

Communication

Synthesis and characterization of a β -diketiminato-supported aluminum dication

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Abstract

A base-stabilized mononuclear aluminum dication has been prepared by extrusion of two triflate anions from a precursor β -diketiminato-supported aluminum bis(triflate) using the tris(2-aminoethyl)amine (tren) ligand.

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1. Introduction

Interest in aluminum cations has been stimulated by their use as catalysts and Lewis acid promoters. Several types of aluminum cations have now been recognized [1]. However, all reported examples are monocationic and, to the best of our knowledge, mononuclear aluminum dications [2] have not been prepared. We describe the first example of such a dication. At the outset, it was clear that the selection of the supporting ligand would be important. Since β -diketiminato ligands have been used effectively for the support of other potentially redox active aluminum entities such as Al(1) [3,4], we opted to employ this ligand class in the present case.

2. Results and discussion

Treatment of $[\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2]\text{AlCl}_2$ [5] with two equivalents of AgOTf in CH_3CN solution at room temperature resulted, after workup, in an 82% yield of pale yellow $[\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2]\text{Al}(\text{OTf})_2$ (**1**). The bis(triflate) **1** was characterized by HRMS and multinuclear NMR spectroscopy.

The reaction of **1** with an equimolar quantity of 2,2'-bipyridine (bipy) in CH_2Cl_2 solution at ambient temperature resulted in the formation of the 1:1 complex **2** in 71% yield (Scheme 1). The X-ray crystal structure of **2** (Fig. 1) shows that it is a neutral six-coordinate complex of **1** with bipy and that both triflate groups remain coordinated. Interestingly, however, the Al(1)–O(1) distance is ~ 0.04 Å longer than the Al(1)–O(4) distance, possibly implying incipient ionization of one of the triflate ligands. One of the consequences of the coordination of the bipy ligand is that the $\text{C}_3\text{N}_2\text{Al}$ ring is significantly distorted and adopts a boat conformation. The dihedral angles of the N(1)–Al(1)–N(2) and C(1)–C(2)–C(3) planes with respect to the N(1)–C(1)–C(3)–N(2) plane are 12.21° and 20.21° , respectively. A further consequence of the steric crowding in **2** is that both C_6F_5 substituents are bent down with respect to the N(1)–C(1)–C(3)–N(2) plane. The two triflate ligands maintain their non-equivalence in solution as evidenced by the observation of distinct ^{19}F NMR chemical shifts ($\delta = -79.73$ and -80.56 ppm).

The ambient temperature reaction of 2,2':6',2''-terpyridine (terpy) with **1** also resulted in the formation of a complex with 1:1 stoichiometry. However, examination of the crystalline product by X-ray diffraction revealed that one of the triflate ligands had been extruded and the aluminum monocation **3** is formed (Fig. 2). The closest anion–cation

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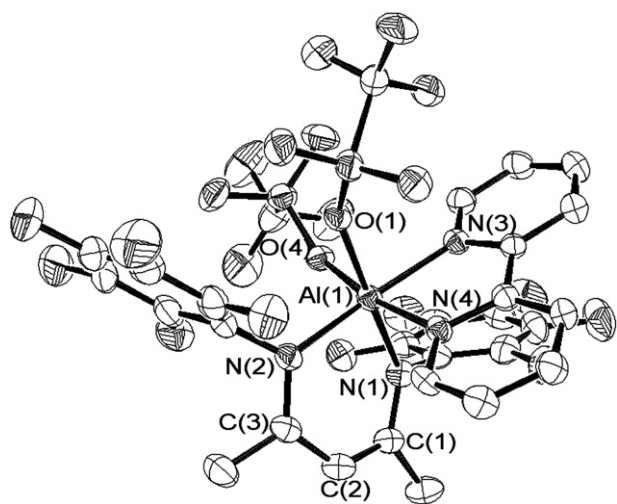
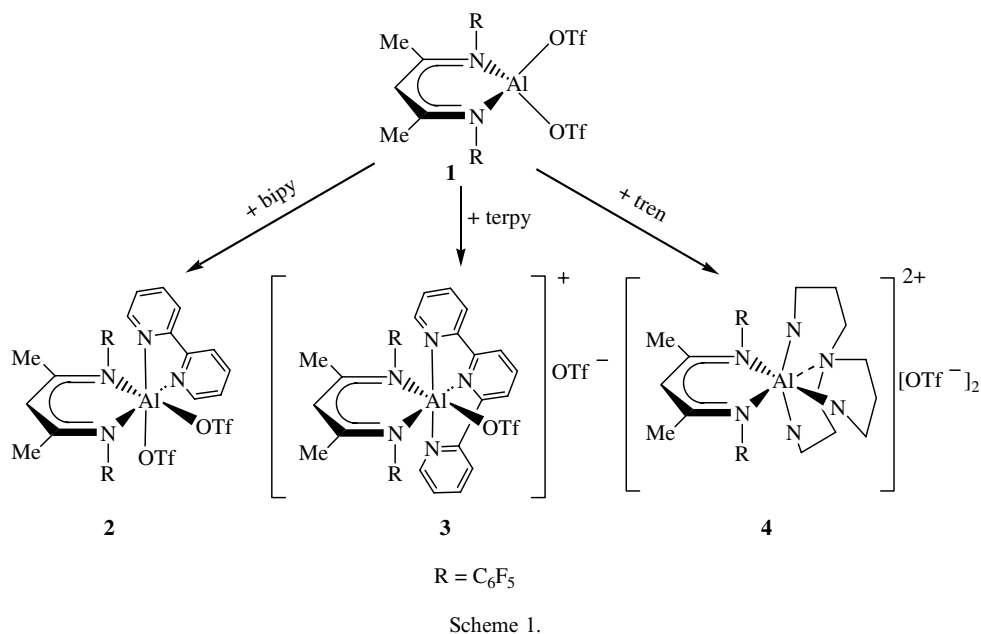


