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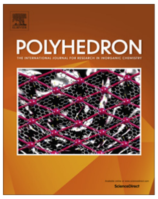

Synthesis and characterization of sterically crowded aryloxides: 'Mitsubishi'-class of tetrametallic aluminum complexes

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ABSTRACT

A new series of tetrameric aluminum molecules with a Mitsubishi structure, composed of two cage-shaped triphenolic ligands with a tripod-chelated structure, have been synthesized and characterized. Transmetalation from the cage-shaped borates was a proper method for the synthesis of these aluminum complexes. All complexes were determined via X-ray crystallography and NMR measurements. These Lewis acidic aluminum complexes catalyze the hetero Diels Alder reaction of the Danishefsky diene with benzaldehyde.

1. Introduction

The elements in Group 13, such as boron (B), aluminum (Al), gallium (Ga) and indium (In), possess derivatives that behave as a Lewis acid and originate from a vacant *p*-orbital. These are versatile metals that are used in precise organic syntheses [1–4]. The properties of these metals are often controlled by the steric or electronic factors of ligands, which play important roles in developing peculiar metal complexes with novel reactivities and properties. The use of the multidentate ligands is one of the promising strategies in ligand design, because the multidentate ligands can reduce the freedom of the metal–ligand coordination and impart higher steric requirements to the resultant metal complexes, compared with monodentate ligands [5–13].

Scott and co-workers reported pioneering studies on the structural control of the coordination geometry of aluminum complexes. They employed a tripodal ligand and synthesized trimeric aluminum complex **1** as the basic platform of a reactive Lewis acid catalyst (Fig. 1(A)) [13]. Recently, we elucidated the effectiveness of a cage-shaped triphenolic ligand to control the Lewis acidity of a boron atom (Fig. 1(A)) [14]. The cage-shaped borate esters with a tripod-chelated structure such as **3** show a higher level of Lewis acidity than that of the planar structure of a common borate **2** due to the weaker electronic communication between O and B atoms induced by the geometric restrictions. As shown in Fig. 1(A), the Lewis acidity of the cage-shaped borate **4** can be electronically tuned by the introduction of substituents, R, such as halogens [15], aryl groups [16], and hetero aromatic rings [17]. They also can be sterically controlled by changing a tether atom, X, from carbon to silicon [18], which allows precise control of the LUMO levels and dihedral angles of $C(Ar_{ipso})—O—B—O$ in the cage. These accessible chemical modification of the tripod ligands is a promising way to design the cage-shaped Lewis acids with a variety of characteristics. Applying this strategy to an aluminum atom instead of a boron atom is a fascinating proposition. It is well known that an aluminum complex with aryloxide or alkoxide ligands can exhibit many types of structures [19–22] ranging from monomeric [23–27], dimeric [25–32], and trimeric [13,28–30,33] to tetrameric [33–36] species depending on the degree of the steric encumbrance incorporated into the ligands (Fig. 1(B)). These facts raised the expectations that our triphenolic ligand with a tripod-chelated structure could impart dramatic influence on the molecular geometry of an aluminum complex. Here, we describe the tetrameric aluminum complexes **6a**–**c** based on cage-shaped triphenolic ligands **5a**–**c**, which contain a central six-coordinate aluminum with three peripheral four-coordinate aluminum atoms (Fig. 1 (C)). The aluminum–oxygen framework in the obtained complexes formed a tri-diamond skeleton, which is reminiscent of Mitsubishi Ltd.'s logo [37]. These previously reported aluminum complexes with a Mitsubishi structure may be viewed as metal alkoxides

