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Monomeric tri-coordinated bis(ferrocenyl) haloalumanes†‡

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The reactions of the sterically demanding ferrocenyl lithium dimer $(Fc*Li)_2$ ($Fc*$ = 2,5-bis(3,5-di-*t*-butyl-phenyl)-1-ferrocenyl) with aluminum trihalides ($AlCl_3$, $AlBr_3$, and AlI_3) to furnish the corresponding monomeric bis(ferrocenyl)haloalumanes are reported. In the case of the reaction with AlI_3, an unexpected intramolecular 1,1′-aluminum migration in the ferrocenyl moiety was found to occur. Their monomeric structures with a tri-coordinated aluminum atom show affinitive Al⋯Fe interactions.

A variety of organoaluminum compounds have shown potential as Lewis-acidic catalysts for the transformation of small molecules.[1] In most cases, however, trivalent organoaluminum compounds can be expected to exist as oligomeric structures or tetra-coordinated compounds with an intra-/inter-molecular coordination due to the stabilization of the vacant p-orbital of the aluminum atom upon coordination, which reduces the intrinsic electrophilicity and/or Lewis acidity. The oligomeric structures of trivalent organoaluminum halides with intermolecularly bridging halogen atoms or Al–C σ-bonds should be of great interest from a coordination-chemistry viewpoint. In particular, ferrocenyl-substituted trivalent aluminum compounds are known to exhibit unique geometries with Al-bridging oligomeric structures and short Fe⋯Al distances.[2–5] For example, the reaction of FcLi (Fc = ferrocenyl) generated *in situ* with an equimolar amount of R_2AlCl (R = CH_3 or CH_2CH_3) afforded the corresponding dialkylferrocenylalumanes ($FcAlR_2$) in the form of Al-bridging dimer **I**.[3] When FcLi was treated with an excess of R_2AlCl, the generated dialkylferrocenylalumane

formed a complex with another molecule of R_2AlCl to yield $Fc(AlR_2)_2Cl$ (**II**).[3] Treatment of FcLi with chlorodimethylalumane ($ClAlMe_2$) followed by addition of pyridine afforded the corresponding ferrocenyldimethylalumane·pyridine complex ($FcMe_2Al$·pyridine; **III**).[3,4] As seen in these examples, the isolable organo-/halo-alumanes can be expected to exhibit in most cases tetra-coordinate geometries. However, in some cases, tri-coordinated bis(ferrocenyl)alumanes were obtained, especially when the tri-coordinated aluminum moiety is surrounded by cluster-like structures (Fig. 1).[4,5]

We aim to synthesize monomeric ferrocenylalumanes that are expected to exhibit ambiphilic properties of high reactivity and thermodynamic stability. That is, these properties arise from the combination of high electrophilicity, attributed to the vacant 3p orbital on the aluminum center, and thermodynamic stability, provided by the intramolecular electronic stabilization from the electron-donating ferrocenyl group. We have already reported the isolation of the sterically demanding ferrocenyl lithium dimer $(Fc*Li)_2$ ($Fc*$ = 2,5-bis(3,5-di-*t*-butyl-phenyl)-1-ferrocenyl),[6] and its synthetic application in the isolation of the corresponding monomeric bis(ferrocenyl)-germylene and -stannylene ($Fc*_2E$:, E = Ge and Sn).[7] These previous results on the application of the $Fc*$ group prompted us to attempt the isolation of monomeric, tri-coordinated ferrocenylalumanes by the introduction of the sterically demanding ferrocenyl group to the aluminum center. The group of Braunschweig has reported the isolation of a tetra-coordinated ferrocenyldiiodoalumane stabilized by substitution with an $Fc*$ group and the coordination of an N-heterocyclic carbene

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†Dedicated to Prof. Dr Shigeru Nagase on the occasion of his 77th birthday.
‡Electronic supplementary information (ESI) available. CCDC 2401680–2401683 and 2403232. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4dt03233k

Fig. 1 Examples of hitherto reported ferrocenylalumanes.

R = CH_3 or C_2H_5

(NHC), Fc*AlI$_2$(NHC), which was obtained from the reaction of Fc*Li with (NHC) → AlH$_3$ followed by iodination with iodomethane.[8] Here, we present the synthesis of bis(ferrocenyl) haloalumanes that bear sterically demanding ferrocenyl groups to avoid self-dimerization/oligomerization (Fig. 2).