Fig. 1. ORTEP view of $\{\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2\}\text{Al}(\text{bipy})(\text{OTf})_2$ (**2**) showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Al(1)–O(1) 1.941(2), Al(1)–O(4) 1.9025(18), Al(1)–N(3) 2.053(2), Al(1)–N(4) 2.047(2), Al(1)–O(4) 1.9025(18), Al(1)–N(3) 2.053(2), Al(1)–N(4) 2.047(2), Al(1)–N(1) 1.989(2), N(1)–C(1) 1.341(3), C(1)–C(2) 1.389(4), C(2)–C(3) 1.389(4), C(3)–N(2) 1.348(3), N(2)–Al(1) 1.975(2), O(1)–Al(1)–O(4) 86.87(8), N(1)–Al(1)–N(2) 90.24(10), Al(1)–N(1)–C(1) 124.37(18), N(1)–C(1)–C(2) 122.6(3), C(1)–C(2)–C(3) 127.3(3), C(2)–C(3)–N(2) 122.3(3), C(3)–N(2)–Al(1) 125.47(18).

contacts are 8.572 Å between Al(1) and O(4), and 6.804 Å between Al(1) and F(16). The Al–O distance for the bound triflate (1.933(3) Å) falls between those found for the bipy complex, **2** (1.9025(18) and 1.941(2) Å). Overall, the terpy complex **3** is less sterically strained than the bipy complex **2**. This is evident from the fact that e.g. the sum of bond angles for the C₃N₂Al ring of **3** (717.0(4)°) is greater than that for **2** (712.3(3)°).

At this point it was clear that the removal of both triflate anions and generation of the targeted base-stabilized dica-

