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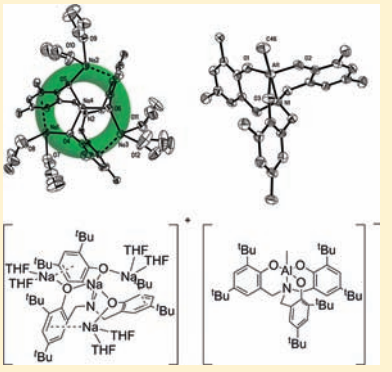
Multimetallic Synergic Sedation of a Labile Sodium Atrane: Synthesis and Characterization of a Tetranuclear Sodium Atrane Cation Complex

Jinfeng Zhang,[†] Ai Liu,[†] XiaoBo Pan, Lihui Yao, Lei Wang, Jianguo Fang, and Jincai Wu*

Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People's Republic of China

Supporting Information

ABSTRACT: A series of sodium and aluminum atrane complexes of $Na_3L(THF)_5$ (**1**), $[AlLMe][Na_4L(THF)_6]$ (**2**), $AlL(THF)$ (**3**), $AlNaLMe(THF)_2$ (**4**), and $AlNaLOBn(THF)_2$ (**5**), wherein L = tris(2-oxy-4,6-di-*tert*-butyl-benzyl)amine, were synthesized and characterized by NMR, X-ray crystallography, and elemental analysis. The trinuclear sodium atrane complex of $Na_3L(THF)_5$ (**1**) is labile at room temperature; however, the tetranuclear sodium atrane cation in complex **2** can be stabilized by a multimetallic synergetic effect due to a firm interaction ring of $-[Na-O-benzene]_3-$. Complex **2** is also the first example of a sodatrane and alumatrane ion-paired complex in which both the cationic and anionic moieties contain an atrane ligand.



1. INTRODUCTION

Multimetallic coordination chemistry has attracted considerable interest due to some special synergic effects. The enzyme of nitrogenase, for example, includes heterometallic complexes (e.g., Fe, Mo, and Co) at the active site in which the multimetallic synergic effect plays a key role in the fixation of atmospheric nitrogen gas.[1] Some heterobimetallic complexes applied as asymmetric catalysts can efficiently promote many reactions through a synergetic cooperation between two different metals,[2] and the heterobimetallic complex of "iBu$_3$Al(TMP)Li" (TMP(H) = 2,2,6,6-tetramethylpiperidine) exhibits high chemo- and regioselectivity in proton abstraction reactions of functionalized aromatic substrates because of alkali-metal−aluminum synergic effects.[3] Recently, Mulvey et al. published extensive and excellent work on the applications of mixed-metal molecular synergy, such as the extraordinary synergic sedation of sensitive cyclic ether and ethene anions by alkali-mediated zincation[4] and the quantitative regioselective tetramagnesiation of ferrocene, ruthenocene, and osmocene (which cannot be directly magnesiated by any known conventional organomagnesium reagent by an alkali-metal-mediated magnesiation approach).[5] They have also reported the activation of arene by multimetallic inverse crown complexes[6] and the self-deprotonation/metalation of the TMP anion in a K−Al heterobimetallic complex, which is unlikely to be reproduced in a homometallic system under a controlled manner.[7]

Recently, our research has focused on the development of multimetallic catalysts for the ring-opening polymerization of cyclic esters. Thus, some multimetallic complexes have been synthesized, and some interesting synergic effects were observed.[8] Here, we report a new synergic effect in the stabilization of a special tetrasodium atrane cation with tripodal aminetris(phenol) as the ligand.

An atrane is tricyclic molecule with three five- or six-membered rings and a transannular bond. Atranes have attracted the interest of many chemists because they can be used to stabilize unusual metal coordination geometries,[9] unusual inorganic functionalities,[10] and catalytically active species.[11] The tripodal aminetris(phenol), when acting as an atrane ligand with one nitrogen and three oxygen coordination atoms, usually binds to a metal in a tetradentate manner to give the settled coordinating environment; five-coordinate trigonal bipyramidal complexes are most commonly observed with another simple coordinated ligand at the apical position. Because of the ease with which steric and electronic modulation are induced by changes in the substituents on the aryl rings, tripodal aminetris(phenol) ligands have been widely used to synthesize many kinds of atranes such as silicon,[12] phosphorus,[13] titanium,[14] tantalum,[15] indium,[16] vanadium,[17] iron,[18] and germanium[19] atranes. Among the known atranes, sodatrane remains relatively unexplored. To the best of our knowledge, the sodium complexes of aminetriethanol reported by Verkade et al. are the only examples of sodatranes,[20]

