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ARTICLE

Structural Characterization of a Dicoordinated Bis(ferrocenyl)aluminum Cation‡

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This study reports on the synthesis and structural characterization of a stable dicoordinated organoaluminum cation. The bis(ferrocenyl)aluminum cation, featuring sterically encumbered ferrocenyl substituents, was isolated and its solid-state structure analyzed using single-crystal X-ray diffraction analysis. The electron-deficient aluminum center could be expected to exhibit strong Lewis acidity, even though stabilized by interactions with the ferrocenyl moieties. This research contributes to the yielding a new type of low-coordinated Group 13 cationic species and their potential utility as Lewis acids.

Introduction

Trivalent compounds of Group-13 elements, such as boranes and aluminum(III) compounds exemplified by aluminum trichloride, display Lewis acidity and/or electrophilicity due to their low-lying vacant p-orbitals, and are widely employed as catalysts in organic synthetic chemistry.[1] To develop more potent Lewis acids and/or electrophiles, significant research efforts have focused on the synthesis of trivalent cationic species of Group-13 elements.[2-8] Although several trivalent Group-13 cations with two or three substituents, stabilized via intermolecular coordination, have been synthesized and isolated, these species are often significantly electronically perturbed by the intermolecular coordination and/or resonance effects from neighboring heteroatom substituents.[2-5] In order to preserve the inherent Lewis acidic/electrophilic character of unsaturated cationic Group-13 species, diorgano-substituted Group-13 cationic species (R_2E^+, E = B, Al, Ga, In, Tl) paired with weakly coordinating anions (WCAs), such as $[B(C_6F_5)_4]^-$,[9] are of considerable interest as research targets, where these species are expected to exhibit high Lewis acidity/electrophilicity due to their vacant p-orbitals (Figure 1).[5-8]

Trivalent dicoordinated boron cationic species are known as borenium ions. Shoji and co-workers have synthesized the first kinetically stabilized diarylborenium cation, using weakly coordinating anions (WCAs) such as $[B(C_6F_5)_4]^-$ and the carborane, $CHB_{11}Cl_{11}^-$, demonstrating that these cations function as effective agents for the activation of small molecules.[6] For instance, the borenium cation Mes_2B^+ (Mes = mesityl) reacts with CO_2, leading to the formation of $MesCO^+$ through C=O bond cleavage.

Given the significant role that aluminum(III) compounds play in synthetic organic chemistry, aluminum cationic species have been extensively investigated. In 2002, Reed and co-workers reported the synthesis of a diethylaluminum cation paired with a carborane anion.[10] Although the vacant p-orbital of the cationic aluminum center is expected to be stabilized by the coordination of halogen atoms from the carborane anion, this species was found to function as an effective Lewis acid, capable of activating ethylene and leading to the formation of corresponding polymers.

In 1993, Schnöckel and co-workers reported $[Cp^*_2Al]^+[Cp^*AlCl_3]^-$ (**I**, Cp* = pentamethylcyclopentadienyl) as the first example of a diorganoaluminum cation paired with a WCA, which was synthesized through a substituent redistribution reaction between $AlCl_3$ and Cp^*_3Al (Figure 2).[11a]

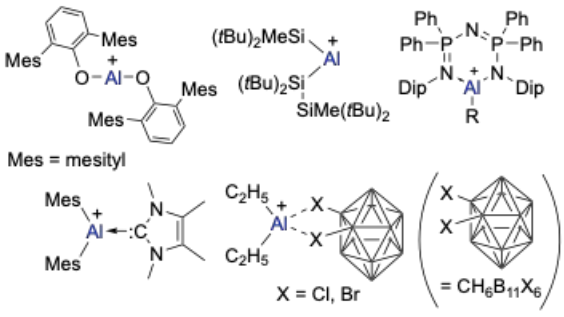

Figure 1. Intra-/inter-molecularly stabilized aluminum cations.

