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Soluble Alumotitanosilicates and Their Zirconium and Hafnium Analogues

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The synthesis of molecular heterometallic alumosilicates in good yields has been achieved by reaction between $LAl(OH{\cdot}thf)(\mu\text{-}O)Si(OH)(OtBu)_2$ (**1**, L = $[HC\{C(Me)N(Ar)\}_2]^-$, Ar = 2,6-$iPr_2C_6H_3$) and group 4 amides. These reactions lead to inorganic cycles (type I) and spirocycles (type II) containing six-membered rings with unprecedented inorganic cores $(O–Al–O–Si–O)_nM$ (n = 1, 2; M = Ti, Zr and Hf). Noteworthy, for the heavier metals, Zr and Hf, higher steric bulk in the alkyl substituent of the amide moiety is required to obtain type I compounds. The solid-state structures for all compounds were determined and reveal a tetrahedral environment for all metal atoms, dihedral angles close to 90° for spirocyclic compounds, and isomorphous structures for the Zr and Hf derivatives.

Introduction

An important component of the earth's crust are multimetallic silicates and alumosilicates, which is reflected in its elemental composition (46.6% O, 27.8% Si, 8.1% Al). Many of these minerals are important catalysts in various chemical processes. In particular, zeolites such as N-erionite, ZSM-5 and Ni-ZSM-5 have been widely used as drying agents, in cracking processes, dehydration reactions, and for hydrogenation or dehydrogenation of alkenes.[1] However, little is known about the catalytic mechanisms of these systems. Thus, it is not surprising that many research groups have focused on the preparation of model compounds to gain a deeper insight into the catalytic process. However, because of the low kinetic barriers for the formation and breaking of the Al–O and Si–O bonds, which are similar for numerous reactions,[2] and because of the high Lewis acidity of aluminum, it is highly difficult to control the degree of association in these compounds. Inseparable mixtures of products are the result of these reactions in most of the cases. The situation is further complicated when two metals are used.

Results and Discussion

Recently, we have reported on the preparation of the unique alumosilicate precursor $LAl(OH{\cdot}thf)(\mu\text{-}O)Si(OH)(OtBu)_2$ (**1**, L = $[HC\{C(Me)N(Ar)\}_2]^-$, Ar = 2,6-$iPr_2C_6H_3$) containing two terminal OH groups attached to the aluminum and silicon atoms.[3] We became interested in whether this precursor can be used for the preparation of molecular heterobimetallic alumosilicates containing the M–O–Si–O–Al–O (M = metal) six-membered ring. To the best of our knowledge, only one similar simple heterobimetallic six-membered ring (Sn–O–Si–O–Ge–O) has been structurally characterized in the siloxane $Ph_2SiOGe(tBu)_2OSn\{(CH_2)_3NMe_2\}_2O$.[4] We have focused on metals of group 4 because of its relevance in heterometallic catalytic transformations.[5] Nevertheless, this choice brings also a synthetic challenge, as, to date, only a few compounds containing the three elements Al, Si, and M (M is titanium or zirconium) have been fully described. In none of these compounds is there an oxygen bridge between any two of these elements.[6] Furthermore, no compound containing Al, Si, and Hf has been structurally authenticated so far. This is obviously because of the high Lewis acidity of the metal atoms and the competition for the formation of the M–O bonds, as reported recently.[7] However, acid–base reactions of **1** with $M(NMe_2)_4$ (M = Ti, Zr) or $M(NEt_2)_4$ (M = Zr, Hf) in different ratios and under different conditions led to the isolation of unprecedented molecular heterobimetallic alumosilicates with the inorganic cores O–Al–O–Si–O–M (type I, M = Ti, Zr, Hf) or $(O–Al–O–Si–O)_2M$ (type II, M = Ti, Zr, Hf) (Scheme 1).

