1)–S(2) 102.5(1), Al(1)–S(1)–Ti(1) 84.7(1), Al(1)–S(2)–Ti(1) 83.6(1), S(1)–Ti(1)–S(2) 89.3(1), $\text{X}_{\text{Cp1}}\text{–Ti(1)–X}_{\text{Cp2}}$ 130.0(2); X = centroid of Cp ring.

Ti–S, 2.059–2.093 Å for $\text{X}_{\text{Cp}}\text{–Ti}$, 129.6–131.6° for $\text{X}_{\text{Cp1}}\text{–Ti–X}_{\text{Cp2}}$ and 86.5–95.9° for S–Ti–S).^[8] The substitution of the SH protons by Li or Ti has a significant influence on the Al–S bond length. The Al–S bond lengths decrease in the series from **1** (2.223 Å and 2.217 Å)^[1] to **4** (2.208 and 2.197 Å), to **2** (2.173–2.186 Å) and finally to **3** (2.123 Å). The partial negative charge on the substituted S atom in **3** causes a shortening of the Al–S bond and thus, increases the electron density on the aluminum center resulting in an elongation of the Al–S(H) bond (2.268 Å).

In summary, we have developed a new strategy for the preparation of heterobimetallic sulfides containing aluminum and isolated four new species. Furthermore, the lithium salts $[\{\text{LAL}[(\text{SLi})_2(\text{thf})_2]\}_2]$ and $[\{\text{LAL}(\text{SH})[\text{SLi}(\text{thf})_2]\}_2]$ are promising precursors for further reactions.

Experimental Section

All manipulations were performed under a dry and oxygen-free atmosphere (N_2 or Ar) using Schlenk-line and glovebox techniques. **2**: Compound **1** (2.000 g, 3.916 mmol) and $\text{LiN}(\text{SiMe}_3)_2$ (1.311 g, 7.832 mmol) were mixed as solids in a flask and subsequently cold THF (70 mL, 0°C) was added. Within a few seconds pale yellow crystals of **2** started to precipitate from the reaction mixture. After 5 min of stirring at 0°C, the reaction mixture was cooled to –20°C and maintained at this temperature for 5–10 min under vigorous stirring to support the crystallization. The time allowed for the crystallization is determined by the color of the solution. The original pale yellow color of the solution turned slowly into a dark brown, which indicates decomposition of the product. Thus, the filtration of the microcrystalline product should occur within the first significant color change of the mother liquor. After washing the crude product with cold THF (5 mL) and drying in vacuo, **2** was obtained as a pale yellow powder. Yield 2.19 g (84%). M.p. 320°C (decomp). ^1H NMR (500 MHz, $[\text{D}_8]\text{THF}$, 25°C, TMS): δ = 1.07 (d, $^3J(\text{H,H})$ = 6.8 Hz, 24H,

CH(CH₃)₂), 1.25 (d, ³J(H,H) = 6.8 Hz, 24H, CH(CH₃)₂), 1.51 (s, 12H, CH₃), 1.77 (m, 16H, O(CH₂CH₂)₂), 3.62 (m, 16H, O(CH₂CH₂)₂), 4.00 (sept, ³J(H,H) = 6.8 Hz, 8H, CH(CH₃)₂), 5.01 (s, 2H, CH), 7.00–7.01 ppm (m, 12H, *m*-, *p*-Ar(H)); ¹³C NMR (125.8 MHz, [D₈]THF, 25 °C, TMS): δ = 24.7 (CH(CH₃)₂), 24.8 (CH(CH₃)₂), 26.4 (O(CH₂CH₂)₂), 27.4 (CH(CH₃)₂), 28.7 (CH₃), 68.2 (O(CH₂CH₂)₂), 98.1 (γ-CH), 124.2, 126.2, 145.1, 146.1 (*i*-, *o*-, *m*-, *p*-C of Ar), 168.1 ppm (C=N); ⁷Li NMR (116.6 MHz, [D₈]THF, 25 °C, LiCl, 1M in D₂O): δ = 1.26 (SLI). Elemental analysis calcd (%) for C₇₄H₁₁₄Al₂Li₄N₄O₈S₄ (1333.71): C 66.64, H 8.62, N 4.20; found: C 65.70, H 8.57, N 4.27.