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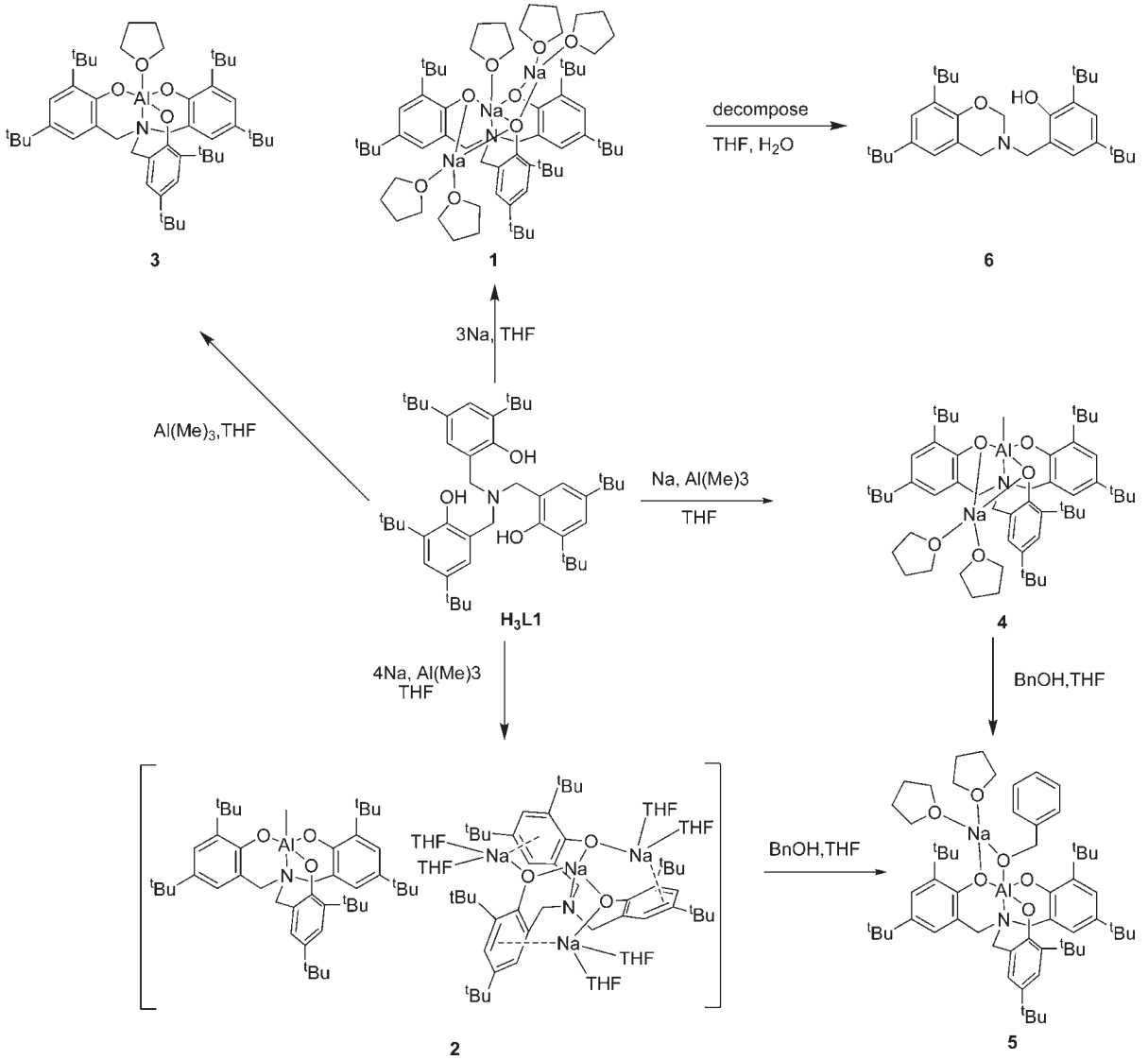
Scheme 1. Synthesis of Complexes 1−5



and aminetris(phenol)-supported sodium atrane has not been previously reported.