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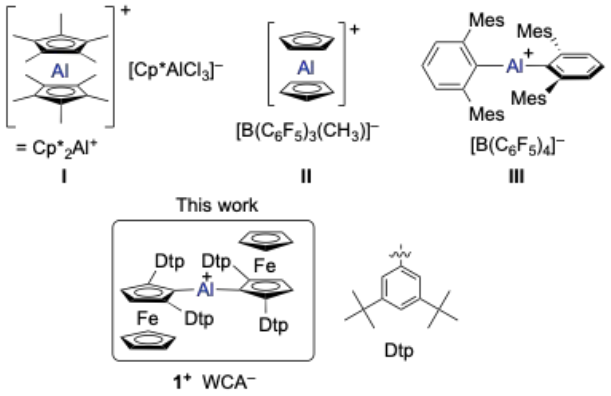


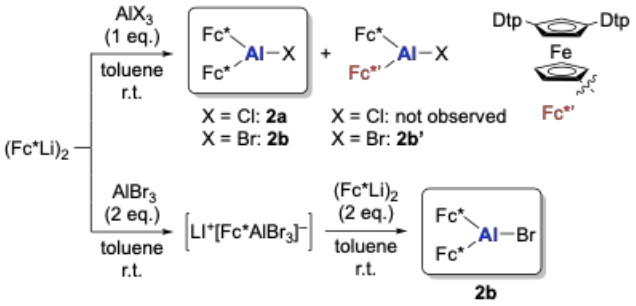
Figure 2. Diorganoaluminum cations **I** – **III** and the targeted bis(ferrocenyl)aluminum cation **1**$^+$.

Although **I** would be considered a trivalent dicoordinated organoaluminum cation, the 3p-orbital of the Al$^+$ center in **I** is likely occupied by the π-electrons of the Cp* moiety. In 1996, Bochmann and co-workers reported the aluminocenium cation Cp_2Al^+ (**II**, Cp = cyclopentadienyl), which demonstrated efficacy as an initiator for the cationic polymerization of isobutene and the copolymerization of isobutene/isoprene.[11b] Subsequently, in 2004, Wehmschulte and co-workers isolated and structurally characterized trivalent diorganoaluminum cation **III**, which bears two sterically demanding aryl substituents.[8] The vacant p-orbital at the central Al atom in **III** was observed to be stabilized by intramolecular π-coordination from the flanking *ortho*-Mes groups of the aryl substituents.

Building upon our development of the sterically encumbered ferrocenyl substituent Fc* (2,5-bis(3,5-di-*tert*-butylphenyl)-1-ferrocenyl),[12] we have previously reported the synthesis and structures of kinetically stabilized bis(ferrocenyl)germylene and -stannylene.[13] These exhibited monomeric structures, devoid of π-coordination from the Dtp (3,5-di-*tert*-butylphenyl) groups on the Fc* ligands to the vacant Ge/Sn centers. Inspired by the structural characteristics of Fc^*_2Ge and Fc^*_2Sn, we sought to explore the synthesis of the bis(ferrocenyl)aluminum cation, $Fc^*_2Al^+$, as we hypothesized that the cationic aluminum center would remain largely unaffected by π-coordination from the flanking Dtp groups. Herein, we present the synthesis of bis(ferrocenyl)aluminum cation **1**$^+$, a diorganoaluminum cation in which the electron-deficient Al center experiences less electronic perturbation compared to previously reported heteroatom-substituted and donor-coordinated aluminum cations.[3,4,11]

Results and discussion

As a strategic approach to synthesize bis(ferrocenyl)aluminum cation **1**$^+$, we initially targeted the synthesis and isolation of bis(ferrocenyl)haloalumanes **2a-c** (Fc^*_2AlX; X = Cl(**a**), Br(**b**), I(**c**)), anticipating their utility as precursors for dehalogenation reactions. While bis(ferrocenyl)chloroalumane **2a** could be isolated from the reaction of $(Fc^*Li)_2$ with $AlCl_3$, the corresponding bromo and iodo analogues, *i.e.*, **2b** (Fc^*_2AlBr) and **2c** (Fc^*_2AlI), proved challenging to isolate due to contamination with the 1,1'-migrated byproducts, *i.e.*, Fc*(Fc*')AlX (**2b'**: X = Br; **2c'**: X = I; Fc*' = 1',3'-bis(3,5-di-*t*-butylphenyl)-1-ferrocenyl) (Scheme 1).[14]

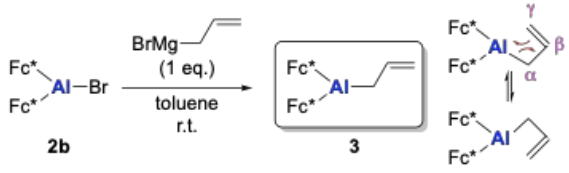


Scheme 1. Synthesis of bis(ferrocenyl)haloalumanes **2a,b**.

