

Synthesis, Characterization, and Reactivity of a Pincer-Type Aluminum(III) Complex

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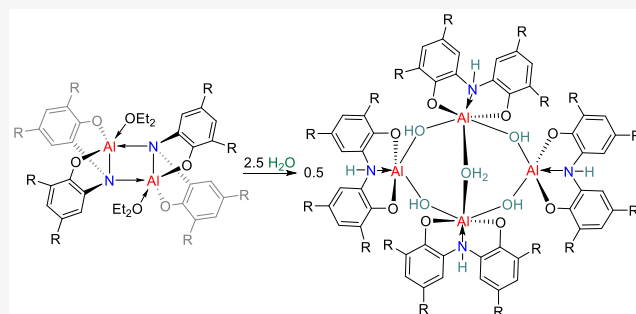
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ABSTRACT: Pincer-type main-group complexes have attractive properties and excellent potential as catalysts. A set of sterically hindered trianionic pincer-type phosphorus complexes have been shown to activate a series of E–H bonds, but the corresponding aluminum species has not been isolated. Herein, we report a novel pincer-type aluminum complex with a $[\text{ONO}]^{3-}$ ligand. This species can react with the O–H bond in alcohol, phenol, and water, leading to the formation of a series of four-, six-, and eight-membered alumoxanes.



1. INTRODUCTION

In the last two decades, reactive main-group compounds have been the objects of significant research,¹ which resembles that conducted with transition-metal complexes. Examples of this include carbenes,² carboene,³ low-oxidation-state species of the group 13 and 14 elements,⁴ and frustrated Lewis pairs (FLPs).⁵ Recently, main-group complexes with a trianionic pincer ligand have attracted increasing interest due to their high stability, activity, and variability. For example, sterically hindered pincer-type phosphorus^{6–10} and bismuth¹¹ compounds not only have unique geometric structures and electronic properties but also exhibit excellent properties in the activation of small molecules and potential applications in catalysis.

Aluminum is the most abundant metal in the Earth's crust, and the combination of aluminum with rigid pincer ligands has attracted the attention of chemists.¹² For example, as reported by Takaya and Iwasawa, the Pd complex **A**, containing a pincer-type Al unit as a ligand (Figure 1), is a catalyst in the hydrosilylation of CO_2 .¹³ The Berben group found that the Al complex **B**, bearing a tridentate bis(imino)pyridine ligand, activates O–H and N–H bonds and catalyzes the conversion of formic acid to H_2 and CO_2 .¹⁴ In addition, they also found that pincer-type Al(III) species, $(\text{P}^{\text{Ph}}\text{I}_2\text{P}^{2-})\text{AlH}$, can also activate

polar chemical bonds.^{14c–f} Recently, Aldridge and Goicoechea and co-workers exploited a dimeric potassium Al complex and its derivatives (**C**), which display unprecedented reactivity toward inert chemical bonds and small molecules.¹⁵ In spite of remarkable progress in this area, pincer-type Al species with trianionic ligands are rare.^{12g}

Alumoxanes, as catalysts or cocatalysts in the polymerization of epoxides, aldehydes, and olefins, have attracted significant interest.¹⁶ However, the synthesis of this type of species is challenging due to the tendency of discrete complexes containing the Al–O–Al moiety to form oligomers.¹⁷

Herein, we report the synthesis, characterization, and reactivity of the novel trianionic pincer-type aluminum complex **2**, which employs bis(3,5-di-*tert*-butyl-2-phenol)-amine ($[\text{ONO}]^{3-}$) as a ligand (Scheme 1). A series of four-, six-, and even eight-membered alumoxanes were isolated by the reactions of complex **2** with alcohol, phenol, and water.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of 2. Complex **2** was prepared by the reaction of **1** with AlBr_3 in the presence of *n*-butyllithium (Scheme 1) and was isolated as a white solid in 69% yield. The structure of complex **2** was characterized by nuclear magnetic resonance (NMR) spectroscopy, single-crystal X-ray diffraction, and high-resolution mass spectrom-

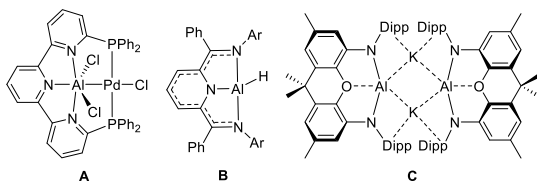
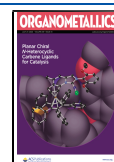


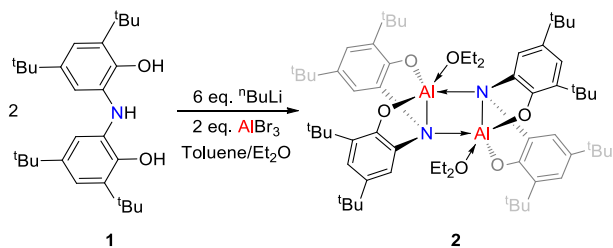
Figure 1. Selected examples of pincer-type aluminum species.