Thus, the reaction between **1** and $Ti(NMe_2)_4$ in a 1:1 ratio gave the monomeric compound $[LAl(\mu\text{-}O)_2Si(OtBu)_2(\mu\text{-}O)Ti(NMe_2)_2]$ (**2**) in a nearly quantitative yield. However, when $Zr(NMe_2)_4$ was used under the same conditions, the

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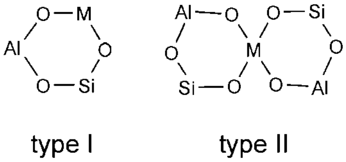
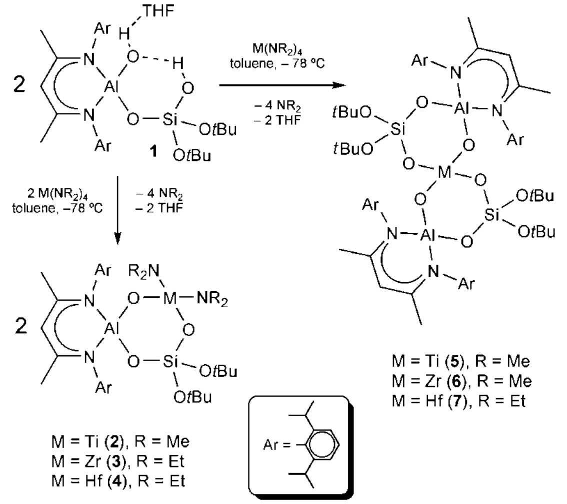


Scheme 1. Type I and II inorganic cores based on **1** (M = Ti, Zr, Hf).

spiro-cyclic compound [{LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)}$_2$Zr] (**6**) was obtained as the only product. An identical result was expected for the reaction of Hf(NEt$_2$)$_4$ with **1** under the same conditions, as the covalent radii of Zr and Hf are very similar (1.56 and 1.57 Å, respectively)[8] and the Hf–O (802 kJ/mol) bond energy is in fact higher than that for Zr–O (776 kJ/mol).[2c] To our surprise, the monomeric species [LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)Hf(NEt$_2$)$_2$] (**4**) was isolated in a high yield. All our attempts to synthesize the monomeric derivative [LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)Zr(NMe$_2$)$_2$] either using an excess of the zirconium precursor, by very slow addition of the solution of **1** into the solution of the zirconium reagent, or using highly diluted solutions of the starting materials led always to the formation of **6** and trace quantities of the desired product [LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O) Zr(NMe$_2$)$_2$]. On the other hand, the reaction of Ti(NMe$_2$)$_4$ and Hf(NEt$_2$)$_4$ with **1** in a 1:2 molar ratio led to the exclusive formation of the spiro-cyclic compounds [{LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)}$_2$M] (**5**, M = Ti, **7**, M = Hf). Therefore, the subtle changes in the alkyl chain from Me to Et in Zr(NMe$_2$)$_4$ and Hf(NEt$_2$)$_4$ could be responsible for this behavior. To confirm our theory, **1** was treated with 1 equiv. of Zr(NEt$_2$)$_4$, and [LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)Zr(NEt$_2$)$_2$] (**3**) was isolated in high yield, thus completing the series. Scheme 2 summarizes the preparation of compounds **2**–**7**.



Scheme 2. Preparation of compounds **2**–**7**.

All compounds are highly soluble in toluene, THF, and CH$_2$Cl$_2$, but only sparingly soluble in hexane or pentane, and crystallize easily from a toluene/hexane mixture. Compounds **3**–**7** have been isolated as colorless crystalline solids, whereas compound **2** is pale yellow. The ^{1}H and ^{13}C NMR spectra for all compounds are consistent with their structure. In the case of compounds **2**–**4**, signals for the alkyl groups of the corresponding NR$_2$ moieties can be observed, which confirms the formation of the monomeric species, but these are essentially absent in the case of compounds **5**–**7**, which corroborates the total elimination of the alkylamino ligands and formation of the spiro-cycles. Moreover, IR and ^{1}H NMR spectra are devoid of the signals for the OH groups, which thus confirms the formation of inorganic oxide rings. Compounds **2**–**7** are thermally stable up to 200 °C, but decomposition of all samples occurred below 250 °C. The ESI-MS spectra reveal $[M + H]^+$ peaks for the spiro-cycles **5**–**7** at m/z = 1381.7586 (**5**), 1424.7183 (**6**) and 1513.7518 (**7**) and $[M + 3\ CH_3CN + H]^+$ peaks at m/z = 1114.5919 for **4**, whereas for compounds **2** (m/z = 844.4780 $[M - NMe_2 + 2\ CH_3CN]^+$) and **3** ($m/z$ = 1033.5116 $[M - NEt_2 + 5\ CH_3CN]^+$), only fragmentation peaks are observed.