Recognizing the potential of bis(ferrocenyl)bromoalumane **2b** as a versatile building block for the synthesis of bis(ferrocenyl)alumanes featuring two Fc* groups, we aimed to isolate **2b** while minimizing contamination from its 1,1'-migrated isomer (**2b'**). Our previous investigations revealed that the reaction of $Li^+[Fc^*AlBr_3]^-$, generated *in situ* from $(FcLi)_2$ and $AlBr_3$, with a trace amount of $AlBr_3$ facilitated 1,1'-aluminum migration to yield $(Fc^*'AlBr_2)_2$.[14] Consequently, by treating a suspension of the insoluble $Li^+[Fc^*AlBr_3]^-$ with a slight deficiency of $(Fc^*Li)_2$, we successfully obtained Fc^*_2AlBr (**2b**) with negligible contamination from **2b'**.

Attempted dehalogenations of Fc^*_2AlX (**2a**: X = Cl; **2b**: X = Br) using $Na^+[B(C_6F_5)_4]^-$ resulted in the formation of complicated mixtures characterized by significantly broadened signals in the ^{1}H NMR spectra. Furthermore, the dechlorination of **2a** with $GaCl_3$ led to the formation of Fc*(Fc*')GaCl,[15] likely via transmetallation and 1,1'-migration. Therefore, we opted to replace the halide leaving group with an allyl group, leveraging the reactivity of allylalumanes, which can be converted to aluminum cations upon electrophilic addition (E^+) with concomitant elimination of $E–CH_2CHCH_2$.[16] Treatment of bis(ferrocenyl)bromoalumane **2b** with allylmagnesium bromide in Et_2O afforded bis(ferrocenyl)allylalumane **3** (Scheme 2). A single-crystal X-ray diffraction (SC-XRD) analysis confirmed the monomeric structure of **3** in the solid state (Figure 3).[17] The ^{1}H NMR spectrum of **3** exhibited equivalent signals for the α and γ protons (δ = 3.00; d, *J* = 10.7 Hz, 4H) and a quintet signal for the β proton (δ = 5.35; quin., *J* = 10.7 Hz, 1H), suggesting a facile exchange of the allyl group on the aluminum atom (Scheme 2).

The reaction of bis(ferrocenyl)allylalumane **3** with 0.90 equivalents of $[Ph_3C]^+[B(C_6F_5)_4]^-$ in benzene yielded bis(ferrocenyl)aluminum cation as $1^+[B(C_6F_5)_4]^-$ in the form of a pale yellow solid that could be isolated in 80% yield (Scheme 3). The limited solubility of $1^+[B(C_6F_5)_4]^-$ in hexane proved advantageous for its purification. Specifically, filtration of the reaction mixture to remove hexane-soluble byproducts enabled the successful isolation of $1^+[B(C_6F_5)_4]^-$. Notably, $1^+[B(C_6F_5)_4]^-$



Scheme 2. Synthesis of bis(ferrocenyl)allylalumane **3**.

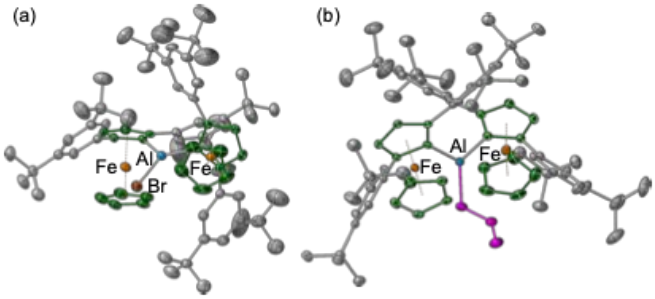
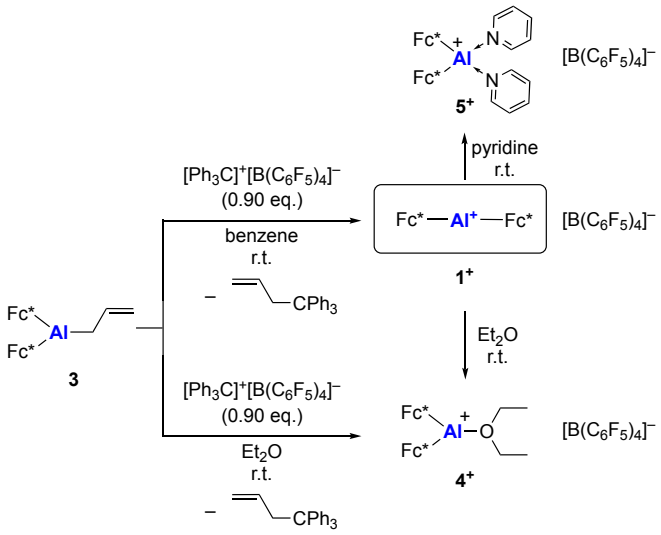