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Scheme 1. Synthesis of Complex 2



etry (HRMS). The ^1H NMR spectrum of **2** suggests a symmetrical structure. Complex **2** is stable under an inert atmosphere both in the solid state and in solution, but it turned purple immediately upon exposure to air, presumably due to the redox nature of the ONO^{3-} ligand.^{8a} Szigethy and Heyduk previously reported that the doubly deprotonated ligand **1**, $[\text{ONHO}]_2\text{M}$ ($\text{M} = \text{Li}, \text{K}$), reacted with AlX_3 ($\text{X} = \text{Cl}, \text{Br}$) to afford the five-coordinate $[\text{ONHO}]\text{AlCl}(\text{Et}_2\text{O})$ or $[\text{ONHO}]\text{AlBr}(\text{THF})$, respectively.¹⁸

The structure of complex **2** obtained from X-ray crystallographic analysis shows that it is a dimer in the solid state (Figure 2).¹⁹ Complex **2** contains a coplanar four-membered

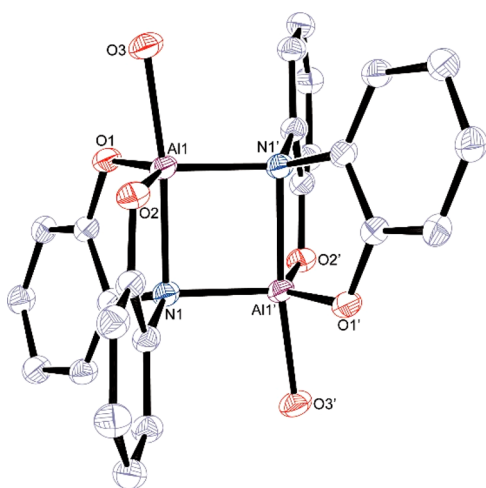
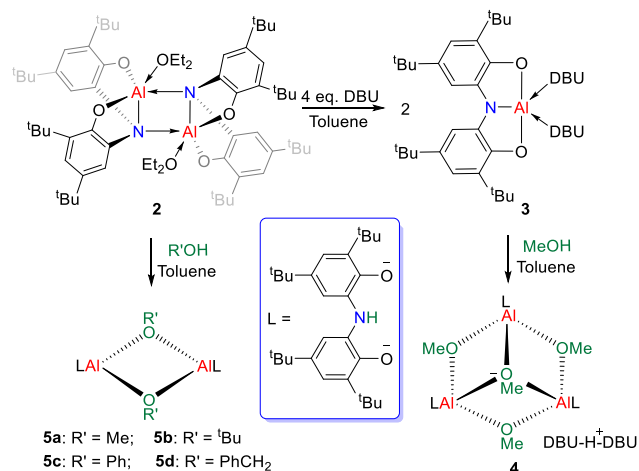


Figure 2. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the ethyl groups in ether, and *tert*-butyl moieties in the ligand are omitted for clarity.

Al_2N_2 core, which was formed by the dimerization of two $[\text{ONO}]\text{Al}$ units. This structural feature is sharply in contrast to the geometry of the analogous pincer boron species $[\text{NNN}]\text{B}$ based on a bis(2-aminophenyl)amine skeleton,²⁰ which shows a planar arrangement of the B atom and the trianionic ligand. The geometry of complex **2** is uncommon but is similar to that observed in pincer-type silicon complexes $\{[\text{ONO}]\text{SiR}\}_2$ reported by the Driess and Greb groups.²¹ The aluminum atoms in complex **2** are pentacoordinated with three O atoms and two N atoms. The $\text{N1}-\text{Al1}-\text{O3}$ angle is $172.92(9)^\circ$ and suggests the presence of a slightly distorted trigonal bipyramidal (TBP) geometry ($\tau = 0.69$). The $\text{Al1}-\text{O1}$ (1.7579(19) Å) and $\text{Al1}-\text{O2}$ (1.7639(18) Å) bond lengths are shorter than the coordinated $\text{Al1}-\text{O3}$ bond distance (1.9702(18) Å). The $\text{Al1}-\text{N1}'$ bond length (1.913(2) Å) is 0.15 Å shorter than the $\text{Al1}-\text{N1}$ distance (2.067(2) Å), which suggests that the formation of complex **2** represents a strong driving force for the dimerization.