2. RESULTS AND DISCUSSION

The trinuclear sodium atrane of complex **1** was designed as a precursor (Scheme 1) for the synthesis of new catalysts for the ring-opening polymerization of lactides. The tripodal aminetris(phenol) (tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine) ligand, however, is not stable under basic conditions: the reaction of aminetris(phenol) and sodium metal/NaH/NaOH gives a mixture of complex **1** and the side product of compound **6** (6,8-di-*tert*-butyl-3-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-2*H*-3,4-dihydrobenz-1,3-oxazine) at room temperature, which can usually be obtained by the reaction of phenol and urotropine under Duff reaction conditions.[21] The purification of complex **1** for sequent decomposition at room temperature is difficult. Low-purity complex **1** can only be obtained by a cooling reaction of NaH and aminetris(phenol) in dry THF at −20 °C, together with approximately 8% of compound **6** as the side product, as evidenced by the analysis of the NMR spectrum. The experiment also shows that H_2O can accelerate the decomposition because the reaction of NaOH and aminetris(phenol) gives compound **6** in 1 h with a conversion of approximately 50% at room temperature. As other researches have previously reported, this aminetris(phenol) ligand is stable after coordination to highly charged metals, such as those in Al^{3+}, Ti^{4+}, or Fe^{3+} complexes. Therefore, the lability of the sodium atrane complex **1** is attributed to the weak coordination interaction between the sodium cation and the aminetris(phenol) ligand. The geometry of the atrane cannot be fixed like other highly Lewis-acidic metal complexes; thus, the aminetris(phenol) ligand decomposes to compound **6**, possibly via an approach similar to that in Scheme 2.

During the synthesis of the heterometallic aluminum sodium alkoxide of complex **5** as a potential initiator for the ring-opening polymerization of lactides,[22] an interesting complex (**2**) was found as a first example of a sodatrane and alumatrane ion-paired complex (Scheme 1). This complex also contains the first example

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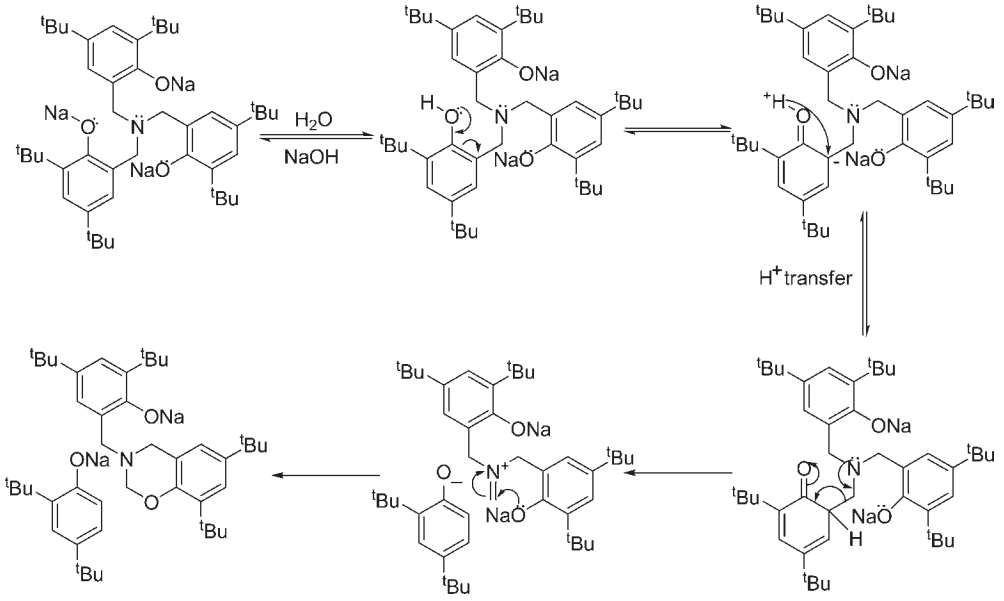
Scheme 2. Possible Decomposition Mechanism of Aminetris(phenol) under Basic Conditions



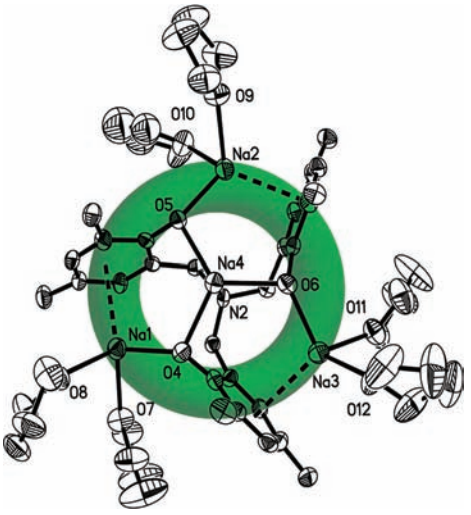


Figure 1. The tetranuclear sodium atrane cation of complex **2** (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms omitted for clarity). The coordination of the oxygen atoms of phenol to Na1/Na2/Na3 and the p−π interaction between the Na^+ and benzene ring of the ligand form a −[Na−O−benzene]$_3$ interaction ring that is colored in green. Selected bond lengths (Å): Na1−O4, 2.222(5); Na1−O8, 2.323(6); Na1−O7, 2.380(6); Na2−O5, 2.216(6); Na2−O10, 2.376(6); Na2−O9, 2.400(7); Na3−O6, 2.197(6); Na3−O11, 2.363(7); Na3−O12, 2.381(6); Na4−O4, 2.222(5); Na4−O6, 2.235(6); Na4−O5, 2.247(7); Na4−N2, 2.447(7).