3: Compound **1** (1.000 g, 1.958 mmol) and LiN(SiMe₃)₂ (0.328 g, 1.958 mmol) were mixed as solids in a flask and subsequently THF (30 mL) was added at ambient temperature. The mixture was stirred for 5 min, all the volatiles were removed in vacuo. The crude product was washed with cold hexane (5 mL) to remove the remaining HN(SiMe₃)₂, yielding **3** as a pale yellow powder. Yield 1.11 g (85 %). M.p. 230 °C (decomp). ¹H NMR (500 MHz, [D₈]THF, 25 °C, TMS): δ = -1.00 (s, 2H, SH), 1.04 (d, ³J(H,H) = 6.8 Hz, 12H, CH(CH₃)₂), 1.21 (d, ³J(H,H) = 6.8 Hz, 12H, CH(CH₃)₂), 1.25 (d, ³J(H,H) = 6.8 Hz, 12H, CH(CH₃)₂), 1.40 (d, ³J(H,H) = 6.8 Hz, 12H, CH(CH₃)₂), 1.69 (s, 12H, CH₃), 1.77 (m, 16H, O(CH₂CH₂)₂), 3.62 (m, 16H, O(CH₂CH₂)₂), 3.77 (sept, ³J(H,H) = 6.8 Hz, 4H, CH(CH₃)₂), 3.85 (sept, ³J(H,H) = 6.8 Hz, 4H, CH(CH₃)₂), 5.13 (s, 2H, CH), 7.06–7.16 ppm (m, 12H, *m*-, *p*-Ar-H); ¹³C NMR (125.8 MHz, [D₈]THF, 25 °C, TMS): δ = 24.3 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 26.4 (O(CH₂CH₂)₂), 28.0 (CH(CH₃)₂), 28.5 (CH(CH₃)₂), 29.6 (CH₃), 68.2 (O(CH₂CH₂)₂), 97.6 (γ-CH), 124.1, 134.3, 126.4, 143.6, 145.7, 146.0 (*i*-, *o*-, *m*-, *p*-C of Ar), 169.0 ppm (C=N); ⁷Li NMR (116.6 MHz, [D₈]THF, 25 °C, LiCl, 1M in D₂O) δ = 0.32 (SLI). IR(KBr pellet): 2552 vw (SH) cm⁻¹. Elemental analysis calcd (%) for C₇₄H₁₁₆Al₂Li₂N₄O₈S₄ (1321.84): C 67.24, H 8.85, N 4.24; found: C 66.45, H 8.45, N 4.52.

4: A solution of [Cp₂TiCl₂] (0.224 g, 0.900 mmol) in THF (20 mL) was added dropwise to a solution of **2** (0.600 g, 0.450 mmol) in THF (40 mL) at -20 °C. During the addition, the color of the solution changed to deep brown-green. After the addition was complete, the reaction mixture was stirred for additional 5 min at -20 °C and then allowed to warm to ambient temperature. The solvent was removed in vacuo and the crude product was extracted twice with cold toluene (15 mL, 5 °C). After filtration, removing of the toluene from the filtrate, washing of the product with a cold toluene:pentane (5 mL, 1:4) mixture and drying in vacuo, **4** was obtained as a brown-green powder. Yield 0.55 g (89 %). Decomposition without melting at 270 °C. ¹H NMR (500 MHz, C₆D₆, 25 °C, TMS): δ = 1.06 (d, ³J(H,H) = 6.8 Hz, 12H, CH(CH₃)₂), 1.64 (s, 6H, CH₃), 1.88 (d, ³J(H,H) = 6.8 Hz, 12H, CH(CH₃)₂), 3.57 (sept, ³J(H,H) = 6.8 Hz, 4H, CH(CH₃)₂), 4.84 (s, 1H, CH), 5.71 (s, 10H, C₅H₅), 7.30(-7.37 ppm (m, 6H, *m*-, *p*-Ar(H)); ¹³C NMR (125.8 MHz, C₆D₆, 25 °C, TMS): δ = 24.0 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 29.1 (CH₃), 94.9 (γ-CH), 118.3 (C₅H₅), 125.0, 128.0, 140.6, 146.0 (*i*-, *o*-, *m*-, *p*-C of Ar), 170.2 ppm (C=N); ²⁷Al NMR (78.2 MHz, C₆D₆, 25 °C, [Al(H₂O)₆]³⁺) δ = 94 ppm. MS (70 eV): *m/z* (%): 686 (8) [*M*⁺], 621 (100) [*M*⁺(Cp)]. Elemental analysis calcd (%) for C₃₉H₅₁AlN₂S₂Ti (686.83): C 68.20, H 7.48, N 4.08; found: C 67.61, H 7.46, N 4.02.

5: preparation like that of **4** from [Cp₂ZrCl₂] (0.263 g, 0.900 mmol) and **2** (0.600 g, 0.450 mmol). The product was isolated as a deep yellow powder. Yield 0.56 g (85 %). Decomposition without melting at 180 °C. ¹H NMR (500 MHz, C₆D₆, 25 °C, TMS): δ = 1.06 (d, ³J(H,H) = 6.8 Hz, 12H, CH(CH₃)₂), 1.65 (s, 6H, CH₃), 1.82 (d, ³J(H,H) = 6.8 Hz, 12H, CH(CH₃)₂), 3.59 (sept, ³J(H,H) = 6.8 Hz, 4H, CH(CH₃)₂), 4.87 (s, 1H, CH), 5.65 (s, 10H, C₅H₅), 7.22–7.32 ppm (m, 6H, *m*-, *p*-Ar(H)); ¹³C NMR (125.8 MHz, C₆D₆, 25 °C, TMS): δ = 24.4 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 29.0 (CH₃), 95.1 (γ-CH), 114.4 (C₅H₅), 124.9, 128.0, 140.1, 146.1 (*i*-, *o*-, *m*-, *p*-C of Ar), 170.6 ppm (C=N); ²⁷Al NMR (78.2 MHz, C₆D₆, 25 °C, [Al(H₂O)₆]³⁺) δ = 101 ppm. MS (70 eV): *m/z* (%): 728 (58) [*M*⁺], 663 (100) [*M*⁺(Cp)].

Elemental analysis calcd (%) for C₃₉H₅₁AlN₂S₂Zr (730.17): C 64.15, H 7.04, N 3.84; found: C 63.09, H 7.30, N 3.83.

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