The molecular structures of compounds **2**–**7** were determined by X-ray diffraction studies. Titanium alumosilicates **2** and **5** crystallize in the monoclinic space groups $P2_1/c$ and $P2_1/n$, respectively, whereas the isomorphous Zr and Hf monomeric derivatives (**3**–**4**) and the isomorphous spiro-compounds **6** and **7** crystallize in the triclinic space group $P\bar{1}$ (Figures 1 and 2 and Figures S1–S4).[9]

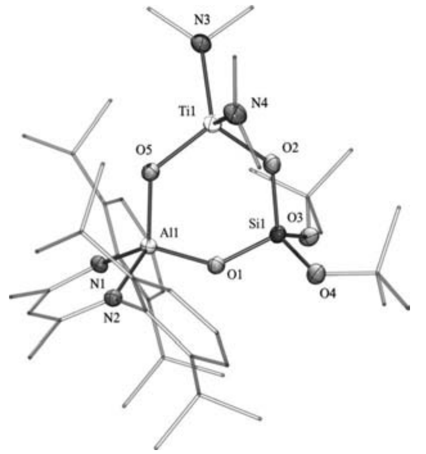


Figure 1. Molecular structure of **2**, hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability only for non-carbon atoms. Al1–N1 1.893(2), Al1–N2 1.909(2), Al1–O5 1.736(2), Al1–O1 1.720(2), Si1–O1 1.609(2), Si1–O2 1.630(2), Si1–O3 1.631(2), Si1–O4 1.627(2), Ti1–O5 1.801(2), Ti1–O2 1.843(2), Ti1–N3 1.879(2), Ti1–N4 1.904(2), N1–Al1–N2 96.6(1), O1–Al1–O5 107.9(1), Al1–O1–Si1 135.8(1), O1–Si1–O2 109.5(1), Si1–O2–Ti1 130.5(1), O2–Ti1–O5 105.5(1), Ti1–O5–Al1 128.3(1).

Compounds **2**–**7** feature unprecedented six-membered inorganic rings that only slightly deviate from planarity [mean deviation: 0.05 (**2**), 0.12 (**3** and **4**), 0.06 Å (average for both rings) (**5**–**7**)]. In addition, the rings in **5**–**7** are nearly perpendicular to each other: 91.9° (with Si2) and 96.9° (with Si2a) for **5**,[10] and 81.1° for **6**, and 81.6° for **7**. In all six heterobimetallic alumosilicates **2**–**7**, the metallic atoms (Al, Ti, Zr, Hf) and the Si atoms possess a distorted tetrahedral geometry, and the greatest distortion is located on the aluminum atoms (the N–Al–N angles are between 96.6 and 98.4°). In-