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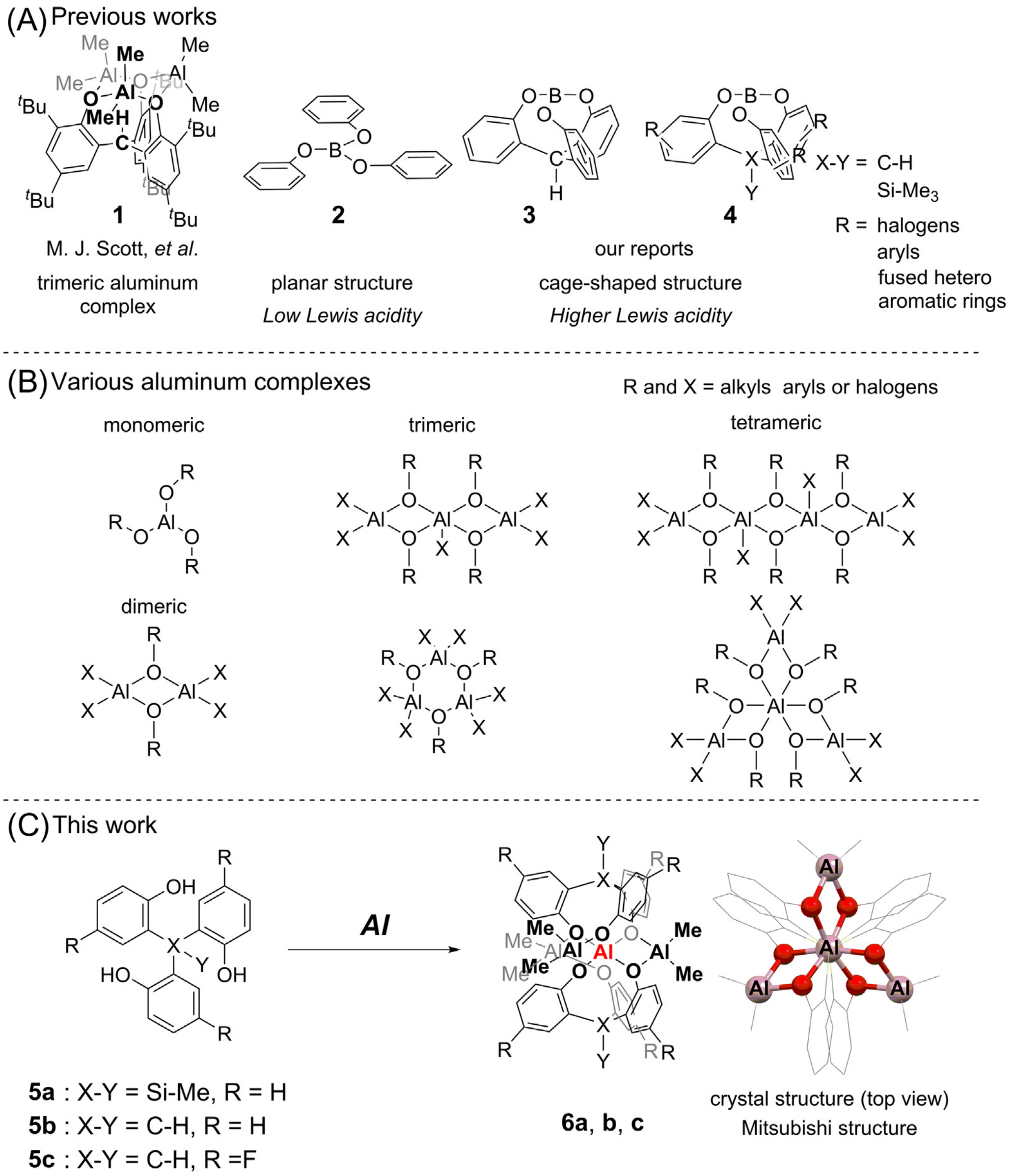

Fig. 1. (A) Scott's trimeric aluminum complex **1** and planar-/cage-shaped borates **2**–**4**, (B) structures of aryloxide or alkoxide aluminum complexes, and (C) this work.

[14,20,21,38–46], whereas those reported here are alkyl aluminum aryloxides based on tripodal ligands.