of a tetranuclear monomeric sodium atrane cation. As far as we know, no other separated ion-paired atrane complexes are known in which both the cationic and anionic moieties contain an atrane ligand. Because of the lability of the trinuclear sodium atrane of complex **1**, the presence of the stable tetrasodium atrane of aminetrisphenoxide attracted our attention, and we assumed that an interesting synergetic effect stabilized the tetranuclear sodium atrane cation in complex **2**.

Complex **2** was obtained by stirring a mixture of 4 equivalents of sodium, 1 equivalent of $AlMe_3$, and 2 equivalents of tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine in THF at 50 °C. Fine crystals of complex **2** were obtained from a saturated solution in THF/hexane at room temperature with 53% yield. Complex **2** contains one sodatrane cation and one alumatrane anion. The structure of the tetrasodium cation in complex **2**, depicted in Figure 1, reveals a well-defined sodatrane composed of a center Na^+ and aminetrisphenoxy. The geometry around the center Na^+ is an unprecedented trigonal pyramid, and the opposite position of N is unoccupied, which is different from the prevalent five-coordinate trigonal bipyramidal metal atrane complex. Intriguingly, this sodatrane can attract three Na^+ ions. Each Na^+ ion is stabilized by the coordination of two THF molecules, one oxygen atom of phenol, and the p−π interaction between the Na^+ and benzene ring of the ligand with an average distance of 2.743(7) Å. The latter two interactions for Na^+ form another ring, −[Na−O−benzene]$_3$−, depicted in Figure 1 as the green ring. As the anion component (Figure 2), the alumatrane apparently binds one methyl group at the apical position of a trigonal bipyramid with a C−Al bond distance of 1.984(7) Å. Compared to the aluminatrane complex **3** (Figure 3), which was synthesized by the reaction of $AlMe_3$ and aminetris(phenol) ligand in THF at 80 °C, the long N1−Al1 bond with a distance of 2.289(7) Å in the anion of complex **2** consists of an electron-rich methyl group anchored on the aluminum center.

Although complex **1** is very labile to moisture, several crystals of complex **1** were picked up from the reaction mixture, which indicated the slight stability of complex **1** in the solid state. The structure of complex **1** drawn in Figure 4 shows that the center Na^+ ion and the ligand form a three-bladed turbine that features sodatrane. The structure also shows that the other two Na^+ ions occupy the two vacancies of the three-bladed turbine with coordination of two oxygen atoms from the ligand and two oxygen atoms from two THF molecules. No p−π interactions occur between the benzene ring and the Na^+ ion, which is different from the tetrasodium atrane cation in complex **2**. Another difference is that the center Na^+ is normally five-coordinate,

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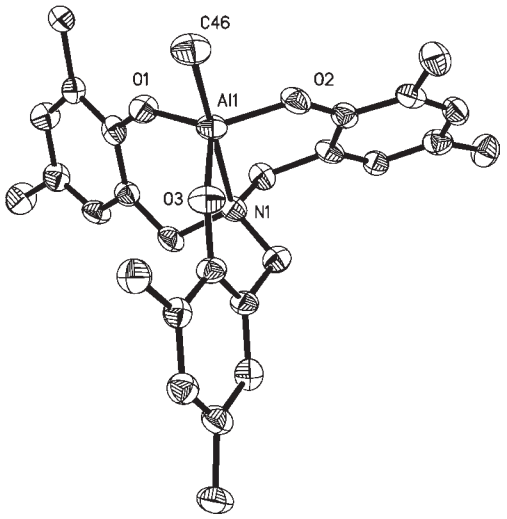

Figure 2. The aluminum atrane anion of complex **2** (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms omitted for clarity). Selected bond lengths (Å): Al1−O1, 1.775(5); Al1−O2, 1.790(6); Al1−O3, 1.801(5); Al1−C46, 1.984(7); Al1−N1, 2.289(7).