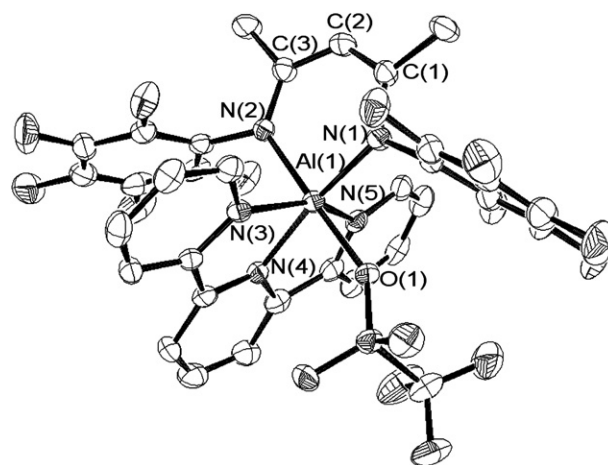


Fig. 2. ORTEP view of the $[\{\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2\}\text{Al}(\text{terpy})(\text{OTf})]^+$ cation (**3**⁺) showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Al(1)–O(1) 1.933(3), Al(1)–N(3) 2.0563(3), Al(1)–N(4) 1.991(3), Al(1)–N(5) 2.060(3), Al(1)–N(1) 1.974(4), N(1)–C(1) 1.328(5), C(1)–C(2) 1.400(6), C(2)–C(3) 1.380(6), C(3)–N(2) 1.357(5), N(2)–Al(1) 1.967(4), N(3)–Al(1)–N(5) 155.70(15), N(3)–Al(1)–N(4) 78.10(14), N(4)–Al(1)–N(5) 77.67(14), O(1)–Al(1)–N(4) 85.37(13), N(1)–Al(1)–N(2) 92.19(15), Al(1)–N(1)–C(1) 126.2(3), N(1)–C(1)–C(2) 122.1(4), C(1)–C(2)–C(3) 128.5(4), C(2)–C(3)–N(2) 123.4(4), C(3)–N(2)–Al(1) 124.6(3).

tion would necessitate the use of a stabilizing tetradentate ligand. Accordingly, **1** was treated with an equimolar quantity of tris(2-aminoethyl)amine (tren) in CH₃CN solution at ambient temperature. The ¹⁹F NMR spectrum of the product (**4**) revealed the presence of only one resonance for the triflate groups (δ –79.65 ppm) thus implying that both triflate anions had been extruded. This conclusion was confirmed by the X-ray crystal structure of **4** (Fig. 3). The two triflate anions are well separated from the aluminum dication. The closest anion–cation contact is 4.302 Å between Al(1) and O(1). The β -diketiminato ring

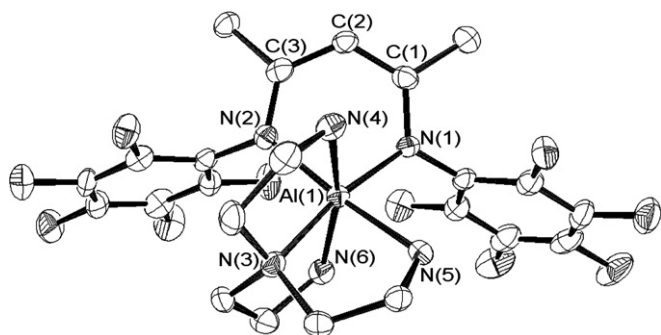


Fig. 3. ORTEP view of the $[\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2]\text{Al}(\text{tren})^{2+}$ cation (**4**⁺) showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.962(5), Al(1)–N(2) 2.052(4), Al(1)–N(3) 2.093(5), Al(1)–N(4) 2.053(5), Al(1)–N(5) 2.086(4), Al(1)–N(6) 2.037(5), N(1)–C(1) 1.365(7), C(1)–C(2) 1.372(7), C(2)–C(3) 1.405(8), C(3)–N(2) 1.354(7), N(2)–Al(1) 2.052(4), N(4)–Al(1)–N(6) 164.4(2), N(1)–Al(1)–N(5) 87.65(18), N(2)–Al(1)–N(3) 102.00(18), N(1)–Al(1)–N(2) 88.18(18), Al(1)–N(1)–C(1) 120.1(3), N(1)–C(1)–C(2) 121.7(5), C(1)–C(2)–C(3) 125.2(5), C(2)–C(3)–N(2) 122.8(5), C(3)–N(2)–Al(1) 118.1(4).

of **4** is significantly more distorted toward the boat conformation than those of the bipy and terpy complexes. Thus, the dihedral angles between the C(1)–N(1)–C(3)–N(2) plane and the N(1)–Al(1)–N(2) and C(1)–C(2)–C(3) planes are 36.87° and 20.59°, respectively, and the sum of bond angles for the C₃N₂ Al ring is 694.2(5)°. Significant distortions are also evident in the roughly octahedral geometry at the six-coordinate aluminum center. For example, the axial bond angle, N(4)–Al(1)–N(6), is 164.4(2)° and the equatorial bond angles range from 81.31(19)° to 102.00(18)°. To minimize the steric interactions with the coordinated tren ligand, both C₆F₅ groups are bent away from the C(1)–N(1)–C(3)–N(2) plane such that the C₆F₅ ring centroids deviate from said plane by an average of 1.348 Å. The corresponding distances for **2** and **3** are 0.801 and 0.316 Å, respectively.

3. Experimental

All reactions were performed under a dry, oxygen-free atmosphere utilizing Schlenk manifold techniques or a drybox. All solvents were dried and distilled under nitrogen prior to use. NMR spectra were recorded at 295 K on a Varian Unity +300 instrument (¹H 300 MHz; ¹³C{¹H} 75 MHz; ¹⁹F 282 MHz; ²⁷Al{¹H} 78 MHz). Low- and high-resolution mass spectra were measured on Finnigan MAT TSQ-700 and VG Analytical ZAB-VE sector instruments, respectively.