Figure 3. Molecular structures of (a) bis(ferrocenyl)bromoalumane **2b** and (b) bis(ferrocenyl)allylalumane **3** in the crystalline state with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity.

demonstrated remarkable stability in the solid state at room temperature under ambient conditions. However, in C_6D_6 solution, $\mathbf{1}^+[B(C_6F_5)_4]^-$ decomposed readily upon exposure to air, resulting in the formation of a green solution characterized by significantly broadened signals in the ^1H NMR spectrum.

The addition of Et_2O or pyridine to $\mathbf{1}^+[B(C_6F_5)_4]^-$ yielded the corresponding adducts, *i.e.*, $\mathbf{4}^+[B(C_6F_5)_4]^-$ or $\mathbf{5}^+[B(C_6F_5)_4]^-$, respectively, which showcases the efficient Lewis acidity of $\mathbf{1}^+[B(C_6F_5)_4]^-$ as a low-coordinated aluminum cation (Scheme 3).[18] While $\mathbf{1}^+$ coordinates one Et_2O molecule, it Is able to accommodate two molecules of pyridine. Notably, the reaction of bis(ferrocenyl)allylalumane **3** with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in Et_2O produced the expected adduct, *i.e.*, $\mathbf{4}^+[B(C_6F_5)_4]^-$.



Scheme 3. Synthesis of bis(ferrocenyl)aluminum cations $\mathbf{1}^+$ and $\mathbf{4}^+$.

Due to the lability and steric bulk of $\mathbf{1}^+$, experimental evaluation of its electrophilicity or Lewis acidity, for instance, *via* fluoride coordination or the Guttmann test,[19] was precluded. Consequently, the Lewis acidity of $\mathbf{1}^+$ was assessed using theoretically calculated fluoride-ion affinity (FIA).[19,20] Recognizing the critical role of solvation effects,[19e] the Conductor-like Polarizable Continuum Model (CPCM) for toluene was employed in these calculations. The FIAs were determined relative to the trimethylsilyl cation (TMS^+) using the following equation: $FIA_{Si}(LA^+) = [E_{zero}(LA^+) + E_{zero}(TMSF)] - [E_{zero}(LA–F) + E_{zero}(TMS^+)]$, where LA^+ = cationic Lewis acid, TMS = $Si(CH_3)_3$, and E_{zero} = zero-point corrected energy. As a result, it was shown that $FIA_{Si}(Fc^*_2Al^+) = –142.7$ kJ/mol and $FIA_{Si}((2,6\text{-}Mes_2C_6H_3)_2Al^+) = –158.1$ kJ/mol, indicating that the di-coordinated organoaluminum cations Fc^*_2Al ($\mathbf{1}^+$) and $(2,6\text{-}Mes_2C_6H_3)_2Al^+$ (**III**) have smaller FIAs (*i.e.*, are weaker Lewis acids) than $(H_3C)_3Si^+$. The results also suggest that $\mathbf{1}^+$ possesses slightly stronger Lewis acidity than **III**. Notably, $\mathbf{1}^+$ is predicted to be marginally more Lewis acidic than $(2,6\text{-}Mes_2C_6H_3)_2Al^+$ (**III**), albeit that the LUMO level of $\mathbf{1}^+$ (–3.80 eV) lies higher than that of $(Mes_2C_6H_3)_2Al^+$ (–4.44 eV). Considering the significantly negative FIA_{Si} value for the previously isolated ferrocenyl silylcation $FcSi^+(t\text{Bu})(CH_3)$ (**V**),[21] where $FIA_{Si}(FcSi^+(t\text{Bu})(CH_3)) = –98.0$ kJ/mol, it appears the ferrocenyl substituent considerably diminishes the Lewis acidity of cationic unsaturated species. Furthermore, the larger (less negative or more positive) FIAs values of less bulky diorgano aluminum cations, such as $FIA_{Si}(Fc_2Al^+) = –102.3$ kJ/mol and $FIA_{Si}(Ph_2Al^+) = +6.2$ kJ/mol, suggest that the steric bulk should reduce their Lewis acidity. Nevertheless $\mathbf{1}^+[B(C_6F_5)_4]^-$ can be regarded as an effective Lewis acid, stronger than $(Mes_2C_6H_3)_2Al^+[B(C_6F_5)_4]^-$ (**III**), although the Lewis acidities of both $\mathbf{1}^+$ and **III** sare markedly reduced compared to silyl cations.