Treatment of the ferrocenyl lithium dimer (Fc*Li)$_2$ (**1**)[6] with 2 eq. of AlX$_3$ (X = Cl and Br; *i.e.*, Fc*Li : AlX$_3$ = 1 : 1) at r.t. afforded insoluble orange solids, which were converted to the corresponding dihaloalumane·thf complexes Fc*AlX$_2$·(thf) (**2a**: X = Cl; **2b**: X = Br), by addition of a small amount of THF (Scheme 1). Although their isolation and purification were very difficult due to their lability and contamination with a small amount of inseparable Fc*H, the products could be identified[9] based on NMR and mass spectral data; moreover, the solid-state structure of **2b**·(thf) was determined unequivocally by single-crystal X-ray diffraction (SC-XRD) analysis.[10] Thus, the insoluble orange solids obtained by mixing **1** and AlX$_3$ are most likely Li$^+$[Fc*AlX$_3$]$^-$ complexes. When a toluene solution of **1** was heated with an equimolar amount of AlCl$_3$ (*i.e.*, Fc*Li : AlCl$_3$ = 2 : 1) at 60 °C for 17 h, bis(ferrocenyl)chloroalumane Fc*$_2$AlCl (**3a**) was obtained in 76% yield. Alternatively, treatment of **1** with the insoluble solid obtained from the reaction of **1** with 2 eq. of AlCl$_3$ also afforded **3a**. Judging from the ^{1}H NMR spectrum, the addition of THF to **3a** furnished **3a**·(thf).

In the expectation of obtaining the bromine analogue, bis (ferrocenyl)bromoalumane Fc*$_2$AlBr (**3b**), the reaction of **1** with an equimolar amount of AlBr$_3$ was examined, which unexpectedly furnished not only **3b** but also **4b** in 79% and 13% NMR yields, respectively. The expected product (**3b**) was identified based on its ^{1}H NMR spectrum and its similarity to that of **3a**. The unexpected product (**4b**) was identified as another type of bis(ferrocenyl)bromoalumane, *i.e.*, Fc*(Fc*′)AlBr (Scheme 2), based on the spectroscopic and SC-XRD analyses of its single crystals, which were obtained from a careful recrystallization of the reaction mixture from hexane (Fig. 3).
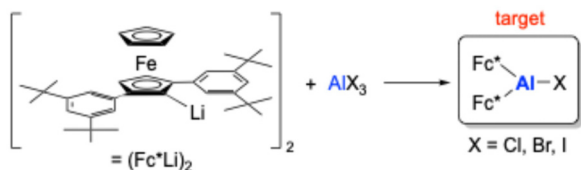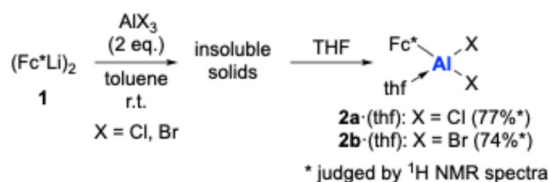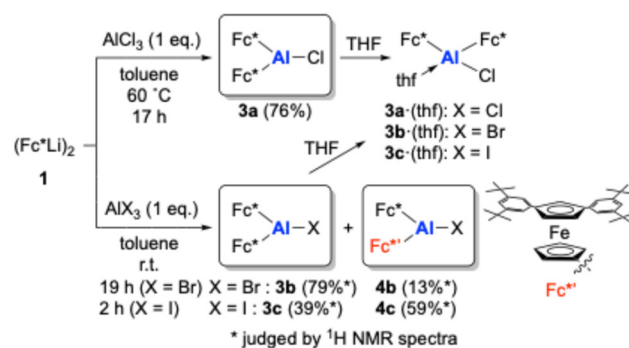

Fig. 2 Targeted compounds: monomeric bis(ferrocenyl)haloalumanes.

Scheme 1 Formation of ferrocenyldihaloalumane·thf complexes **2a** (X = Cl) and **2b** (X = Br).

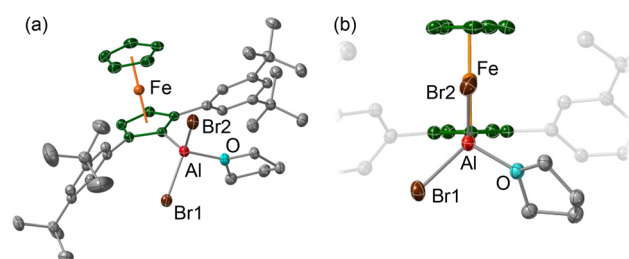**Scheme 2** Synthesis of bis(ferrocenyl)haloalumanes.

Fig. 3 (a) Molecular structure of **2b**·(thf) in the crystalline state with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. (b) Depiction of the geometry of the core moiety of **2b**·(thf). Selected bond lengths (Å): Al–Br1, 2.3196(5); Al–Br2, 2.3057(5).