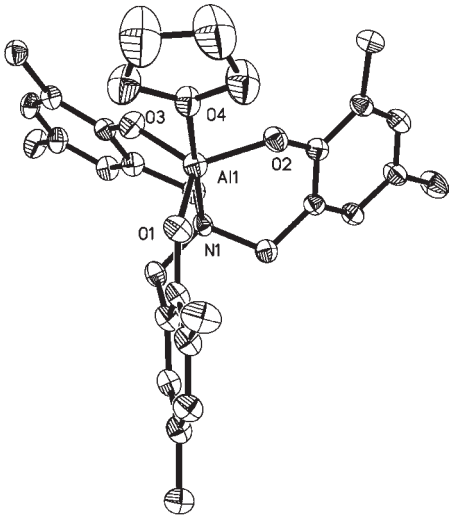

Figure 3. Molecular structure of complex **3** as 30% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms omitted for clarity). Selected bond lengths (Å): Al1−O1, 1.752(5); Al1−O3, 1.753(4); Al1−O2, 1.760(4); Al1−O4, 1.976(4); Al1−N1, 2.026(5).

as are the other atrane metal complexes, whereas the center Na^+ in complex **2** is unwontedly four-coordinate.

Complex **1** can be considered the precursor of complex **2** despite its lability. As another precursor of complex **2**, complex **4** can be obtained by heating a mixed solution of 1 equivalent of sodium, 1 equivalent of $AlMe_3$, and the ligand. Therefore, we propose that the formation mechanism of complex **2** involves the extraction of Na^+ from complex **4** to complex **1**. A stable tetranuclear sodium cation then forms; i.e., alumatrane binds Na^+ loosely. The driving force for the formation of the ion-paired complex **2** is possibly the greater stability of the tetrasodium atrane cation relative to the trisodium atrane. The tetrasodium atrane cation is stable even in hot THF solution, whereas pure complex **1** cannot be obtained in hot THF solution. A greater amount of compound **6** appears under the same conditions, even

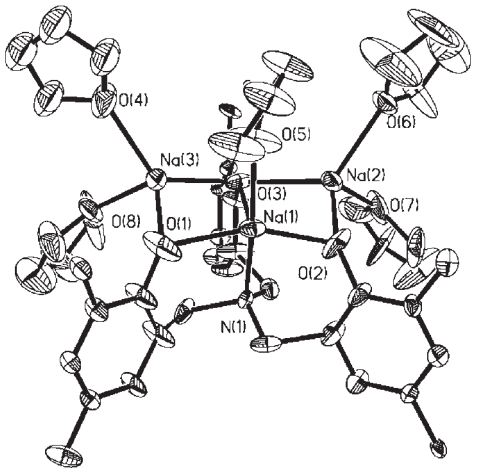

Figure 4. Molecular structure of complex **1** as 30% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms omitted for clarity). Selected bond lengths (Å): Na1−O1, 2.222(11); Na1−O2, 2.133(11); Na1−N1, 2.367(5); Na1−O3, 2.442(5); Na1−O5, 2.281(7).

after recrystallization. Therefore, a synergetic effect stabilizes the tetrasodium atrane cation in complex **2**, which we attribute primarily to the firm interaction ring of $-[Na-O-benzene]_3-$ that resulted from the p−π interaction and the coordination of oxygen. Compared to complex **1**, the additional p−π interactions between the Na^+ and benzene ring of the ligand in complex **2** can fix the position of phenol and decrease the nucleophilicity of oxygen and nitrogen atoms; the tetrasodium atrane can therefore be stabilized.

To check this synergetic effect in the tetranuclear sodium cation, the reaction of aminetris(phenol) ligand with 1 equivalent of $NaB(Ph)_4$ and 3 equivalents of NaH was conducted at 0 °C in a mixed solvent of CH_3OH and THF for 0.5 h. The mixture was then warmed to room temperature under a moist air atmosphere. The results show that the ligand is stable and that no compound **6** can be found by analysis of the NMR and mass spectra of the reaction mixture. One mass peak at 1047.8 was observed, which is attributed to the tetrasodium cation $[Na_4L(THF)_4]^+$ (Figure S1, Supporting Information).

We also attempted to use complex **2** to synthesize a catalyst. The reaction between complex **2** and BnOH was conducted and gave complex **5**. Understandably, the benzyloxy that is substituted for the methyl group is so basic that one Na^+ is attracted back to the alumatrane anion from the tetrasodium atrane cation to form the neutral complex **5**. Complex **5** can also be obtained by reflux of a mixture of BnOH and complex **4** in THF. The structure of complex **5** shows that the benzyloxy bridges sodium and aluminum atoms. The benzyloxy also locates at the apical position of a trigonal bipyramid (Figure 5). Complex **5** can work as an initiator for the ring-opening polymerization of lactide/lactone, which will be reported in a forthcoming paper.

In conclusion, the first example of a sodatrane and alumatrane ion-paired complex **2** is reported. The trinuclear sodium atrane of complex **1** is very labile; however, the tetranuclear sodium atrane cation in complex **2** is stable, possibly because of the multimetallic synergetic effect.