2.2. Construction of Four- and Six-Membered Alumoxanes. Although complex **2** has a strong tendency to dimerize, it can react with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to form a monomeric product, probably due to the steric effect of DBU. Treatment of DBU with complex **2** in toluene leads to the monomer **3** coordinated with two DBUs, which was isolated in 90% yield (Scheme 2). Complex **3** could

Scheme 2. Synthesis of Monomeric Complex 3 from 2 and Their Reactivity toward Alcohol and Phenol



also be prepared by the reaction of **1** with AlBr_3 in the presence of 5 equiv of DBU (see the Supporting Information for details). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show that the coordinated Et_2O in complex **2** was replaced by DBU in complex **3**.

The molecular structure of **3** was further confirmed by an X-ray crystallographic analysis (Figure 3). The Al atom in

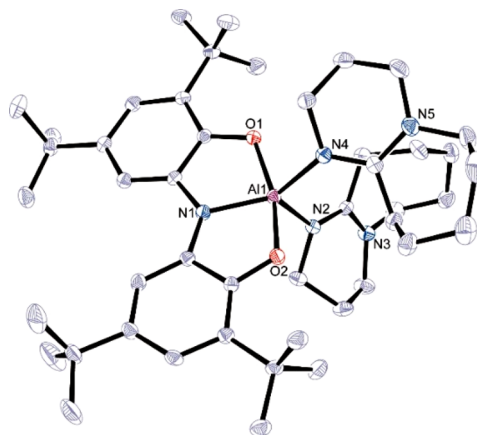


Figure 3. Molecular structure for the anion of **3** with thermal ellipsoids at the 50% probability level. Solvent and hydrogen atoms are omitted for clarity.

complex **3** adopts a slightly distorted TBP geometry with two axial Al–O bonds and three equatorial Al–N bonds. The $\text{Al1}-\text{N2}$ (1.989(2) Å) and $\text{Al1}-\text{N4}$ (1.986(2) Å) bond lengths are slightly longer than the $\text{Al1}-\text{N1}$ distance (1.8872(19) Å). Complex **3** represents a novel example of a pincer-type aluminum(III) species with a trianionic ligand.

Previous studies have shown that trianionic pincer-type phosphorus complexes could activate a series of E–H

bonds.^{6–9} Thus, we examined the reaction of **3** with methanol. Treatment of a toluene solution of **3** with an excess of methanol at RT generated **4** as a colorless crystalline powder in 64% yield (Scheme 2). Complex **4** was characterized by NMR and HRMS, and its structure was confirmed by single-crystal X-ray diffraction (Figure 4). Complex **4** can be viewed as a

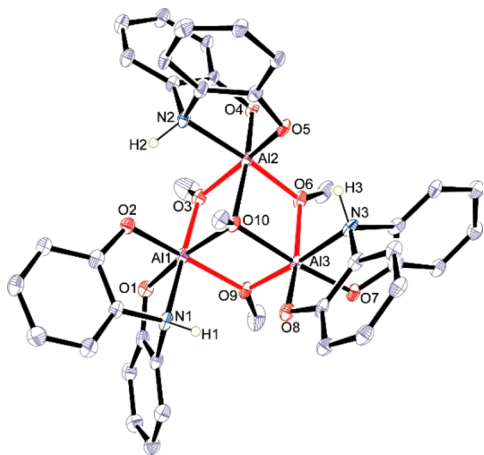


Figure 4. Molecular structure for the anion of **4** with thermal ellipsoids at the 50% probability level. Solvent, hydrogen atoms on carbon, and *tert*-butyl moieties in the ligand are omitted for clarity.

trimer of an [ONHO]Al unit by four bridging OMe groups and two DBU molecules connected by hydrogen bonds. The Al centers in **4** are hexacoordinated and adopt a slightly distorted octahedral geometry. The six Al–O(μ_2) bonds have an average length of 1.878(6) Å and are consistent with those between the Al–O bonds involving the bridging oxygen atoms (1.886(3) Å). However, the three Al–O(μ_3) bond lengths (2.003(4), 2.012(4), and 2.034(4) Å) are very close to the bond length of Al1–O3 (1.9702(18) Å) in complex **2**, indicating the dative nature of the bonds between O10 and Al1, Al2, and Al3. One protonated molecule of DBU is connected to the second DBU by hydrogen bonding, and the proton signal from DBU–H–DBU was observed at 9.43 ppm in the ¹H NMR spectrum of complex **4**. This reaction represents a new route for the synthesis of organoaluminum.

