Mixed-Metal Complexes

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# Preparation of Heterobimetallic Oxide–Hydroxide–Hydrogensulfides [LAl(OH)(μ-O)MCp$_2$(SH)] (M = Ti, Zr)**

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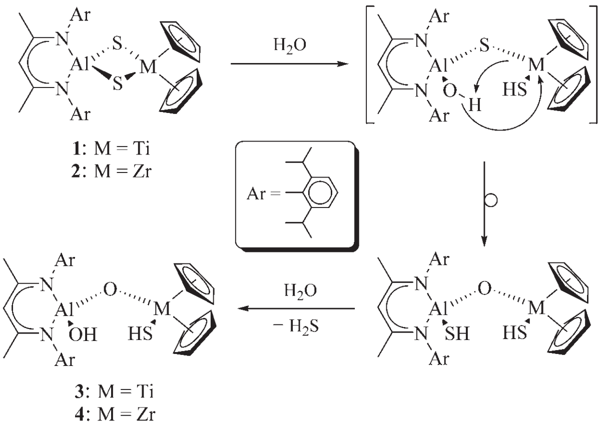
*Dedicated to Professor Thomas B. Rauchfuss*

Recently we reported the preparation of heterobimetallic sulfides that contained aluminum atoms [LAl(μ-S)$_2$MCp$_2$] (M = Ti, **1**; M = Zr, **2**; L = HC[C(Me)N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$; Cp = C$_5$H$_5$).[1] The X-ray crystal structural analysis of the titanium compound **1** confirmed the presence of a highly strained {Al(μ-S)$_2$Ti} four-membered ring (S-Al-S 102.5(1), Al-S-Ti 84.7(1) and 83.6(1), S-Ti-S 89.3(1)°). The ring strain and the short Al···Ti separation (3.118 Å) prompted us to examine the reactivity of **1** and **2** with water in expectation of a nucleophilic attack that would lead to the opening of the ring and to the isolation of compounds containing the {LAl(EH)(μ-E)M(EH)Cp$_2$} framework (E = O or S depending on the degree of hydrolysis). Such species could serve as unique precursors for the preparation of trimetallic systems comparable with the alumoxane [(μ-O)[LAl(μ-O)]$_2$AlMe], which is prepared from [(μ-O)[LAl(OH)]$_2$] and AlMe$_2$H.[2] Although a few dinuclear systems that contain the {M′(EH)-(μ-E)M(EH)} arrangement have been described (M′ = Al,[2] Fe,[3a] Ge,[3b,c] In,[3d] Re,[3e] Ru,[3f] Sn,[3g] V,[3h] Zr[3i]) none has been structurally characterized that contains two different metal atoms stabilized by organic ligands.

The addition of two equivalents of water to a solution of **1** or **2** in THF at room temperature led, after overnight stirring, to the precipitation of a crystalline material. H$_2$S was identified as a by-product. The solid product was filtered off, dried in vacuo, and isolated as pale brown (Ti) or pale yellow (Zr) microcrystals. The $^1$H NMR spectroscopic, EI mass spectrometric, and X-ray crystal structural analysis of these products confirmed that the ring-opening reaction had occurred, but revealed the presence of two derivatives in the samples. The major component (about 85 %) was identified as [LAl(OH)(μ-O)MCp$_2$(SH)] (M = Ti, **3**; M = Zr, **4**) whereas the minor component (about 15 %) was the intermediate of the hydrolysis, [LAl(SH)(μ-O)MCp$_2$(SH)]. One of the first steps of the hydrolytic ring opening is the formation of an unobserved intermediate [LAl(OH)(μ-S)MCp$_2$(SH)], which subsequently rearranges into [LAl(SH)(μ-O)MCp$_2$(SH)]. The driving force for this intramolecular rearrangement is the high oxophilicity of the metal centers and the higher stability of the {Al-O-Ti} frame compared to {Al-S-Ti}.[4] Compound [LAl(SH)(μ-O)MCp$_2$(SH)] reacts with a second equivalent of water with elimination of H$_2$S to form **3** or **4** (Scheme 1).



**Scheme 1.** Preparation of compounds **3** and **4**.

After elucidating the course of the hydrolysis, we focused on the optimization of the hydrolysis conditions. The presence of the intermediates in the final product can be explained by the low solubility of the bridged species in THF and their crystallization from the mother liquor before the reaction was complete. Thus, the use of THF/CH$_2$Cl$_2$ (1:1) in the reaction mixture led to the formation of pure **3** or **4**. It is surprising that in these reactions, the Al–S bond is more reactive than the M–S bond. [LAl(SH)$_2$] reacts smoothly with two equivalents of water to give [LAl(OH)$_2$] with elimination of H$_2$S,[5] but the reaction is relatively slow and needs at least 20 minutes to reach completion at room temperature. It was reported that even traces of moisture in systems that contain Ti–S or Zr–S bonds lead to fast hydrolysis of these bonds.[6] As reported earlier, the alumoxane [{LAl(OH)}$_2$O][2] is stable, whereas [LAl(OH)$_2$] decomposes even under an inert atmosphere.[7] It seems that the presence of at least one bridging oxygen atom is necessary for the stabilization of the species containing the {AlO$_2$} unit.