3. EXPERIMENTAL SECTION

General Procedures. All solvents were dried before use. Commercial chemicals were purchased and used without further purification.

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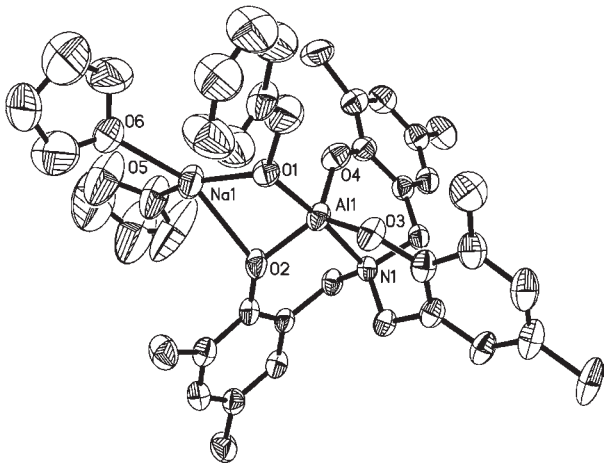

Figure 5. Molecular structure of complex **5** as 30% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms omitted for clarity). Selected bond lengths (Å): Al1−O2, 1.773(3); Al1−O1, 1.794(3); Al1−O6, 1.822(3); Al1−O3, 1.835(3); Al1−N1, 2.130(3); Al1−Na1, 3.077(3); Na1−O6, 2.267(3); Na1−O4, 2.299(4); Na1−O5, 2.300(4); Na1−O3, 2.410(3).

Tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine was prepared according to the method reported in the literature.[23] Mass spectroscopic data were obtained from a Bruker APEX II (FT-ICR MS), and NMR spectra were recorded using spectrometers of the Varian Mercury Plus family.

Synthesis of Complex ***1***. A solution of tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine (0.671 g, 1.0 mmol) and NaH (0.076 g, 3.15 mmol) was stirred in THF (15 mL) at −20 °C under a N_2 atmosphere for 12 h. The solvent was then removed under vacuum conditions to afford a white solid. For the subsequent decomposition of complex **1** at room temperature, only mixtures of complex **1** and compound **6** (about 8%) were obtained. ^{1}H NMR ($CDCl_3$, 200 MHz) for the mixture of **1** and **6**: δ (ppm) 7.27−7.19 (b, Ar−H), 6.89 (s, Ar-*H*), 6.85(s, Ar-*H*), 6.81(s, Ar-*H*), 4.84 (s, OCH_2N), 4.05(s, NCH_2, 4H), 3.64(s, NCH_2), 1.44 (s, t-Bu), 1.40 (s, t-Bu), 1.35 (s, t-Bu), 1.27 (s, t-Bu) 1.25(s, t-Bu). NMR data for compound **6**, ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 9.81 (s, O-*H*, 1H), 7.27 (d, J = 1.8 Hz, Ar-*H*, 1H), 7.21 (d, J = 1.8 Hz, Ar-*H*, 1H), 6.85 (d, J = 2.1 Hz, Ar−H, 1H), 6.81 (d, J = 2.4 Hz, Ar-*H*, 1H), 4.84 (s, OCH_2N, 2H), 4.05(S, NCH_2, 4H), 1.44 (s, t-Bu, 9H), 1.40 (s, t-Bu, 9H), 1.28 (s, t-Bu, 9H), 1.26 (s, t-Bu, 9H). ^{13}C NMR ($CDCl_3$, 300 MHz): 154.10, 149.92, 142.89, 141.06, 136.89, 135.88, 124.33, 123.42, 122.30, 120.48, 117.89, 79.64, 55.49, 49.99, 34.91, 34.30, 34.17, 31.64, 31.53, 29.69, 29.62.