2. Synthesis of Mitsubishi-type aluminum complexes

2.1. Direct treatment of the triphenolic ligand with $AlMe_3$

First, we attempted to synthesize a monomeric cage-shaped aluminum complex similar to the cage-shaped borates **2** and **3** [14]. However, the treatment of the triphenolic ligand **5a** with 1.0 equivalent $AlMe_3$ in CH_2Cl_2/THF selectively afforded a tetrameric aluminum complex **6a** with a Mitsubishi structure as an isolable product regardless of the stoichiometry. The observation of the reaction mixture via ^{27}Al NMR measurement indicated that a broad signal at around 230 ppm emerged in the early reaction stages, and is believed to have come from a trimeric aluminum species such as **7a**. The signal then was gradually converted into a set of sharp signals at 52.0 ppm and a broad signal at around 100.0 ppm, which corresponds to the two types of aluminum atoms in the tetrameric complex **6a** (see below). Under dilute or low-temperature conditions, the generation of **7a** was observed prior to that of **6a**, which suggests that the trimeric complex **7a** is one of the kinetically-controlled products that is shifted to the thermodynamically favored tetrameric complex **6a**. After optimizing the reaction condition, a 2.0 equivalent of $AlMe_3$ was suitable for the synthesis of the complex **6a**, giving the product quantitatively (Scheme 1(A)). Unfortunately, this method can only accomplish the synthesis of complex **6a**; a change in the tether atom of the ligand from silicon to carbon, such as **5b** and **5c**, yielded unidentified products, presumably due to a decrease in the ligand flexibility derived from the downsizing of the tether atom.

2.2. Transmetalation via the cage-shaped borates

In order to establish versatility in the synthesis of the tetrameric aluminum complexes with a Mitsubishi structure, we developed a transmetalation method where the cage-shaped borate **4**

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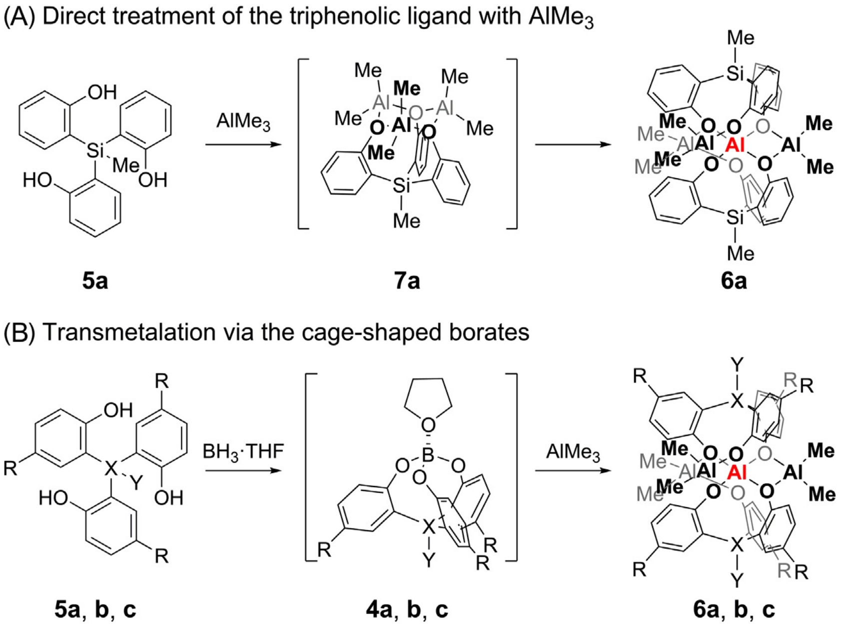


Scheme 1. The synthetic scheme for **6a**–**c**. (A) Direct treatment of the triphenolic ligand with trimethylaluminum and (B) transmetalation via cage-shaped borates.

was generated *in situ* and employed as a precursor. As shown in Scheme 1(B), the treatment of the cage-shaped borate **4a** with an excess of $AlMe_3$ gave the desired tetrameric aluminum complex **6a**, quantitatively. Moreover, the class of the tether atom of carbons **6b** and **6c** was obtained under the same conditions. This is the first example of a transmetalation reaction of cage-shaped borates to other metal complexes. It should be noted that the cage-shaped borates play a template-like role in forming these tetrameric aluminum complexes with a Mitsubishi structure. The moderate fixation of metal by the tripodal ligands may promote reorganization from the monomeric cage-shaped borate to a tetrameric aluminum complex.