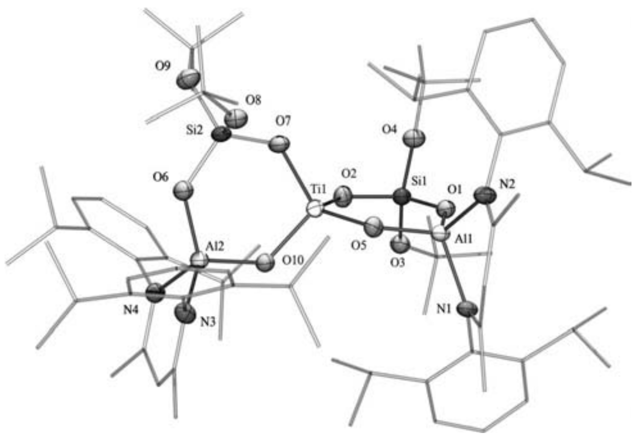


Figure 2. Molecular structure of **5**, hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability only for non-carbon atoms. Al1–N1 1.892(2), Al1–N2 1.889(3), Al2–N3 1.878(3), Al2–N4 1.886(3), Al1–O1 1.717(2), Al1–O5 1.736(2), Al2–O6 1.716(2), Al2–O10 1.736(2), Si1–O1 1.616(2), Si1–O2 1.626(2), Si1–O3 1.616(2), Si1–O4 1.625(2), Si2–O6 1.619(5), Si2–O7 1.648(5), Si2–O8 1.619(5), Si2–O9 1.624(5), Ti1–O2 1.830(2), Ti1–O5 1.779(2), Ti1–O7 1.834(2), Ti1–O10 1.783(2), N1–Al1–N2 98.4(1), N3–Al2–N4 98.3(1), O1–Al1–O5 109.4(1), Al1–O1–Si1 131.9(1), O1–Si1–O2 109.8(1), Si1–O2–Ti1 134.7(1), O2–Ti1–O5 102.8(1), Ti1–O5–Al1 130.1(1), O6–Al2–O10 110.4(1), Al2–O6–Si2 131.1(2), O6–Si2–O7 109.0(3), Si2–O7–Ti1 133.4(2), O7–Ti1–O10 102.6(1), Ti1–O10–Al2 129.8(1).

side the inorganic ring, the obtuse angles on all three oxygen atoms compensate for the tetrahedral geometry on the metal and silicon atoms (the tetrahedral angle 109.5° is smaller than the inner angle in a regular hexagon: 120°) (see Tables S1 and S2).

Because of the lack of any similar compounds, only the fragments of the inorganic rings can be compared with the literature data. From this point of view, M–(μ-O)–Al (M = group 4 metal) is the most interesting part of the ring. To date, only a few compounds with the Al–(μ-O)–M unit (M = Ti,[11a–11f] M = Zr,[11a,11c–11e,11g–11i] M = Hf[11b]) have been structurally characterized. The Al–O and M–O bonds (M = Ti **2** and **5**, M = Zr **3** and **6**, M = Hf **4** and **7**) are in agreement with those observed in the literature; however, compounds **2**–**7** contain the most acute Al–O–M angles observed up to date. The Al–O–Ti angles observed are between 142.2° [LAlMe(μ-O)TiCpMe$_2$][11e] and 175.6° {LAlMe(μ-O)]$_2$Ti(NMe$_2$)$_2$}[11d] and the values for Al–O–Zr and Al–O–Hf are 144.4–175.6° {[LAlEt(μ-O)ZrCp$_2$Me][11h] and [[LAlMe(μ-O)]$_2$ZrBz$_2$],[11c] Bz = benzyl} and 158.4° [LAlMe(μ-O)HfCp$_2$Me],[11b] respectively.

Conclusions

We have prepared unprecedented molecular alumotitanosilicates and their heavier congeners. These compounds are the first examples that include aluminum, silicon, and a group 4 metal connected by oxygen bridges. In addition, these compounds may be very useful for the preparation of alumotitanosilicate materials. Such experiments are already underway.

Experimental Section

Materials: All preparations were performed in a dry and oxygen-free atmosphere (N$_2$) by using Schlenk and glove-box techniques. Solvents were purified in an Mbraun SPS by using Grubs columns. LAl(OH·thf)(μ-O)Si(OH)(O*t*Bu)$_2$ and Zr(NEt$_2$)$_4$ were prepared according to literature procedures,[3,12] whereas M(NR$_2$)$_4$ (Ti, Zr, R = Me, Hf, R = Et) were purchased from Aldrich and used as received.

Physical Methods: ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECLIPSE 300 NMR spectrometer, and the ^{29}Si NMR spectra on a VNMR 500 MHz Varian Unity. Mass spectra (ESI-HRMS) were recorded by using a Bruker micrOTOF II spectrometer coupled with a MBraun UniLab glove-box.