The reactions of complex **2** with alcohol and phenol were also examined. Treatment of complex **2** in toluene with methanol at RT led to rapid consumption of **2** and isolation of **5a** in 53% yield. The ¹H and ¹³C{¹H} NMR spectra of **5a** indicate a symmetrical environment for the [ONHO]^{2–} ligand. The signal of N–H was observed at 4.72 ppm in the ¹H NMR spectrum. Complex **2** also reacts with *tert*-butyl alcohol, phenol, and benzyl alcohol under similar conditions, leading to products **5b–d** (Scheme 2). Complexes **5b–d** are diamagnetic, and their ¹H and ¹³C{¹H} NMR spectra are similar to that of **5a** (see the Supporting Information).

The structure of complex **5b** was further confirmed by single-crystal X-ray diffraction and is a dimer in the solid state (Figure 5). This centrosymmetric structure was formed by the double donor/acceptor O→Al interaction, which is consistent with the NMR spectra. The Al atoms are coordinated by four O atoms and one N atom and adopt a distorted TBP geometry with a N1–Al1–O3 angle of 176.71(9)°. The Al1–O3 (1.810(2) Å) and Al1–O3' (1.8710(19) Å) bond lengths are close to the Al–O bond lengths found in alumoxanes²² and are obviously longer than the Al1–O1 (1.776(2) Å) and Al–

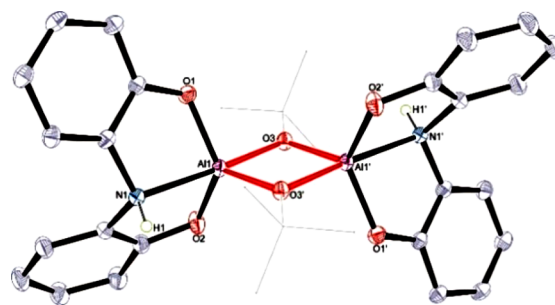
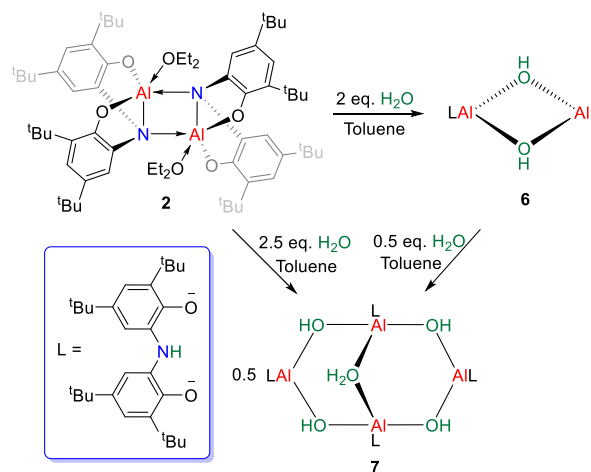


Figure 5. Molecular structure of **5b** with thermal ellipsoids at the 50% probability level. Hydrogen atoms on carbon and *tert*-butyl moieties in the ligand are omitted for clarity.

O2 (1.775(2) Å) bond lengths. The Al1–N1 bond length (2.139(2) Å) is larger than the sum of the covalent single-bond radii of Al and N atoms (1.92 Å), indicating a weak interaction between N1 and Al1. Therefore, the reactions of complex **2** with alcohol and phenol generate a series of novel four-membered organoalumoxanes. The different products between the reactions of **2** and **3** with MeOH are probably due to the two Lewis base DBU ligands in complex **3**.

2.3. Construction of Four- and Eight-Membered Alumoxanes. The activation of the O–H bond in water in a controlled manner by main-group compounds is challenging. The facile reaction of alcohol and phenol with complex **2** led to an exploration of its reactivity toward H₂O. The addition of 2 equiv of H₂O to a solution of **2** in toluene led to an immediate color change from colorless to light blue, from which complex **6** was isolated in 41% yield (Scheme 3).