Compound **4b** could be formed *via* 1,1′-Al-migration on one of the Fc* substituents. Furthermore, treatment of ferrocenyl lithium dimer **1** with AlI$_3$ afforded the corresponding bis(ferrocenyl)iodoalumanes **3c** and **4c**, similar to the case of the reaction of **1** with AlBr$_3$; however, the reaction is not very clean, as evident from several small signals due to unknown by-products in the ^{1}H NMR spectra of the reaction mixture. Notably, the formation ratio of **3c** and **4c** in the reaction mixture was found to depend on the reaction conditions (Table S1‡). Using a higher reaction temperature (60 °C) and/or longer reaction time increased the formation ratio of **3c** relative to **4c**. The use of a slightly higher/lower amount of AlI$_3$ increased/decreased the ratio of **4c** relative to **3c**, indicating that a small amount of residual AlI$_3$ promotes the 1,1′-Al-migration on the ferrocenyl moiety as a Lewis acid. When a small amount of AlBr$_3$ was added to the mixture of **3b** and **4b** (5 : 3), no significant change in their ratio was evident from the ^{1}H NMR spectra after leaving the sample to stand for 6 days at room temperature. Accordingly, it seems feasible to discard the possibility that **3b** and **4b** are transformed into each other in the presence of AlBr$_3$. Overall, the results of the reactions suggest that AlX$_3$ can promote the formation of 1,1′-Al-migrated products **4**, while AlX$_3$ seems unable to directly transform **3** into **4**.[11]

When isolated **3b** was treated with an equimolar amount of AlBr$_3$ in C$_6$D$_6$, ferrocenyldibromoalumane dimer (Fc*′AlBr$_2$)$_2$ (**5b**) was formed quantitatively (Scheme 3).[9,10] According to Scheme 1, the initially formed Li$^+$[Fc*AlBr$_3$]$^-$ would generate a
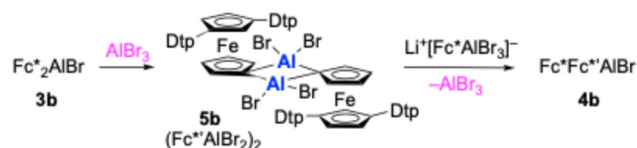
Scheme 3 Reaction of **3b** with $AlBr_3$ to yield dibromoalumane dimer **5b**, which could subsequently be converted to **4b**.

Table 1 Structural parameters of bis(ferrocenyl)haloalumanes

X		Al–C/Å	Fe···Al/Å	Al–X/Å	a^a/°	b^b/°
Exp.						
3a	Fc*	1.957(5)	3.623(1)	2.129(2)	0.06	64.6
Cl	Fc*	1.948(4)	3.387(1)		12.5	42.1
4b	Fc*	1.944(4)	3.605(1)	2.294(1)	1.27	57.5
Br	Fc*′	1.904(3)	2.974(1)		29.6	26.7
4c	Fc*	1.952(7)	3.614(3)	2.510(3)	2.26	59.7
I	Fc*′	1.904(10)	2.988(4)		29.1	26.2
Calc.^{c}						
3a	Fc*	1.924	3.629	2.128	3.34	64.6
Cl	Fc*	1.925	3.253		16.9	42.1
4a	Fc*	1.930	3.626	2.134	5.77	57.5
Cl	Fc*′	1.900	3.029		26.6	26.7
3b	Fc*	1.925	3.646	2.294	4.32	59.7
Br	Fc*	1.927	3.292		15.1	26.2
4b	Fc*	1.929	3.629	2.297	6.07	64.6
Br	Fc*′	1.899	3.036		26.3	42.1
3c	Fc*	1.926	3.661	2.518	5.09	57.5
I	Fc*	1.929	3.315		14.2	26.7
4c	Fc*	1.929	3.633	2.516	6.13	59.7
I	Fc*′	1.900	3.037		26.3	26.2

^{a} Dip-angle ($\alpha = 180° - (\angle Cp_{cent}–Cp_{ipso}–E)$). ^{b} Dihedral angle between the Cp and Al planes. ^{c} Optimized at the B3PW91-D3(BJ)/def2TZVPP level.

small amount of Fc*Li and $AlBr_3$ as well as $Fc*AlBr_2$ and LiBr *in situ*; it would thus be possible that **5b** reacts with Fc*Li generated from $Li^+[Fc*AlBr_3]^-$ to furnish Fc*Fc*′AlBr (**4b**). Thus, the transformation of **3b** to **4b** promoted by a small amount of $AlBr_3$ should most likely be interpreted in terms of intermediate **5b**, which would be formed by the reaction of **3b** with $AlBr_3$, although the detailed mechanism for the formation of **5b** from **3b** is still unclear at present.