The isomorphous compounds **3** and **4** crystallize in the monoclinic space group $P2_1/n$, with one molecule in the asymmetric unit (Figure 1).[8] We were not able to crystallize pure **4**, thus data for **4** contaminated with about 15 % of the intermediate [LAl(SH)(μ-O)Zr(SH)Cp$_2$] were used. The OH moiety on the Al atom and the SH groups on the Ti (**3**) and Zr (**4**) atoms adopt a *cis* conformation and are involved in an intramolecular hydrogen bond O–H···S (**3** 2.66 Å; **4** 2.80 Å). The Al–O(H) (**3** 1.726 Å; **4** 1.720 Å) and Al–O(M) (**3** 1.717 Å; **4** 1.713 Å) bond lengths are similar to those in [LAl(OH)$_2$] (1.711 and 1.695 Å),[9] [{LAl(OH)}$_2$O] (1.694–1.741 Å),[2] and in the trimeric alumoxane [(μ-O)[LAl(μ-O)]$_2$(MeAl)] (1.726–1.708 Å),[2] but considerably shorter than those in the μ-OH derivatives (1.787–1.928 Å).[10] The O-Al-O angles (**3** 114.0°; **4** 114.7°) are similar to those of

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[**] L = HC[C(Me)N(Ar)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

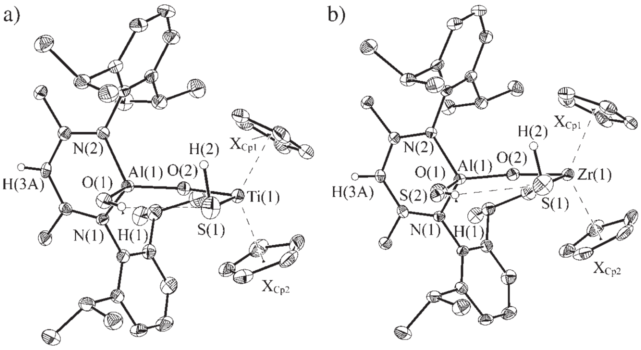

***Figure 1.*** XP plots at the 50% probability level of **3** (a) and **4** (b; the presence of the reaction intermediate that contains an SH group on the aluminum atom, the proton of which could not be localized, is obvious). Hydrogen atoms except those of the SH and OH groups and the H(3A) protons are omitted for clarity. Selected bond lengths [Å] and angles [°]: **3**: Al(1)-N(1) 1.897(2), Al(1)-N(2) 1.901(2), Al(1)-O(1) 1.726(2), Al(1)-O(2) 1.719(2), O(1)-H(1) 0.85(2), Ti(1)-O(2) 1.820(2), Ti(1)-S(1) 2.482(1), S(1)-H(2) 1.25(3), Ti(1)-$X_{Cp1}$ 2.107(3), Ti(1)-$X_{Cp2}$ 2.098(3); N(1)-Al(1)-N(2) 95.7(1), O(1)-Al(1)-O(2) 114.0(1), Al(1)-O(1)-H(1) 119(3), Al(1)-O(2)-Ti(1) 148.9(1), O(2)-Ti(1)-S(1) 97.3(1), Ti(1)-S(1)-H(2) 100(2), $X_{Cp1}$-Ti(1)-$X_{Cp2}$ 128.6(2). **4**: Al(1)-N(1) 1.895(2), Al(1)-N(2) 1.898(2), Al(1)-O(1) 1.720(6), Al(1)-S(2) 2.08(1), Al(1)-O(2) 1.713(2), O(1)-H(1) 0.85(2), Zr(1)-O(1) 1.939(2), Zr(1)-S(1) 2.573(1), S(1)-H(2) 1.19(3), Zr(1)-$X_{Cp1}$ 2.237(3), Zr(1)-$X_{Cp2}$ 2.240(3); N(1)-Al(1)-N(2) 96.1(1), O(1)-Al(1)-O(2) 114.7(2), O(2)-Al(1)-S(2) 112.2(4), Al(1)-O(1)-H(1) 122(3), Zr(1)-S(1)-H(1) 100(2), Al(1)-O(2)-Zr(1) 147.2(1), O(2)-Zr(1)-S(1) 98.7(1), $X_{Cp1}$-Zr(1)-$X_{Cp2}$ 128.0(2).