3.1. Preparation of $[\text{CH}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2]\text{Al}(\text{OTf})_2$ (**1**)

Solid AgOTf (0.680 g, 2.656 mmol) was added to 40 mL of an acetonitrile solution containing 0.700 g (1.328 mmol) of $[\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2]\text{AlCl}_2$ at ambient temperature in the absence of light. The reaction mixture was left to stir for 2 d, after which it was filtered through Celite® and the solvent was removed under reduced pressure resulting

in 0.820 g (82%) of pale yellow solid **1**. This solid was used in subsequent reactions without further purification. MS (CI⁺, CH₄): m/z 755 [M+H]⁺. HRMS (CI⁺, CH₄). Calc. for C₁₉H₈AlF₁₆N₂O₆S₂, m/z 754.9384. Found: 754.9389. ¹H NMR (CD₃CN): δ 2.26 (s, 6H, CH₃), 5.54 (s, 1H, γ-CH). ¹⁹F NMR (CD₃CN): δ –79.45 (s, 6F, OTf), –145.68 to –164.50 (m, 10F, C₆F₅). ²⁷Al NMR (CD₃CN): δ –5.40.

3.2. Preparation of

$[\text{CH}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2]\text{Al}(\text{bipy})(\text{OTf})_2$ (**2**)

Solid 2,2'-bipyridine (0.021 g, 0.134 mmol) was added to 10 mL of a methylene chloride solution containing 0.100 g (0.132 mmol) of **1**. The reaction mixture was allowed to stir overnight, after which it was filtered. Hexane (10 mL) was added to the filtrate resulting in the formation of 0.852 g (71%) of pale yellow crystalline **2** after 2 d. MS (CI⁺, CH₄): m/z 911 [M+H]⁺. HRMS (CI⁺, CH₄). Calc. for C₁₉H₁₆AlF₁₆N₄O₆S₂, m/z 911.0071. Found: 911.0064. ¹H NMR (CD₃CN): δ 1.28 (s, 6H, CH₃), 5.50 (s, 1H, γ-CH), 7.90 (m, 2H, 5,5'-CH), 8.45 (m, 2H, 4,4'-CH), 8.52 (m, 2H, 3,3'-CH), 8.90 (m, br, 2H, 6,6'-CH). ¹⁹F NMR (CD₃CN): δ –79.73 and –80.56 (s, 6F, OTf), –143.98 to –151.13 (m, o-F, 4F), –158.29 to –161.04 (m, p-F, 2F), –164.26 to –164.78 (m, m-F, 4F). ²⁷Al NMR (CD₃CN): δ 13.09 (broad, s).

3.3. Preparation of

$[\text{CH}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2]\text{Al}(\text{terpy})(\text{OTf})_2$ (**3**)

This compound was prepared in a similar fashion to **2** using **1** (0.100 g, 0.132 mmol) and 2,2':6',2''-terpyridine (0.031 g, 0.133 mmol). Yield of pale yellow crystalline **3** = 0.097 g (74%). MS (CI⁺, CH₄): m/z 838 [M–OTf]⁺. HRMS (CI⁺, CH₄). Calc. for C₃₃H₁₈AlF₁₃N₅O₃S, m/z 838.0738. Found: 838.0732. ¹H NMR (CD₃CN): δ 1.65 and 1.67 (s, 3H, CH₃), 2.25 and 2.26 (s, 3H, CH₃), 5.74 (s, 1H, γ-CH), 8.05 (m, 2H, 2,4'-6,4''-CH), 8.42 (m, 2H, 2,5'-6,5''-CH), 8.45 (m, 1H, 4-CH), 8.50 (m, 2H, 3-5-CH), 8.52 (m, 2H, 2,6'-6,6''-CH), 8.99 (m, 2H, 2,3'-6,3''-CH). ¹⁹F NMR (CD₃CN): δ –79.53 and –80.35 (s, 6F, OTf), –144.64 and –146.67 (d, o-F, 4F, ³J_{FF} = 16.9 Hz), –154.74 and –158.40 (m, p-F, 2F), –161.74 and –163.04 (m, m-F, 4F). ²⁷Al NMR (CD₃CN): δ 17.72 (broad, s).