The molecular structures of bis(ferrocenyl)haloalumanes **3a**, **4b**, and **4c** in the crystalline state were determined by SC-XRD analyses (Fig. 4). The obtained structural parameters[10] are summarized in Table 1 together with those theoretically optimized (B3PW91-D3(BJ)/def2TZVPP) for the bis(ferrocenyl)haloalumanes Fc*(R)AlX (X = Cl(**a**), Br(**b**), and I(**c**); R = Fc*(**3**) and Fc*′(**4**)).[9] The experimentally observed structural parameters are reproduced well by the theoretical calculations, indicating that the observed structural features should be due to the intrinsic nature of the compounds with negligible per-
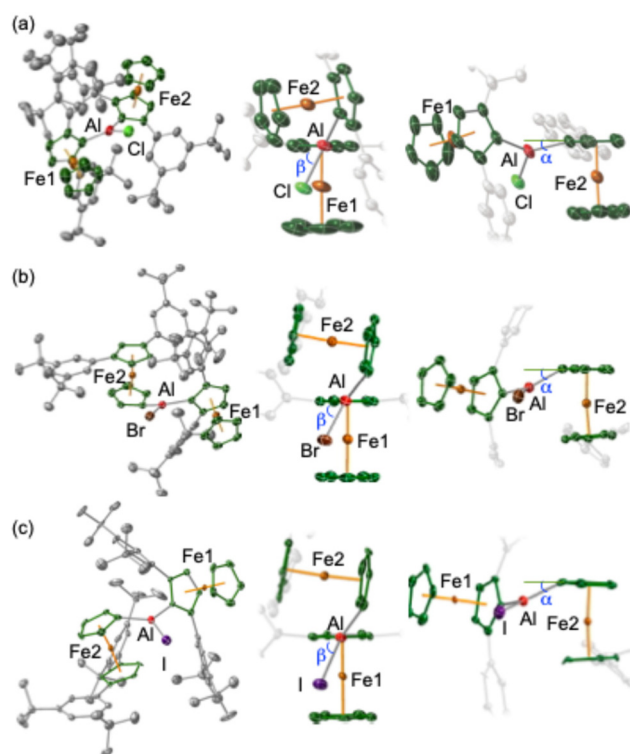
Fig. 4 Molecular structures and the depictions of the central moieties of (a) **3a**, (b) **4b**, and (c) **4c** in the crystalline state with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity.

turbation from packing forces. All of the obtained bis(ferrocenyl)haloalumanes exhibit monomeric tricoordinated structures in the crystalline states due to the sterically demanding ferrocenyl groups on the aluminum center. In all cases (**3a**, **4b**, and **5b**), the sum of the bond angles around the aluminum center is ~360° (Table 1); however, the central aluminum atoms deviate from the Cp planes (α) and approach one of the Fe atoms of the ferrocenyl groups. Notably, the shortened Al···Fe distances should not be attributed to crystal-packing forces, given that this characteristic structural feature was also reproduced by the theoretical calculations in the gas phase (Table 1). Generally, the deviation of the central atom (E) from the Cp-plane in a ferrocenyl-substituted compound ($\alpha = 180° - (\angle Cp_{cent}–Cp_{ipso}–E)$) is known as the "dip-angle",[2b,12] which indicates the electrophilicity/Lewis acidity at the central atom,[13] since the deviation should most likely be interpreted in terms of a 3-center-2-electron bond among the $C(Cp_{ipso})$, Fe, and E atoms (*e.g.*, α in $FcBMe_2$ = 13.0°, $FcSi(tBu)Me^+$ = 44.8°, and $FcSnMe_2^+$ = 41.6°).[12]