X-Ray Crystallography: Selected crystallographic data are presented in Table S2. Single crystals were mounted on a Bruker APEX DUO diffractometer equipped with an Apex II CCD detector at 100 K. Frames were collected by using omega scans and integrated with SAINT.[13a] Absorption correction (SADABS)[13a] was applied. The structures were solved by direct methods (SHELXS)[13b] and refined by the full-matrix least-squares on F^2 with SHELXL-97.[13b] Weighted R factors, R_w, and all goodness-of-fit indicators, S, were based on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions, with C–H distances of 0.93 and 0.98 Å for sp^2- and sp^3-hybridized carbon atoms, respectively, with U_{iso} tied do the parent atom.

LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)M(NR$_2$)$_2$ (2: M = Ti, R = Me; 3: M = Zr, R = Et; 4: M = Hf, R = Et): A solution of LAl(OH·thf)(μ-O)Si(OH)(O*t*Bu)$_2$ (0.30 g, 0.41 mmol) in toluene (15 mL) was added dropwise to a stirred solution of Ti(NMe$_2$)$_4$ (0.10 g, 0.45 mmol) for **2**, Zr(NEt$_2$)$_4$ (0.17 g, 0.45 mmol) for **3**, or Hf(NEt$_2$)$_4$ (0.20 g, 0.43 mmol) for **4**, in toluene (40 mL) at –78 °C. The reaction mixture was allowed to reach room temperature and stirred for an additional 12 h, which resulted in a clear yellow solution. After all volatiles were removed, the crude product was rinsed with cold hexane (5 mL) and dried under vacuum. The product was recrystallized from toluene.

LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)Ti(NMe$_2$)$_2$ (2): Yellow crystals. Yield: 0.29 g (89%). M.p. 215 °C (dec.). ESI-HRMS: calcd. for $C_{43}H_{75}AlN_5O_5SiTi$ [M – NMe$_2$ + 2 CH$_3$CN]$^+$ 844.48317; found 844.47798; error 6.1 ppm. ^{1}H NMR (300.53 MHz, C$_6$D$_6$, 20 °C): δ = 1.11 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.12 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.22 [s, 18 H, CH(C*H*$_3$)$_2$], 1.46 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.52 (*s*, 6 H, C*H*$_3$), 1.71 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$], 2.95 [s, 12 H, N(C*H*$_3$)$_2$], 3.34 [sept., $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.48 [sept., $^3J_{H,H}$ = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$], 4.93 (s, 1 H, γ-*H*), 7.09–7.22 (m, 6 H, *H* of Ar) ppm. ^{13}C{^{1}H} (75.57 MHz, C$_6$D$_6$, 20 °C): δ = 23.8, 24.1, 24.9, 25.2 [CH(*C*H$_3$)$_2$], 28.1, 29.0 [N(*C*H$_3$)], 31.6 [C(*C*H$_3$)$_3$], 44.5 (NC*C*H$_3$), 71.4 [*C*(CH$_3$)$_3$], 97.3 (γ-*C*), 124.6, 124.7, 140.8, 144.7, 144.9 (*C* of Ar), 171.4 (*C*=N) ppm. ^{29}Si{^{1}H} (99.33 MHz, C$_6$D$_6$, 20 °C): δ = –96 [O$_2$*Si*(O*t*Bu)$_2$] ppm.

[LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)Zr(NEt$_2$)$_2$] (3): White crystals. Yield: 0.30 g (82%). M.p. 236–238 °C (dec.). ESI-HRMS: calcd. for $C_{51}H_{84}AlN_8O_5SiZr$ [M – NEt$_2$ + 5 CH$_3$CN]$^+$ 1033.51909; found 1033.51164; error 7.2 ppm. ^{1}H NMR (300.52 MHz, C$_6$D$_6$, 20 °C): δ = 1.09 [d, 6 H, $^3J_{H,H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$], 1.14 [d, 6 H, $^3J_{H,H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$], 1.22 [s, 18 H, C(C*H*$_3$)$_3$], 1.22 [t, 12 H, $^3J_{H,H}$ = 6.9 Hz, N(CH$_2$C*H*$_3$)$_2$], 1.47 [d, 6 H, $^3J_{H,H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$], 1.49 (s, 6 H, C*H*$_3$), 1.69 [d, 6 H, $^3J_{H,H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$], 3.01 [dq, 4 H, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 6.9 Hz, N(C*H*$_2$CH$_3$)$_2$], 3.14 [dq, 4 H, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 6.9 Hz, N(C*H*$_2$CH$_3$)$_2$], 3.37 [sept, 2 H,