3.4. Preparation of

$[\text{CH}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2]\text{Al}(\text{tren})][2 \cdot \text{OTf}]$ (**4**)

This compound was prepared in a similar fashion to **2** using 0.100 g (0.132 mmol) of **1** and tris(2-aminoethyl)amine (0.020 g, 0.137 mmol). Yield of pale green crystalline **4** = 0.092 g (77%). MS (ESI⁺): m/z 601 [M²⁺–H⁺]⁺. HRMS (ESI⁺). Calc. for C₂₃H₂₄AlF₁₀N₆, m/z 601.1718. Found: 601.1726. ¹H NMR (CD₃CN, [M] = 0.040): δ 1.99 (s, 6H, CH₃), 2.74 (t, 6H, N–CH₂, ³J_{HH} = 5.4 Hz), 2.97 (t, 6H, H₂N–CH₂, ³J_{HH} = 5.7 Hz),

5.34 (s, 1H, γ -CH), 5.38 (s, br, 6H, NH₂). ¹³C NMR (CD₃CN, saturated solution): 20.47 (s, CH₃), 38.52 (s, CH₂-NH₂), 52.25 (s, N-CH₂), 98.74 (s, H-C(γ)), 120.90 (q, CF₃, ¹J_{CF} = 319 Hz), 137.04, 140.23 and 143.50 (C₆F₅), 165.53 (s, C-N). ¹⁹F NMR (CD₃CN, saturated solution): δ -79.65 (s, 6F, OTf), -151.72 (d, *o*-F, 4F, ³J_{FF} = 16.1 Hz), -163.64 (t, *p*-F, 2F, ³J_{FF} = 20.3 Hz), -166.02 (m, *m*-F, 4F). ²⁷Al NMR (CD₃CN): no signal detected.

3.5. Crystal data

For **2**: C₂₉H₁₅AlF₁₆N₄O₆S₂, *M_r* = 910.57; *a* = 34.635(5), *b* = 12.688(5), *c* = 17.564(5) Å³; α = 90°, β = 103.128(5)°, γ = 90°; *V* = 7517(4) Å³; *Z* = 8; space group *C2/c* (monoclinic); *T* = 153(2) K; λ = 0.71073 Å; μ = 0.291 mm⁻¹; ρ_{calc} = 1.609 g cm⁻³; $2\theta_{\text{max}}$ = 55.00°; *F*(000) = 3632; 14331 measured reflections, 8618 independent (*R*_{int} = 0.0364); *R*₁ = 0.0530, *wR*₂ = 0.1362; largest difference peak and hole 0.421/−0.398 e Å⁻³. For **3** · (CH₂Cl₂)₃: C₃₇H₂₄AlCl₆F₁₆N₅O₆S₂, *M_r* = 124.41; *a* = 19.758(5), *b* = 13.678(5), *c* = 19.512(5) Å; α = 90°, β = 113.289(5)°, γ = 90°; *V* = 4843(2) Å³; *Z* = 4; space group *P2₁/c* (monoclinic); *T* = 153(2) K; λ = 0.71073 Å; μ = 0.571 mm⁻¹; ρ_{calc} = 1.704 g cm⁻³; $2\theta_{\text{max}}$ = 55.00°; *F*(000) = 2480; 19427 measured reflections, 10976 independent (*R*_{int} = 0.0720); *R*₁ = 0.0670, *wR*₂ = 0.1692; largest difference peak and hole 0.797/−0.816 e Å⁻³. For **4** · (CH₂Cl₂)₂: C₂₇H₂₃AlCl₄ F₁₆N₆O₆S₂, *M_r* = 1064.41; *a* = 11.195(2), *b* = 21.287(4), *c* = 17.378(4) Å; α = 90°, β = 100.34(3)°, γ = 90°; *V* = 4073.9(14) Å³; *Z* = 4; space group *P2₁/c* (monoclinic); *T* = 153(2) K; λ = 0.71073 Å; μ = 0.537 mm⁻¹; ρ_{calc} = 1.745 g cm⁻³; $2\theta_{\text{max}}$ = 54.00°; *F*(000) = 2152; 14891 measured reflections, 8853 independent (*R*_{int} = 0.0696); *R*₁ = 0.0763, *wR*₂ = 0.1971; largest difference peak and hole 0.965/−0.933 e Å⁻³. The crystal data were collected on a Nonius Kappa CCD diffractometer at

153(2) K. The structures were solved by direct methods (SIR-97) [6] and refined by full-matrix, least-squares techniques on *F*² using SHELX-97 [7].

4. Supplementary material

CCDC 645182, 645180 and 645181 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.

Acknowledgements

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