Synthesis of Complex ***2***. A solution of tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine (0.671 g, 1.0 mmol) and sodium (0.050 g, 2.2 mmol) was stirred in THF (15 mL) at 50 °C under a N_2 atmosphere until the sodium dissolved completely. Then, $Al(Me)_3$ (0.6 mL, 1 mol/L in hexane) was slowly added to the solution. After the mixture was stirred for 12 h, the solvent was removed under vacuum conditions to afford a white solid. The white solid was dissolved in a mixture solvent of 5 mL THF and 10 mL hexane. The solution was then filtered through Celite, and the filtrate was stored for several days at room temperature. Colorless crystals were obtained. Yield: 0.52 g (53%). Anal. Calcd for $C_{115}H_{183}N_2AlNa_4O_{12}$: C, 72.48; H, 9.73; N 1.47. Found: C, 72.01; H, 9.33; N, 1.20. ^{1}H NMR ($CDCl_3$, 300 Hz): δ (ppm) 7.18(s, Ph, 3H), 7.07 (s, Ph, 6H), 6.75−6.74 (m, Ph, 3H), 4.19−4.15 (d, J = 12 Hz, NCH_2, 6H), 3.60 (b, OCH_2CH_2, 8H), 2.59−2.55 (d, J = 12 Hz, NCH_2, 6H), 1.84 (b, OCH_2CH_2, 24H), 1.40 (s, t-Bu, 27H), 1.33 (s, t-Bu, 27H), 1.26 (s, t-Bu, 54H), −0.737 (s, $AlCH_3$, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 136.9, 136.6, 130.88, 127.0, 123.4, 122.1, 121.7, 68.1, 59.9, 35.1, 34.8, 33.8, 31.9, 29.5, 25.3.

Synthesis of Complex ***3***. A solution of tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine (0.671 g, 1.0 mmol) and 1.2 mmol $Al(Me)_3$ (1.0 mol/L in hexane) was stirred in toluene (10 mL) at 80 °C under a N_2 atmosphere for 12 h. The solvent was removed under vacuum conditions to afford a white solid. Colorless crystals were obtained by cooling a hot THF solution of complex **3**. Yield: 0.62 g (81%). Anal. Calcd for $C_{49}H_{74}NAlO4$: C, 76.62; H, 9.71; N 1.82. Found: C, 76.34; H, 9.53; N, 1.60. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 7.22 (s, Ph, 3H), 6.83 (s, Ph, 3H), 4.50(b, OCH_2CH_2, 4H), 4.16−4.18(b, NCH_2, 3H), 3.58−3.60 (b, NCH_2, 3H), 2.09 (b, OCH_2CH_2, 4H), 1.41 (s, t-Bu, 27H), 1.26 (s, t-Bu, 27H). ^{13}C NMR ($CDCl_3$, 50 MHz): 154.95, 139.07, 137.11, 123.76, 123.59, 121.56, 71.60, 58.69, 34.91, 34.00, 31.69, 29.75, 25.30.

Synthesis of Complex ***4***. A solution of tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine (0.671 g, 1.0 mmol) and sodium (0.025 g, 1.2 mmol) was stirred in THF (10 mL) at 50 °C under a N_2 atmosphere until the sodium dissolved completely. Then, $Al(Me)_3$ (1.2 mL, 1 mol/L in hexane) was slowly added to the solution. After the mixture was stirred for 12 h, the solvent was removed under vacuum conditions to afford a white solid. The white solid was dissolved in hexane. The hexane solution was then filtered through Celite, and the filtrate was stored for several days at room temperature. Colorless crystals were obtained. Yield: 0.53 g (61%). Anal. Calcd for $C_{54}H_{85}NAlNaO_5$: C, 73.85; H, 9.76; N 1.59. Found: C, 74.01; H, 9.83; N, 1.80. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.14−7.13 (d, J = 4.0 Hz, Ar-*H*, 3H), 6.79−6.78 (d, J = 4 Hz, Ar-*H*, 3H), 4.16−4.13(d, J = 12.0 Hz, NCH_2,3H), 3.53 (b, OCH_2CH_2, 12H), 2.71−2.68 (d, J = 12.0 Hz, NCH_2, 3H), 1.75 (b, OCH_2CH_2, 12H), 1.40 (s, t-Bu, 27H), 1.25 (s, t-Bu,27H), −0.703 (s, $AlCH_3$, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 155.8, 137.8, 136.7, 123.3, 122.9, 122.5, 68.1, 59.9, 34.7, 33.9, 31.7, 29.6, 25.4.

Synthesis of Complex ***5***. *Method A.* To a rapidly stirred solution of complex **4** (0.53 g, 0.61 mmol) in toluene (25 mL) was added BnOH (1 mL, 1 M in toluene) at 50 °C. Stirring was continued for 12 h, and the solvent was removed under vacuum conditions to afford a white solid. The white solid was dissolved in a mixture of 5 mol of THF and 20 mL of hexane. The mixture solution was then filtered through Celite, and the filtrate was stored for several days at room temperature. Colorless crystals were obtained. Yield: 0.42 g (71%).