3. Results and discussion

3.1. NMR studies

In the ^{1}H NMR spectra of **6**, the absence of the —OH resonance of the triphenolic ligands **5** was clear. The $\delta(^{1}H)$ of X_{tether}–Y at the tether position showed typical signals for forming a cage-shaped complex, as the downfield shift of the $\delta(^{1}H)$ of Si—Me for **6a** (0.95 → 1.12 ppm) and the upfield shift of the $\delta(^{1}H)$ of C—H for **6b** (6.07 → 5.41 ppm) and **6c** (6.08 → 5.50 ppm) were observed in comparison with those of the free ligands **5a**–**c**. In addition, the ^{1}H NMR signals of the aromatic protons of **6** maintained a C_3 symmetry similar to those of free ligands, which implies the formation of a product with high symmetry. The highly symmetric structures of the obtained complexes was also consolidated by the ^{27}Al NMR measurement. The ^{27}Al NMR spectra of **6** showed two signals at around ~100 ppm and ~55 ppm for Al atoms, with coordination numbers of four and six, respectively, by the integration values of these signals. Compared with the previously reported ^{27}Al NMR spectra of the methyl aluminum alkoxides with a Mitsubishi structure [43,44], the upfield shift of the $\delta(^{27}Al)$ four-coordinate aluminum atom (~150 ppm) and the downfield shift of the $\delta(^{27}Al)$ six-coordinate aluminum atom (~11 ppm) were observed. We believe the ring current effect from the aryl groups in ligand **5** caused this discrepancy. Examination of the molecular geometry suggests that the complex has an idealized D_3 symmetry in a solution state.

3.2. Molecular geometries

The highly symmetric structure of complex **6** was successfully identified by X-ray crystallography. The ORTEP diagrams of complex **6** are shown in Fig. 2. Although the data for **6a** remained the unsolved alerts, the others were uneventfully solved. The geometry around the aluminum atoms is shown in Fig. 3. Selected bond lengths and bond angles are included in Table 1.

In Figs. 2(A) and 3(A), the geometry of the aluminum–oxygen framework clearly exhibits a Mitsubishi structure with an almost D_3 symmetry, which is consistent with the high symmetry observed via the NMR measurements. The X_{tether}–Y bonds at the tether position of **6** have an *anti*-orientation against the coordinated aluminum atoms (Fig. 2(B)), which reveals distinct differences with the trimeric aluminum complex **1** of a *syn*-orientation, as reported by Scott and coworkers [13]. The molecular structure consists of a central six-coordinate aluminum atom and three peripheral four-coordinate aluminum atoms. The peripheral aluminum atoms occupy an equilateral-triangular plane and the six-coordinate aluminum atoms are located at the center of the triangular plane. The two triphenolic ligands approach from either side of the triangular plane of the peripheral aluminums and each of the oxygen atoms of the ligand bidentately coordinates both of the central and peripheral aluminum atoms. The central aluminum atom is designated a 3^{+} cation surrounded by six oxygen atoms from three monoanioic $[Me_2Al(OAr_{upper})(OAr_{bottom})]^{-}$ (Ar = triphenolic ligand) groups in a slightly distorted octahedral configuration.