The structural features of **3a–c** and **4a–c** should be discussed based on both the experimental and theoretical results. The haloalumanes that bear two Fc* groups exhibit almost C_2-symmetric structures, similar to those of $Fc*_2Ge:$ and $Fc*_2Sn:$.[7] While the Al-centers of **3a–c** are sterically congested as in the case of $Fc*_2Ge:$ and $Fc*_2Sn:$, those of **4a–c** have enough space to exhibit effective conjugation with the Cp moiety of the Fc*′ group. The Al–C(Fc*) distances are almost the same (*e.g.*, **3a** (SC-XRD): Al–C(Fc*) = 1.957(5) and 1.948(4) Å) with slightly different Al···Fe distances (*e.g.*, **3a** (SC-XRD): Al···Fe = 3.623(1) and 3.387(1) Å). Conversely, unsymmetrically substituted bis(ferrocenyl)haloalumanes **4a**, **4b**, and **4c** (Fc*(Fc*′)AlX; X = Cl, Br, and I) showed unsymmetrical structural features. For

example, **4b** showed clearly different Al–C(Fc*/Fc*′) distances (1.944(4)(Fc*) and 1.904(3)(Fc*′) Å) and remarkably different Al···Fe distances (3.605(1) (Fc*) and 2.974(1) (Fc*′) Å), where the Fc*′ group approaches the Al atom with shortened Al–C/Al–Fe distances, causing a large dip-angle α in the Fc*′ moiety (α(Fc*′) = 29.6° and α(Fc*) = 1.27° for **4b**). Moreover, the dihedral angles between the Cp(Fc*′) and Al-planes (β) are significantly smaller (*e.g.*, **4b**: β in Al–Cp(Fc*′) = 26.7°) than those between the Cp(Fc*) and Al-planes (*e.g.*, **4b**: β in Al–Cp(Fc*) = 57.5°), indicating effective conjugation between the π(Cp of Fc*′)-orbital and the vacant p-orbital of the Al atom relative to those in the Al–Cp(Fc*) moiety. The slightly longer Al–X bonds in the Fc*(Fc*′)AlX systems relative to those in the corresponding Fc*$_2$AlX systems should most likely be assessed in terms of effective π-coordination from π(Cp–Fc*′) electrons to the vacant p-orbital of the Al atom due to the lower steric hindrance, which would weaken the donating resonance contribution of the lone pair of the X atom to the vacant p-orbital of the Al atom.

Conclusions

Tricoordinated bis(ferrocenyl)haloalumane derivatives were obtained from the reaction of the sterically demanding ferrocenyl lithium dimer (Fc*Li)$_2$ (Fc* = 2,5-bis(3,5-di-*t*-butyl-phenyl)-1-ferrocenyl) with aluminum trihalides (AlCl$_3$, AlBr$_3$, and AlI$_3$). Some of the obtained compounds were structurally characterized by single-crystal X-ray diffraction analysis. We found that the bis(ferrocenyl)bromoalumane and bis(ferrocenyl)iodoalumane undergo an intramolecular 1,1′-Al migration at the Fc* ligand to yield the corresponding unsymmetrically substituted isomers Fc*(Fc*′)AlX (X = Br and I). These isolated bis(ferrocenyl)haloalumanes exhibit planar tricoordinated structures, suggesting remarkable electrophilicity/Lewis acidity due to the vacant 3p-orbital at the Al center. Further investigations into the reactivity of the obtained bis(ferrocenyl)haloalumanes are currently in progress in our laboratories.

Author contributions

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

Data availability

The data supporting this article have been included as part of the ESI.‡ Crystallographic data for **2b**·(thf), **3a**, **4b**, **4c**, and **5b** can be obtained *via* **https://www.ccdc.cam.ac.uk** at the Cambridge Crystallographic Data Centre (CCDC) under reference numbers CCDC 2401680 (**2b**·(thf)), 2401681 (**3a**), 2401682 (**4b**), 2401683 (**4c**), and 2403232 (**5b**).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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9 Chemical data of the newly obtained compounds and details of experimental procedures as well as theoretical calculations are shown in the ESI.‡

10 Supplementary crystallographic data for **2b**·(thf), **3a**, **4b**, **4c**, and **5b** were deposited at the Cambridge Crystallographic Data Centre (CCDC) under reference numbers CCDC 2401680 (**2b**·(thf)), 2401681 (**3a**), 2401682 (**4b**), 2401683 (**4c**), and 2403232 (**5b**).

11 Calculated relative energies (kcal mol^{-1}) of Fc*Fc*′AlX (**4**) *vs.* the corresponding Fc*$_2$X (**3**): **4a** (X = Cl): ΔE_{zero} = +0.49, ΔG = +0.82; **4b** (X = Br): ΔE_{zero} = −0.18, ΔG = +0.23; **4c** (X = I): ΔE_{zero} = −0.65, ΔG = −0.23; all calculated at the B3PW91-D3(BJ)/def2TZVPP level.

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13 It is difficult to discuss the Lewis acidity of the bis(ferrocenyl)haloalumanes because the complexation with a base would be perturbed by the steric hindrance. On the other hand, the electrophilicity can be estimated based on their low-lying LUMO levels, which are shown in Fig. S24.‡