Scheme 3. Reactions of Complex 2 with Water



Complex **6** was shown by NMR, HRMS, and single-crystal X-ray diffraction (Figure 6) to have an Al₂O₂ structure similar to that of complex **5**. The signals in the ¹H NMR spectrum for protons on nitrogen and oxygen in complex **6** are observed at 4.87 and 3.01 ppm, respectively. However, addition of 2.5 equiv of H₂O to a toluene solution of **2** at RT resulted in the formation of complex **7**, which was isolated as white crystals in 47% yield (Scheme 3). The tetranuclear complex **7** can also be formed by the dimerization of the dinuclear complex **6** in the presence of H₂O. NMR characterization of complex **7** was hindered by its extremely poor solubility, and accordingly, HRMS and single-crystal X-ray diffraction were used to verify

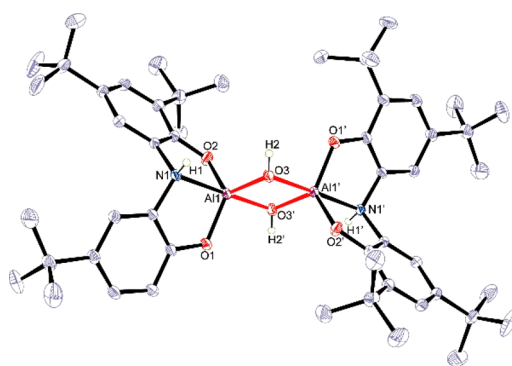


Figure 6. Molecular structure for the anion of **6** with thermal ellipsoids at the 50% probability level. Solvent and hydrogen atoms on carbon are omitted for clarity.

its structure (Figure 7). Berben's group previously reported that the pincer-type ($^{\text{Ph}}\text{I}_2\text{P}^{2-}$)AlH complex **B** (Figure 1)

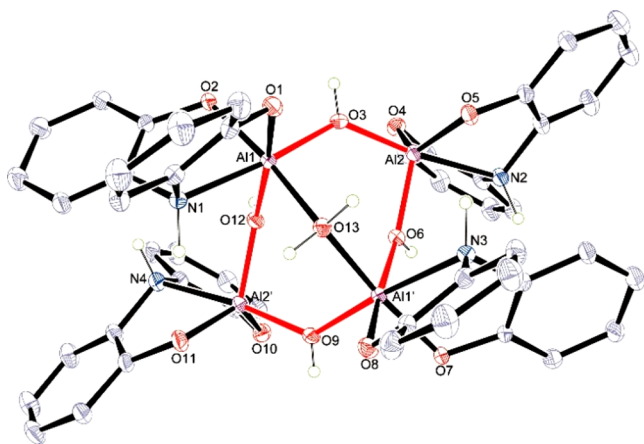


Figure 7. Molecular structure of **7** with thermal ellipsoids at the 50% probability level. Solvent, hydrogen atoms on carbon, and *tert*-butyl moieties in the ligand are omitted for clarity.

reacted with water to afford an alumoxane via aluminum–nitrogen synergistic O–H bond activation.^{14c} The formation of complexes **6** and **7** and the results reported by Berben's group probably indicate the potential of pincer-type Al species in water activation.

Complex **7** is a tetramer consisting of four $[\text{ONHO}]^{2-}$ aluminum units bridged by four hydroxide fragments and two aluminum atoms, Al1 and Al1', bridged by a H_2O molecule. The Al2 and Al2' atoms are pentacoordinated and adopt an approximately TBP geometry ($\tau = 0.78$), while Al1 and Al1' are hexacoordinated with a distorted-octahedral geometry. The average Al–N bond length is 2.12 Å, indicating a weak interaction between Al and N atoms. The eight Al– μ -OH bond lengths ranging from 1.796(3) to 1.926(3) Å in complex **7** are comparable to those observed in **4**, **5b**, and **6**. The Al1–O13 and Al1'–O13 bond distances are 1.8572(13) Å, which are shorter than the Al^{III} –OH₂ bond distances reported in H_2O -AlL (L = tris(2-oxy-3,5-dimethylbenzyl)amine) (1.93(4) Å).²³ Consequently, complex **7** can be viewed as a novel eight-membered alumoxane formed by the reaction of complex **2** with the O–H bond in water.

3. CONCLUSION

In summary, we have developed a novel pincer-type aluminum species **2** based on a trianionic $[\text{ONO}]^{3-}$ ligand. Complex **2** exhibits excellent reactivity toward alcohol, phenol, and water. Significantly, due to the steric hindrance of the ONO pincer ligand and the high coordination number of aluminum, a set of four-, six-, and eight-membered alumoxanes could be isolated. This study not only provides an effective method for the construction of novel alumoxanes of this type but also shows that pincer-type main-group compounds have great potential in synergistic catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00325>.

Experimental procedures, characterization of new compounds, and spectroscopic data (PDF)

Accession Codes

CCDC 1992366–1992371 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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