Method B. A solution of tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine (0.671 g, 1.0 mmol) and sodium (0.050 g, 2.2 mmol) was stirred in THF (15 mL) at 50 °C under a N_2 atmosphere until the sodium dissolved completely. Then, $Al(Me)_3$ (0.6 mL, 1 mol/L in hexane) was slowly added to the solution. After the mixture was stirred for 12 h, the solvent was removed under vacuum conditions to afford a white solid. The white solid was dissolved in 15 mol of toluene, and BnOH (1 mL, 1 M in toluene) was added. After the mixture was stirred for 24 h, the solvent was removed under vacuum conditions to afford a white solid. The white solid was dissolved in 5 mol of THF and 20 mL of hexane. The mixture was then filtered through Celite, and the filtrate was stored for several days at room temperature. Colorless crystals were obtained. Yield: 0.51 g (52%). Anal. Calcd for $C_{60}H_{89}NAlNaO_6$: C, 74.27; H, 9.25; N 1.44. Found: C, 74.60; H, 9.73; N, 1.21. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 7.57, 7.54(d, $PhCH_2$, 2H), 7.36−7.33 (m, $PhCH_2$, 3H), 7.17 (s, Ph, 3H), 6.8 (s, Ph, 3H), 5.39−5.33 (d, J = 12.8 Hz, Ph−CH_2, 1H), 5.10−5.03 (d, J = 12.8 Hz, Ph−CH_2, 1H), 4.21−4.14 (d, J = 13.2 Hz, NCH_2, 3H), 3.48 (b, OCH_2CH_2, 8H), 2.75−2.69 (d, J = 13.2 Hz, NCH_2, 3H), 1.73 (b, OCH_2CH_2, 8H), 1.42 (s, t-Bu, 27H), 1.25 (s, t-Bu,27H). ^{13}C NMR ($CDCl_3$, 50 MHz): 156.1, 148.58, 137.8, 136.5, 128.5, 127.8, 127.3,126.9, 125.5, 123.3, 122.9, 122.5, 68.1, 65.4, 59.9, 34.7, 34.5, 33.9, 31.7, 29.8, 25.3.

Crystallographic Studies. The X-ray single-crystal data collections were performed at room temperature on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by

Table 1. Crystal Data and Structure Refinements for Complexes of 1, 2, 3, and 5

	1	2	3	5
formula	$C_{65}H_{106}NNa_3O_8$	$C_{119}H_{191}AlNNa_4O_{13}$	$C_{49}H_{74}AlNO_4$	$C_{60}H_{89}AlNNaO_6$
fw	1098.48	1968.61	768.07	970.29
temp	296(2)	296(2)	296(2)	296(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2(1)$	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$
a, Å	11.073(6)	16.87(4)	14.368(5)	17.507(13)
b, Å	26.684(15)	20.35(5)	19.641(7)	16.057(12)
c, Å	11.873(7)	21.04(5)	16.530(6)	22.567(17)
α, deg	90.00	73.39(3)	90.00	90.00
β, deg	104.451(7)	87.13(3)	92.672(4)	102.29(3)
γ, deg	90.00	70.489(2)	90.00	90.00
V, Å^3	3397(3)	6413(27)	4660(3)	6198(8)
Z	2	2	4	4
density (calcd) g·cm^{-3}	1.074	1.020	1.095	1.040
absorb. coeff. mm^{-1}	0.085	0.082	0.085	0.084
$F(000)$	1200	2144	1680	2112
θ range	2.25−27.93	3.16−25.00	2.11−22.65	1.57−26.10
index ranges	$-14 \le h \le 14$	$-20 \le h \le 19$	$-14 \le h \le 15$	$-21 \le h \le 21$
	$-35 \le k \le 34$	$-19 \le k \le 24$	$-21 \le k \le 18$	$-19 \le k \le 16$
	$-15 \le l \le 14$	$-25 \le l \le 25$	$-17 \le l \le 17$	$-26 \le l \le 27$
data/restr./params	13424/324/628	19794/0/1240	6147/0/484	12107/0/622
GOF	0.782	0.718	1.026	0.842
final R indices	0.0742	0.0788	0.0843	0.0700
$[I > 2\sigma(I)]$	0.1663	0.1361	0.2224	0.1887
peak and hole e.Å^{-3}	0.176−0.176	0.299−0.160	0.896 −0.605	0.892−0.240
CCDC number	824606	824607	824605	824608

direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs.[24] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The crystal data and refinement results are summarized in Table 1.

■ ASSOCIATED CONTENT

Supporting Information. CIF file giving crystallographic data for **1**, **2**, **3**, and **5** with CCDC reference numbers of 824606, 824607, 824605, and 824608. Mass spectrum of the reaction mixture of aminetris(phenol) ligand with 3 equivalents of NaH and 1 equivalent of $NaB(Ph)_4$ in THF and CH_3OH. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 86 931 8912580. Fax: 86 931 8912582. E-mail: wujc@lzu.edu.cn.

Author Contributions

[†]These authors contributed equally to this work.

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