$^3J_{H,H}$ = 6.8 Hz, C*H*(CH$_3$)$_2$], 3.48 [sept, 2 H, $^3J_{H,H}$ = 6.8 Hz, C*H*(CH$_3$)$_2$], 4.88 (s, 1 H, γ-*H*), 7.11–7.19 (m, 6 H, *H* of Ar) ppm. ^{13}C{^{1}H} (75.57 MHz, C$_6$D$_6$, 20 °C): δ = 15.9 [N(CH$_2$*C*H$_3$)$_2$], 23.8, 24.1, 24.7 [CH(*C*H$_3$)$_2$], 24.9 (*C*H$_3$), 25.0 [CH(*C*H$_3$)$_2$], 27.8, 28.8 [*C*H(CH$_3$)$_2$], 31.3 [C(*C*H$_3$)$_3$], 45.0 [N(*C*H$_2$CH$_3$)$_2$], 71.0 [*C*(CH$_3$)$_3$], 97.2 (γ-*C*), 124.4, 140.9, 144.4, 144.6 (*C* of Ar), 171.0 (*C*=N) ppm; ^{29}Si{^{1}H} (99.33 MHz, C$_6$D$_6$, 20 °C): δ = –97 [O$_2$*Si*(O*t*Bu)$_2$] ppm.

[LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)Hf(NEt$_2$)$_2$] (4): White powder. Yield: 0.31 g (77%). M.p. 213 °C (dec.). ESI-HRMS: calcd. for C$_{51}$H$_{89}$AlN$_7$O$_5$SiHf [M + H + 3 CH$_3$CN]$^+$ 1114.5976; found 1114.5919; error 5.1 ppm. ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 °C): δ = 1.10 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.15 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.23 [s, 18 H, C(C*H*$_3$)$_3$], 1.23 [t, $^3J_{H,H}$ = 7.0 Hz, 12 H, N(CH$_2$C*H*$_3$)$_2$], 1.50 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.51 (s, 6 H, 2 C*H*$_3$), 1.69 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 3.01 [dq, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 7.0 Hz, 4 H, N(C*H*$_2$CH$_3$)$_2$], 3.14 (dq, $^2J_{H,H}$ = 13.2, $^3J_{H,H}$ = 7.0 Hz, 2 H, NC*H*$_2$CH$_3$), 3.38 [sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.48 [sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 4.91 (s, 1 H, γ-*H*), 7.11–7.22 (m, 6 H, *H* of Ar) ppm. ^{13}C{^{1}H} (75.57 MHz, C$_6$D$_6$, 20 °C): δ = 16.3 [N(CH$_2$*C*H$_3$)$_2$], 24.0, 24.3, 25.0 [CH(*C*H$_3$)$_2$], 25.2 (*C*H$_3$), 25.2 [CH(*C*H$_3$)$_2$], 28.1, 29.0 [*C*H(CH$_3$)$_2$], 31.5 [C(*C*H$_3$)$_3$], 44.9 [N(*C*H$_2$CH$_3$)$_2$], 71.3 [*C*(CH$_3$)$_3$], 97.5 (γ-*C*), 124.6, 124.7, 141.2, 144.6, 144.8 (*C* of Ar), 171.3 (*C*=N) ppm. ^{29}Si{^{1}H} (99.33 MHz, C$_6$D$_6$, 20 °C): δ = –95 [O$_2$*Si*(O*t*Bu)$_2$] ppm.

[LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)]$_2$M (5: M = Ti, 6: M = Zr, 7: M = Hf): A solution of Ti(NMe$_2$)$_4$ (0.06 g, 0.27 mmol) for **5**, Zr(NMe$_2$)$_4$ (0.07 g, 0.26 mmol) for **6**, or Hf(NEt$_2$)$_4$ (0.13 g, 0.28 mmol) for **7**, respectively, in toluene (10 mL) was added dropwise to a stirred solution of LAl(OH·thf)(μ-O)Si(OH)(O*t*Bu)$_2$ (0.40 g, 0.54 mmol) in toluene (40 mL) at –78 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred for additional 16 h, which resulted in a yellow solution. After all volatiles were removed, the crude product was rinsed with cold hexane (5 mL), filtered, and then dried under vacuum to give a white powder. The product was recrystallized from toluene.

[LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)]$_2$Ti (5): Yield: 0.26 g (70%). M.p. 250 °C (dec.). ESI-HRMS: calcd. for C$_{74}$H$_{119}$Al$_2$N$_4$O$_{10}$Si$_2$Ti [M + H]$^+$ 1381.75796; found 1381.75860; error: –0.5 ppm. ^{1}H NMR (300.53 MHz, C$_6$D$_6$, 20 °C): δ = 1.08 [s, 18 H, C(C*H*$_3$)$_3$], 1.11 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.16 [s, 18 H, C(C*H*$_3$)$_3$], 1.17 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.34 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.41 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.48 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.52 (s, 6 H, C*H*$_3$), 1.54 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.68 (s, 6 H, C*H*$_3$), 1.71 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.93 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 3.14 [sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.38 [sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.64 [sept, $^3J_{H,H}$ = 6.6 Hz, 2 H, C*H*(CH$_3$)$_2$], 4.19 [sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 5.05 (s, 2 H, γ-*H*), 6.99–7.42 (m, 12 H, *H* of Ar) ppm. ^{13}C{^{1}H} (75.57 MHz, C$_6$D$_6$, 20 °C): δ = 23.4, 23.9, 24.2, 24.7, 24.8, 24.9, 25.9, 26.2 [CH(*C*H$_3$)$_2$], 26.7, 27.5 (*C*H$_3$), 28.4, 28.7, 28.8, 28.9 [*C*H(CH$_3$)$_2$], 31.5, 31.6 [C(*C*H$_3$)$_3$], 71.0, 71.1 [*C*(CH$_3$)$_3$], 98.7 (γ-*C*H), 124.0, 124.3, 125.1, 125.23, 127.1, 127.5, 128.3, 143.4, 144.5, 146.0 (*C* of Ar), 170.8, 172.4 (*C*=N) ppm. ^{29}Si{^{1}H} (99.33 MHz, C$_6$D$_6$, 20 °C): δ = –96 [O$_2$*Si*(O*t*Bu)$_2$] ppm.

[{LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)}$_2$Zr] (6): Yield: 0.29 g (75%). M.p. 232–234 °C (dec.). ESI-HRMS: calcd. for C$_{74}$H$_{119}$Al$_2$N$_4$O$_{10}$Si$_2$Zr [M + H]$^+$ 1424.71689; found 1424.71828; error –1.0 ppm. ^{1}H NMR (300.53 MHz, C$_6$D$_6$, 20 °C): δ = 1.09 [s, 18 H, C(C*H*$_3$)$_3$], 1.10 [d, 6 H, $^3J_{H,H}$ = 7.0 Hz, CH(C*H*$_3$)$_2$], 1.16 [s, 18 H, C(C*H*$_3$)$_3$], 1.17 [d, 6 H, $^3J_{H,H}$ = 6.6 Hz, CH(C*H*$_3$)$_2$], 1.33 [d, 6 H, $^3J_{H,H}$ = 6.6 Hz, CH(C*H*$_3$)$_2$], 1.45 [d, 6 H, $^3J_{H,H}$ = 7.0 Hz, CH(C*H*$_3$)$_2$], 1.49 [d, 6 H, $^3J_{H,H}$ = 6.6 Hz, CH(C*H*$_3$)$_2$], 1.50 (s, 6 H, C*H*$_3$), 1.54 [d, 6 H, $^3J_{H,H}$ = 6.6 Hz, CH(C*H*$_3$)$_2$], 1.64 (s, 6 H, C*H*$_3$), 1.64 [d, 6 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$], 1.95 [d, 6 H, $^3J_{H,H}$ = 6.7 Hz, CH(C*H*$_3$)$_2$], 3.18 [sept, 2 H, $^3J_{H,H}$ = 7.0 Hz, C*H*(CH$_3$)$_2$], 3.41 [sept, 2 H, $^3J_{H,H}$ = 6.7 Hz, C*H*(CH$_3$)$_2$], 3.58 [sept, 2 H, $^3J_{H,H}$ = 6.6 Hz, C*H*(CH$_3$)$_2$], 4.10 [sept, 2 H, $^3J_{H,H}$ = 6.6 Hz, C*H*(CH$_3$)$_2$], 5.00 (s, 2 H, γ-C*H*), 7.10–7.32 (m, 12 H, *H* of Ar) ppm. ^{13}C{^{1}H} (75.57 MHz, C$_6$D$_6$, 20 °C): δ = 23.2, 23.9, 24.0, 24.3, 24.7, 24.9, 25.5, 25.7 [CH(*C*H$_3$)$_2$], 26.7, 28.1 (*C*H$_3$), 28.6, 28.7, 28.8, 28.9 [*C*H(CH$_3$)$_2$], 31.6, 31.6 [C(*C*H$_3$)$_3$], 70.7, 70.9 [*C*(CH$_3$)$_3$], 98.4 (γ-*C*), 124.1, 124.4, 124.7, 124.9, 140.1, 141.6, 144.5, 145.5, 145.6 (*C* of Ar), 170.8, 171.8 (*C*=N) ppm; ^{29}Si{^{1}H} (99.33 MHz, C$_6$D$_6$, 20 °C): δ = –95 [O$_2$*Si*(O*t*Bu)$_2$] ppm.