[LAl(OH)$_2$], [{LAl(OH)}$_2$O], and [(μ-O)[LAl(μ-O)]$_2$(MeAl)] (108.3–115.3°);[2,9] the Al-O-M angles are 148.9° for **3** and 147.2° for **4**. The Ti–O (1.820 Å) and Ti–S (2.482 Å) bond lengths and the O-Ti-S angle (97.3°) are similar to those reported for other [Cp$_2$TiOS] fragments: Ti–O 1.845–1.872 Å; Ti–S 2.314–2.467 Å; O-Ti-S 87.7–97.9°.[11] Furthermore, in the zirconium derivative the Zr–O (1.939 Å) and Zr–S (2.573 Å) bond lengths and the O-Zr-S angle (98.7 Å) are similar to those reported previously for species that contain the {Cp$_2$ZrOS} moiety: Zr–S 2.459–2.554 Å; Zr–O 1.941–2.199 Å; O-Zr-S 92.6–103.3°.[6b,12]

In summary, the heterobimetallic sulfides [LAl(μ-S)$_2$MCp$_2$] are ideal precursors for the preparation of the heterobimetallic oxide–hydroxide–hydrogensulfides **3** and **4** by hydrolysis. The presence of two free reactive functionalities in a *cis* arrangement makes them potential starting materials for the heterotrimetallic oxide–sulfides. Such reactions are the subject of our ongoing research.

## *Experimental Section*

All manipulations were performed under a dry and oxygen-free atmosphere (N$_2$ or Ar) by using Schlenk-line and glovebox techniques.

**3**: H$_2$O (26 μL, 1.46 mmol) was added quickly to a solution of **1** (0.50 g, 0.73 mmol) in THF/CH$_2$Cl$_2$ (45 mL, 1:1) at room temperature. The suspension was stirred for 10 h and filtered. All the volatile species were removed under vacuum to leave a brown solid residue, which was treated twice with cold toluene (5 mL). After filtration and drying in vacuo, **3** was obtained as a light brown powder. Yield 0.31 g (60%); m.p.: 227 °C (decomp); $^1$H NMR (500.13 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 1.07$ (s, 1H, OH), 1.10 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, CH(C$H_3$)$_2$), 1.20 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 6H, CH(C$H_3$)$_2$), 1.37 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, CH(C$H_3$)$_2$), 1.44 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 6H, CH(C$H_3$)$_2$), 1.77 (s, 6H, CH$_3$), 2.08 (s, 1H, SH), 3.03 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, C$H$(CH$_3$)$_2$), 3.49 (sept, $^3J_{\text{H-H}} = 6.7$ Hz, 2H, C$H$(CH$_3$)$_2$), 5.20 (s, 1H, γ-CH), 5.36 (s, 10H, Cp–$H$), 7.04–7.20 ppm (m, 6H, *m*-, *p*-Ar–$H$); $^{13}$C NMR (125.77 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 23.6$, 24.2, 24.4, 24.7 (CH($C$H$_3$)$_2$), 26.1, 27.5 ($C$H(CH$_3$)$_2$), 28.7 (CH$_3$), 97.5 (γ-CH), 113.9 (C of Cp) 124.0, 125.2, 127.3, 140.9, 142.9, 145.6 (*i*-, *o*-, *m*-, *p*-C of Ar), 170.6 ppm (C=N); IR (KBr pellet): $\tilde{\nu} = 3551$ br (OH), 2574 vw (SH) cm$^{-1}$; EI MS (70 eV): *m/z* (%): 623 (10, [$M-$Cp]$^+$), 605 (50, [$M-$Cp$-$H$_2$O]$^+$); elemental analysis calcd for C$_{39}$H$_{53}$AlN$_2$O$_2$STi (688.78 g mol$^{-1}$): C 68.0, H 7.8, N 4.1; found: C 67.5, H 8.0, N 4.2%.