As shown in Fig. 2 and Table 1, the structures of the three complexes are almost identical. For three complexes, no significant difference in the average bond distances of the $Al_{peripheral}$—O (1.834(4)–1.861(3) Å), $Al_{central}$—O (1.880(4)–1.895(4) Å) and the average bond angles of O—$Al_{peripheral}$—O (78.65(13)–77.8(18)°) is observed, which also demonstrates the similarities in the previously reported methyl aluminum alkoxides with a Mitsubishi structure [43,44]. In contrast, the average distance between the central aluminum and the tether atom of the triphenolic ligand ($Al_{central}$–X_{tether}) varies according to the size of the tether atom, 3.753 Å for **6a** (X_{tether} = Si) versus 3.553–3.571 Å for **6b** and **6c** (X_{tether} = C), which reflects the flexibility of the cage-shaped ligand. This fine structural control of

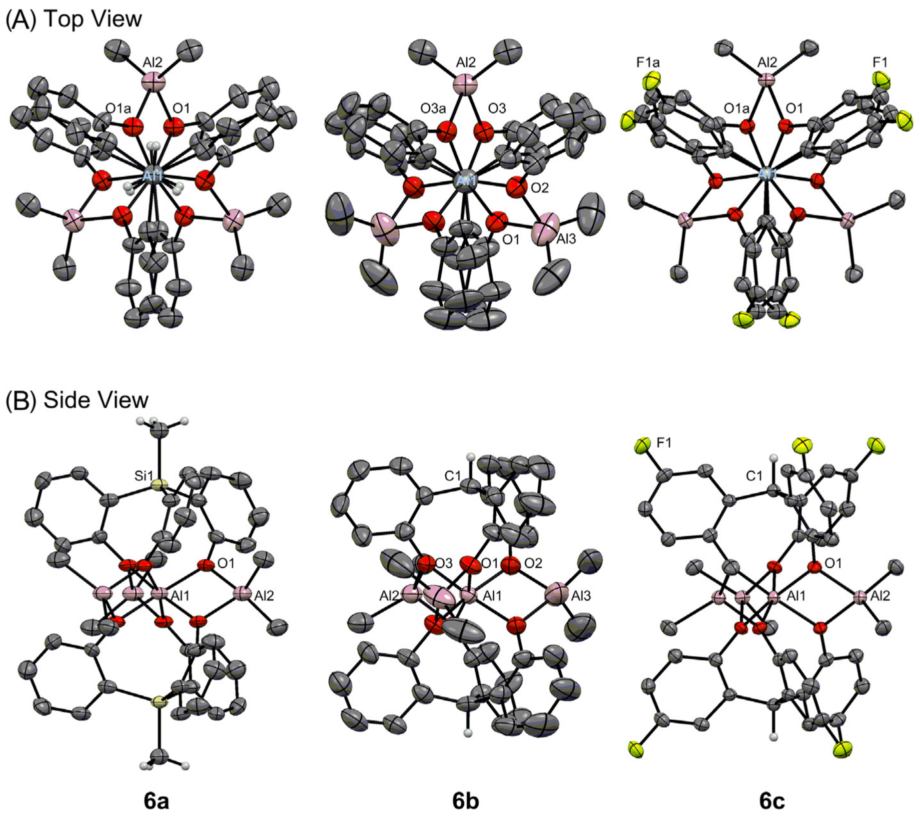


Fig. 2. ORTEP diagrams of the molecular structures of **6a**–**c** showing 50% thermal ellipsoid probability. (A) Top view and (B) side view. Hydrogen atoms, except for those at the tether positions, are omitted for clarity.