The molecular structure of $\mathbf{1}^+[B(C_6F_5)_4]^-$ and $\mathbf{4}^+[B(C_6F_5)_4]^-$ was examined by SC-XRD analyses (Figure 4).[22] Both aluminum cations existing as discrete monomeric ion pairs in the crystalline state. Notably, the aluminum atom in $\mathbf{4}^+$ adopts a tri-coordinated planar geometry (sum of bond angles around Al = 360.0°), wherein the Al atom resides within the plane of the cyclopentadienyl (Cp) rings. In contrast, the central aluminum atom in $\mathbf{1}^+$ deviates significantly from the Cp planes, thus displaying a pronounced approach toward the iron atoms of both Fc* groups.

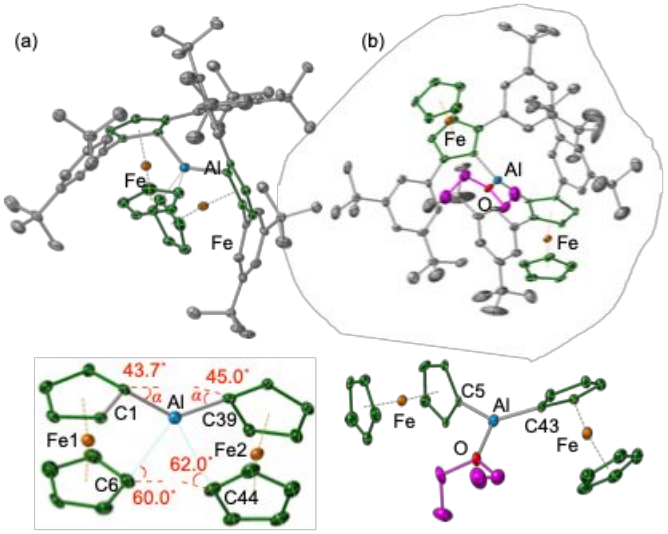


Figure 4. Molecular structures of (a) bis(ferrocenyl)aluminum cation $\mathbf{1}^+[B(C_6F_5)_4]^-$ and (b) bis(ferrocenyl)aluminum cation ether complex $\mathbf{4}^+[B(C_6F_5)_4]^-$ in the crystalline state with thermal ellipsoids at 50% probability; $[B(C_6F_5)_4]^-$ and hydrogen atoms are omitted for clarity. Selected atomic distances (Å): (a) Al–C1, 1.921(6); Al–C6, 2.668(6); Al–C39, 1.906(6); Al–C44, 2.734(5), (b) Al–C5, 1.944(6); Al–C43, 1.939(6); Al–O, 1.836(4).

This structural distortion in **1**$^+$ is not attributable to crystal-packing forces or the steric bulk of the Dtp groups. This conclusion is supported by theoretical optimizations of Fc*$_2$Al$^+$ (**1**$^+$) and Fc$_2$Al$^+$ (**IV**; Fc = ferrocenyl) in the gas phase (B3PW91-D3(bj)/6-311G(3d)), which replicate the observed geometrical features, including short Fe···Al distances.

In ferrocenyl-substituted unsaturated species, such as boranes, the deviation of the central atom (E) from the Cp plane, quantified as the "dip angle" (α = 180˚ – ($\angle Cp_{cent}$–Cp_{ipso}–E)),[23] serves as an indicator of electrophilicity/Lewis acidity at the central atom. The dip angles α for **1**$^+$ (43.7°, 45.0°) are significantly larger than those observed in Fc*$_2$AlX (**2a** (X = Cl): α = 0.06˚, 12.5˚; **2b** (X = Br): α = 0.09˚, 13.1˚),[14] indicating substantial Lewis acidity/electrophilicity for **1**$^+$. Conversely, iEt$_2$O complex **4**$^+$, the electron-deficient aluminum center is stabilized by σ- and π-coordination from Et$_2$O, leading to reduced Lewis acidity/electrophilicity and a planar arrangement of the Al atom with the Cp rings (α = –7.8°, –7.0°). Furthermore, the shorter Al–O(OEt$_2$) (1.836(4) Å) bonds in **4**$^+$ compared to those in Ph$_3$Al·(OEt$_2$) (Al–O(OEt$_2$) 1.924(1) Å), suggest a strong coordination of the Et$_2$O molecule to the cationic aluminum center.