**4**: The synthesis of **4** was similar to that of **3**. Compound **4** was obtained from the reaction of H$_2$O (25 μL, 1.37 mmol) with **2** (0.50 g, 0.69 mmol) as a pale yellow powder. Yield 0.31 g (62%); m.p.: 235 °C (decomp); $^1$H NMR (500.13 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 0.36$ (s, 1H, OH), 1.11 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CH(C$H_3$)$_2$), 1.21 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CH(C$H_3$)$_2$), 1.38 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CH(C$H_3$)$_2$), 1.39 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CH(C$H_3$)$_2$), 1.65 (s, 1H, SH), 1.77 (s, 6H, C$H_3$), 3.04 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, C$H$(CH$_3$)$_2$), 3.50 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, C$H$(CH$_3$)$_2$), 5.20 (s, 1H, γ-C$H$), 5.46 (s, 10H, Cp-$H$), 7.04–7.20 ppm (m, 6H, *m*-, *p*- Ar-$H$); $^{13}$C NMR (125.77 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 23.5$, 24.4, 24.5, 24.6 (CH($C$H$_3$)$_2$), 27.5, 28.6 ($C$H(CH$_3$)$_2$), 28.7 (CH$_3$), 97.4 (γ-CH), 111.8 (C of Cp) 124.0, 125.1, 127.3, 140.6, 143.2, 145.5 (*i*-, *o*-, *m*-, *p*- C of Ar), 170.6 ppm (C=N); IR (KBr pellet): $\tilde{\nu} = 3560$ br (OH), 2562 vw (SH) cm$^{-1}$; EI-MS (70 eV): *m/z* (%): 665 (5, [$M-$Cp]$^+$), 647 (50, [$M-$Cp$-$H$_2$O]$^+$); elemental analysis calcd for C$_{39}$H$_{53}$AlN$_2$O$_2$SZr (732.12 g·mol$^{-1}$): C 64.0, H 7.3, N 3.8; found: C 63.5, H 7.4, N 3.9%.

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[4] One can argue that the unobserved intermediate could be [LAl(SH)(μ-S)MCp$_2$(OH)], rather than [LAl(OH)(μ-S)MCp$_2$(SH)]. However, the higher stability of the Ti–SH bond towards hydrolysis, the shielding of the Ti center by two Cp rings, and the easy replacement of the Al–SH group by an Al–OH moiety in the next reaction step support our conclusion.

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[8] a) Crystal data for **3**: $C_{39}H_{53}AlN_2O_2STi$ (688.77), monoclinic, space group $P2_1/n$, $a = 10.903(2)$, $b = 20.543(4)$, $c = 16.222(3)$ Å, $\beta = 99.02(3)°$, $V = 3589(1)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.275$ Mg m$^{-3}$, $F(000) = 1472$, $\lambda = 1.54178$ Å, $T = 100(2)$ K, $\mu(Cu_{K\alpha}) = 3.075$ mm$^{-1}$. Of the 22938 measured reflections, 5087 were independent ($R_{int} = 0.0495$). The final refinements converged at $R1 = 0.0397$ for $I > 2\sigma(\mathrm{I})$, $wR2 = 0.1125$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of $-0.260/+0.477$ e Å$^{-3}$; b) crystal data for **4**: $C_{39}H_{53}AlN_2O_{1.87}S_{1.13}Zr$ (734.14), monoclinic, space group $P2_1/n$, $a = 11.064(2)$, $b = 20.627(3)$, $c = 16.242(3)$ Å, $\beta = 97.76(3)°$, $V = 3673(1)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.328$ Mg m$^{-3}$, $F(000) = 1548$, $\lambda = 1.54178$ Å, $T = 100(2)$ K, $\mu(Cu_{K\alpha}) = 3.548$ mm$^{-1}$. Of the 15708 measured reflections, 5150 were independent ($R_{int} = 0.0351$). The final refinements converged at $R1 = 0.0291$ for $I > 2\sigma(\mathrm{I})$, $wR2 = 0.0764$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of $-0.447/+0.399$ e Å$^{-3}$; c) data for the structures were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector. Intensity measurements were performed on a rapidly cooled crystal ($0.40 \times 0.30 \times 0.30$ mm$^3$) in the range $7.00 \leq 2\theta \leq 117.92°$ (**3**) and in the range $6.96 \leq 2\theta \leq 117.94°$ (**4**; $0.10 \times 0.05 \times 0.05$ mm$^3$). The structures were solved by direct methods (SHELXS-97)[13] and refined against all data by full-matrix least-squares on $F^2$.[14] All the C–H hydrogen atoms except H(3A) were included in geometrically idealized positions and refined with the riding model. Localization of the H(3A) hydrogen from the electron-density map in both structures proved to be more accurate than its fixing in the idealized position and led to a lowering of the $R1$ and w$R2$ values. The hydrogen atoms of the OH and SH moieties in **3** and **4** were localized from the difference electron-density map and refined isotropically with $U_{ij}$ tied to the parent atom. The Al–SH proton belonging to the $[LAl(SH)(\mu\text{-}O)ZrCp_2(SH)]$ in the crystal of **4** could not be localized due to its low content (about 15%). CCDC-270756 (**3**) and CCDC-270757 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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