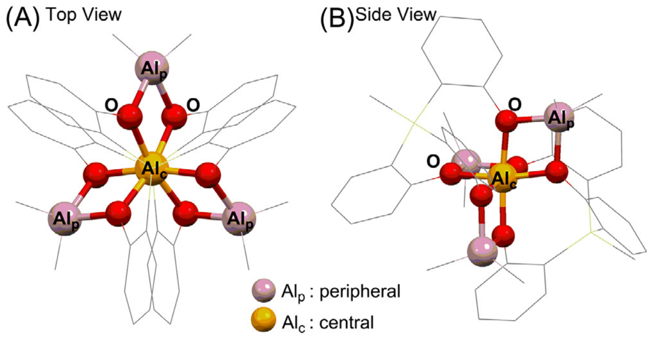
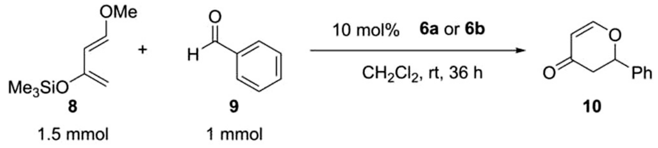


Fig. 3. The coordination geometry around the aluminum atoms of **6a**. (A) Side view and (B) Top view. Selected aluminum and oxygen atoms are depicted as a ball and stick model, and the other atoms are depicted as a wireframe model; hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (mean values reported for **6b**) and bond angles (mean values reported for **6b**) for **6a**–**c**.

	6a	**6b**	**6c**
$Al_{peripheral}$–O/Å	1.853(4)	1.834(4)	1.861(3)
$Al_{central}$–O/Å	1.895(4)	1.880(4)	1.891(3)
$Al_{central}$–X_{tether}/Å	3.753	3.553	3.571
O–$Al_{peripheral}$–O/°	78.4(2)	77.8(18)	78.65(13)
O_{ax}–$Al_{central}$–O_{eq}/°	76.33(13)	75.7(16)	77.15(12)
O_{ax}-$Al_{central}$-O_{ax}/°	169.05(12)	166.1(11)	166.60(17)

Table 2
Hetero Diels–Alder reaction catalyzed by **6a** or **6b**.



Entry	Catalyst	Yield of **10**
1	**6a**	29%
2	**6b**	53%

such a complicated Mitsubishi-type complex shows the effectiveness of the cage-shaped ligand with the accessibility of chemical modification. The geometries around the six-coordinate aluminum atom possess a distorted octahedral coordination (Fig. 3(B)); the angles between O atoms occupying the axial positions of the central aluminum atom vary from 180 ° for a perfect octahedron (169.05(12)° for **6a**, 166.1(11)° for **6b** and 166.60(17)° for **6c**).

3.3. Application to the Lewis acid catalyzed reaction

To estimate Lewis acid catalytic ability, a hetero Diels-Alder reaction of the Danishefsky diene **8** with benzaldehyde **9** was examined in the presence of a tetrameric aluminum complex **6a** or **6b** [15,47,48]. The results are shown in Table 2. Both complexes catalyzed the reaction and complex **6b** afforded a much higher yield of the product **10** compared with that given by **6a**. It seemed strange that the tetrameric aluminum complexes **6** would possess Lewis acidity because the aluminum atoms in complex **6** have no vacant *p*-orbital, which is perfectly filled by the coordination of the methyl groups or oxygen atoms of the triphenolic ligands. While the mechanistic details remain unclear, there may be a disproportionate pathway from the tetrameric aluminum complex **6** to the monomeric or trimeric aluminum species with Lewis acidity under the reaction conditions.

4. Conclusions

Tetrameric aluminum molecules with a Mitsubishi structure based on two cage-shaped triphenolic ligands were synthesized and characterized. The transmetalation from a cage-shaped borate to the tetrameric aluminum complex enabled us to evaluate the structural properties from among a series of cage-shaped Mitsubishi-type aluminum complexes. The molecular geometry was perfectly determined by X-ray crystallography and NMR measurements, which showed a near D_3 symmetry of three tetrahedrally four-coordinated and one octahedrally six-coordinated aluminum atoms. These aluminum complexes exhibited the Lewis acidity and catalyzed the hetero Diels Alder reaction of the Danishefsky diene with benzaldehyde.

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Appendix A. Supplementary data

CCDC 1486007, 1486008 and 1486009 contain the supplementary crystallographic data for **6a**, **6b** and **6c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.10.019.

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