Intriguingly, the crystal structure of **1**$^+$ reveals close proximity between the carbon atoms (C_{Cp}, C6 and C44) of the free cyclopentadienyl (Cp) rings within the Fc* groups, suggesting non-negligible orbital interactions between the Fe–C_{Cp} moieties and the vacant 3p orbital of the aluminum atom. This observation implies that the ferrocenyl groups, through highly bent C–Al bonds, effectively stabilize the vacant orbitals by orienting the Fe–C_{Cp} orbitals toward the 3p orbital of the aluminum center. This phenomenon is reminiscent of the ferrocenyl silyl cation FcSi$^+$(CH$_3$)(*t*Bu) (**V**),[21] which also exhibits a significant dip angle (α = 45.3°) at the Si$^+$–C(Fc) moiety and close proximity between the free Cp carbon and the Si$^+$ center. These structural features in **V** have been interpreted in terms of two effective three-center-two-electron (3c-2e) bonding interactions involving the Fe–C–Si atoms. Analogously, the pronounced bending and large dip angles in **1**$^+$ can be attributed to two 3c-2e bonding interactions, not only between Al$^+$–C1–Fe1 and Al$^+$–C39–Fe2, but also within the C6(H)–Fe1–Al$^+$ and C44(H)–Fe2–Al$^+$ moieties.

Atoms-in-molecules (AIM) calculations[24] for both **1**$^+$ and Fc$_2$Al$^+$ (**IV**) corroborated this hypothesis, by revealing bond critical points (BCPs) not only at the midpoints of the Al–C_{ipso} bonds (C_{ipso}: *ipso*-carbon of the Fc* group) but also between the Al and C_{Cp} atoms (Figure 5). Moreover, ring critical points (RCPs) were identified within the Al– C_{ipso}-Fe– C_{Cp} rings in both **1**$^+$ and **IV**. Natural-bond-orbital (NBO) calculations[25] for **1**$^+$ provided further information on the bonding situation, depicting it as a combination of two Fc*$^-$ anions and an Al^{3+} cation. The predominant bonding contributions between Fc*$^-$ and Al^{3+} were attributed to three orbital interactions: (i) d(Fe) → 3p(Al) (18.2 kcal/mol), (ii) lone pair at C_{ipso} → 3p(Al) (75.2 kcal/mol), and (iii) 3c-2e bond (C_{ipso}–Fe–C_{Cp}) → 3p(Al) (18.4 kcal/mol) (Figure 6).

Considering these structural features and theoretical results, we concluded that the cationic aluminum center in **1**$^+$ is effectively stabilized by broadened orbital interactions involving the C_{ipso}, C_{Cp}, and Fe atoms. This contrasts with the stabilization mechanism in the aryl-substituted dicoordinated aluminum cation **III** ((2,5-Mes$_2$C$_6$H$_3$)$_2$Al$^+$), where π-coordination from the flanking ortho mesityl groups, estimated to be 13 and 18 kcal/mol, plays the primary role.[8]