[{LAl(μ-O)$_2$Si(O*t*Bu)$_2$(μ-O)}$_2$Hf] (7): Yield: 0.33 g (81%). M.p. 225 °C (dec.). ESI-HRMS: calcd. for C$_{74}$H$_{119}$Al$_2$N$_4$O$_{10}$Si$_2$Hf [M + H]$^+$ 1513.75651; found 1513.75178; error: 3.1 ppm. ^{1}H NMR (300.53 MHz, C$_6$D$_6$, 20 °C): δ = 1.08 [s, 18 H, C(C*H*$_3$)$_3$], 1.10 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.16 [s, 18 H, C(C*H*$_3$)$_3$], 1.18 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.34 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.44 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.48 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.52 (s, 6 H, C*H*$_3$) 1.54 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.63 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.65 (s, 6 H, C*H*$_3$), 1.93 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 3.18 [sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.40 [sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.62 [sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 4.10 [sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 5.02 (s, 2 H, γ-C*H*), 6.99–7.41 (m, 12 H, *H* of Ar) ppm. ^{13}C{^{1}H} (75.57 MHz, C$_6$D$_6$, 20 °C): δ = 23.3, 23.9, 24.1, 24.4, 24.7, 24.9, 25.5, 25.7 [CH(*C*H$_3$)$_2$], 26.6, 28.2 (CH$_3$), 28.4, 28.7, 28.8, 28.9 [*C*H(CH$_3$)$_2$], 31.5, 31.6, [C(*C*H$_3$)$_3$], 70.8, 70.9 [*C*(CH$_3$)$_3$], 98.4 (γ-*C*H), 124.1, 124.4, 124.8, 124.9, 127.0, 127.4, 140.2, 141.7, 143.6, 144.6, 145.6, 145.6 (*C* of Ar), 170.8, 171.9 (*C*=N) ppm. ^{29}Si{^{1}H} (99.33 MHz, C$_6$D$_6$, 20 °C): δ = –94 [O$_2$*Si*(O*t*Bu)$_2$] ppm.

Supporting Information (see footnote on the first page of this article): Complete ^{1}H NMR spectra, ESI-HRMS mass spectra for all compounds, molecular structures of compounds **2**–**7** and further X-ray details are presented.

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[9] Selected crystallographic details and selected bond lengths for compounds **2**–**7** are in the Supporting Information. For full details see CCDC-794271 (**2**), -794272 (**3**), -794273 (**4**), -794274 (**5**), -794275 (**6**), -794276 (**7**). 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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