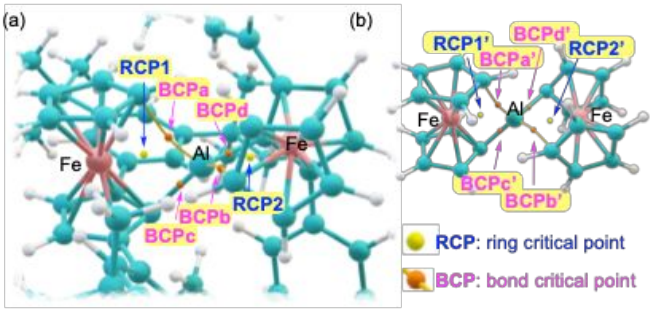


Figure 5. Calculated ring critical points (RCPs) and bond critical points (BCPs) of (a) Fc*$_2$Al$^+$ (**1**$^+$) and (b) Fc$_2$Al$^+$ (**IV**). $\rho(r)$, $\nabla^2\rho(r)$: (a) **RCP1**: 0.025, 0.045; **RCP2**: 0.025, 0.042; **BCPa**: 0.032, 0.025; **BCPb**: 0.033, 0.025; **BCPc**: 0.080, 0.39; **BCPd**: 0.080, 0.39. (b) **RCP1'**: 0.030, 0.057; **RCP 2'**: 0.030, 0.057; **BCPa'**: 0.041, 0.017; **BCPb'**: 0.041, 0.017; **BCPc'**: 0.086, 0.41; **BCPd'**: 0.086, 0.41.

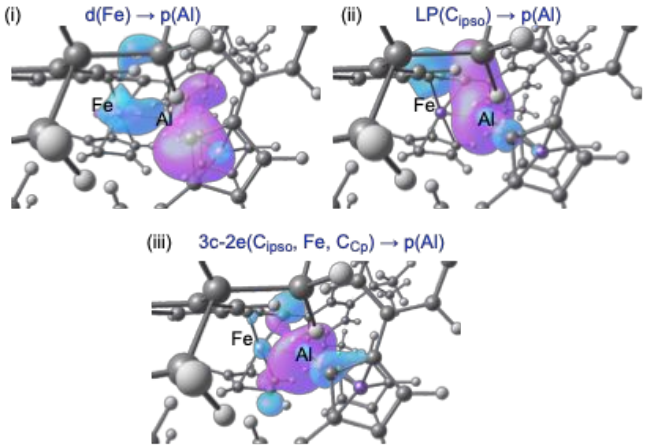


Figure 6. NBO interactions in **1**$^+$. (i) d(Fe) ⟶ 3p(Al), 18.2 kcal/mol; (ii) C_{ipso} ⟶ 3p(Al), 75.2 kcal/mol; (iii) 3c-2e (C_{ipso}–Fe–C_{Cp}) ⟶ 3p(Al), 18.4 kcal/mol.

Conclusions

We have successfully isolated the sterically encumbered bis(ferrocenyl)aluminum cation **1**$^+$[B(C$_6$F$_5$)$_4$]$^-$, demonstrating its stability as a dicoordinated organoaluminum cation. Although the low-coordinated cationic aluminum center should be considerably thermodynamically stabilized by the ferrocenyl moieties through C_{ipso}–Fe–C_{Cp} orbital interactions, resulting its smaller FIA_{Si} value relative to the silyl cations, it is still expected to exhibit an effective electrophilicity/Lewis acidity. Ongoing investigations are focused on exploring the reactivity and applications of **1**$^+$[B(C$_6$F$_5$)$_4$]$^-$ as a potentially effective Lewis acid.

Author contributions

The project was designed and conducted by T.S. Experimental work was carried out by T.A.; theoretical calculations were carried out by K.S. and T.S.. K.S. and S.M. partially collected the analytical data. All authors contributed to writing the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI. Crystallographic data for **2b**, **3**, **1**$^{+}$[B(C_6F_5)$_4$]$^{-}$, **4**$^{+}$[B(C_6F_5)$_4$]$^{-}$, **5**$^{+}$[B(C_6F_5)$_4$]$^{-}$, and Fc*(Fc*')GaCl can be obtained via https://www.ccdc.cam.ac.uk at the Cambridge Crystallographic Data Centre (CCDC) under reference numbers CCDC-2441652-2441657, respectively.

Acknowledgements

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Notes and references

‡ Dedicated to Yosuke Yamamoto on the occasion of his 70th birthday.

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COMMUNICATION

Structural Characterization of a Dicoordinated Bis(ferrocenyl)aluminum Cation‡

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Data availability

The data supporting this article have been included as part of the ESI. Crystallographic data for **2b**, **3**, **1**$^{+}$[B(C$_6$F$_5$)$_4$]$^{-}$, **4**$^{+}$[B(C$_6$F$_5$)$_4$]$^{-}$, **5**$^{+}$[B(C$_6$F$_5$)$_4$]$^{-}$, and Fc*(Fc*')GaCl can be obtained via https://www.ccdc.cam.ac.uk at the Cambridge Crystallographic Data Centre (CCDC) under reference numbers CCDC-2441652-2441657, respectively.