Dalton Transactions

PAPER



Cite this: DOI: 10.1039/c5dt03895b



View Article Online

Unsolvated Al(C_6F_5)₃: structural features and electronic interaction with ferrocene[†]

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Alkyl/aryl ligand exchange between AlEt₃ and B(C₆F₅)₃ in hexanes enables the formation and isolation of the unsolvated Al(C₆F₅)₃ as a crystalline solid, the structure of which has been determined by single-crystal X-ray diffraction analysis. Instead of forming the anticipated Al…F contacts with the seemingly more accessible *meta*- and *para*-F's of $-C_6F_5$ groups, two Al(C₆F₅)₃ molecules form a dimeric structure with double Al…F interactions between the Al center of one molecule and the *ortho*-F atom of the $-C_6F_5$ group on the other molecule. This mode of interactions is apparently linked to the thermal and shock sensitivity of the unsolvated Al(C₆F₅)₃ in the solid state. To compare with the B(C₆F₅)₃/ferrocene frustrated Lewis pair system, the complexation between Al(C₆F₅)₃ and ferrocene has also been studied, which affords a stable adduct formed through the η^1 -coordination of Al to one of the C_{CP} atoms, similar to the alane–toluene or benzene complex.

Received 5th October 2015, Accepted 29th October 2015 DOI: 10.1039/c5dt03895b

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Introduction

Installation of pentafluorophenyl (-C₆F₅) groups onto group 13 elements, typically B and Al,¹⁻⁵ provides a powerful approach to construct highly Lewis acidic catalysts⁶⁻⁹ with considerable stability. Such an enhancement in both acidity and stability is largely due to the attached strongly electron-withdrawing -C₆F₅ groups that render a more electron deficient B or Al center and also offer steric protection and less polar element-carbon bonds around B or Al. For instance, the strongly Lewis acidic and chemically robust $B(C_6F_5)_3$ serves as the most widely studied Lewis acid in the emerging frustrated Lewis pair (FLP) chemistry.¹⁰⁻¹² Its heavier and less explored congener Al(C₆F₅)₃ was recognized to possess higher Lewis acidity^{13,14} and hence also considered as a desired candidate in the FLP type chemistry in recent years.^{15–23} Although B(C₆F₅)₃ was reported in the literature to be a stronger Lewis acid than $Al(C_6F_5)_3^{2,24}$ a large number of observations from both experimental and computational studies indicate that $Al(C_6F_5)_3$ is a stronger Lewis acid.1,13,14,25-28 One possible reason for the Lewis acidity discrepancy could be the unique ability of $Al(C_6F_5)_3$ to form stable adducts with even very weak donor molecules (vide infra), while the structure of the uncomplexed, unsolvated $Al(C_6F_5)_3$ is currently unknown.

Recently we demonstrated that $Al(C_6F_5)_3$, which is known to form an isolable adduct with toluene or benzene,²⁹ can also form an isolable complex with triethylsilane,²⁵ a weaker donor (base) than toluene; in sharp contrast, $B(C_6F_5)_3$ is not capable of forming a stable adduct with either weak basic donor for SC-XRD measurement.³⁰ Interestingly, in this alane-silane complex, a secondary Al---F contact was also present, which indicates that, even upon complexation with a donor such as Et_3SiH , $Al(C_6F_5)_3$ tends to seek for additional stabilization through Al…F interactions. On the other hand, although the unsolvated $Al(C_6F_5)_3$ has been synthesized by transmetalation or alkyl/aryl ligand exchange between AlEt₃ and $B(C_6F_5)_3$ in non-coordinating solvents such as hexanes,¹⁻³ its solid state structure has never been obtained and analysed. Instead, the structural characterization of Al(C₆F₅)₃ was performed through SC-XRD analysis of its adduct with toluene or benzene.²⁹ Notably, the bonding interaction in the alane-toluene adduct features η^1 -coordination at the *para*-position of toluene (Chart 1), which resembles the coordination behavior of the Et₃Si⁺·toluene adduct.^{31,32} Other observations, such as silane complexation and the related catalysis, also suggest that the properties of Al(C_6F_5)₃ are more comparable to those of Et₃Si⁺,

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, USA. E-mail: Eugene.Chen@Colostate.edu; Fax: (+1) 970-491-1801 †Electronic supplementary information (ESI) available: NMR spectra and X-ray structural data. CCDC 1429349 and 1429350. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03895b



Chart 1 Known alane complexes with weak donors.

and less comparable to those of $B(C_6F_5)_3$.²⁵ Given the high level of interest and difficulty in pursuing the "free" Et_3Si^+ cation, owing to the high tendency of such silylium ions to interact with its environments,³³⁻³⁵ such as their pendent groups, coordinating solvents, and counterions, it would be of great interest to investigate the structural features of its neutral analogue, the unsolvated $Al(C_6F_5)_3$.

Results and discussion

Isolation and characterization of unsolvated Al(C₆F₅)₃

To isolate the unsolvated crystalline $Al(C_6F_5)_3$, $B(C_6F_5)_3$ was suspended in hexanes and one equivalent of AlEt₃ was added. The gradual dissolution of B(C₆F₅)₃ indicates the B/Al aryl/ alkyl ligand exchange³⁶ between B and Al. After full dissolution of $B(C_6F_5)_3$, the clear solution mixture was capped tight and left undisturbed for 2 days at room temperature in a glovebox. Colourless crystals were developed, decanted, and washed with hexanes. The resulting crystals had limited solubility in noncoordinating solvents such as hexanes and cyclohexane. Nevertheless, the ¹H and ¹⁹F NMR spectra of a saturated solution of $Al(C_6F_5)_3$ in C_6D_{12} were recorded, indicating that no other component was present except the alane (Fig. S1-3[†]). The ¹⁹F NMR signals at δ -124.9, -146.7 and -157.6 ppm were downfield shifted (for meta- and para-F's), compared to those of the silane- and toluene-alane complexes. Notably, these signals are relatively broad, presumably due to the exchange between the tricoordinate and tetracoordinate environments at the Al center with the fluorine atoms of the $-C_6F_5$ group (vide infra).

To investigate the possible Al…F contacts in the solid state, we performed SC-XRD analysis of the unsolvated alane. As expected, there are strong Al-F interactions. But to our surprise and delight, instead of forming Al---F contacts with the meta- or para-fluorine atoms, which are considered to be less crowded and more accessible, two of the alane molecules adopt a dimeric structure via the ortho-F bridge (Fig. 1). In such geometry, the Al center of one molecule receives dative fluorine interaction from the other alane molecule, and in the meantime it also serves as the fluorine donor to the latter. Such double Al…F interactions within the dimer afford a distorted boat shape 8-membered Al₂C₄F₂ heterocycle consisting of Al, F, and two adjacent C atoms on the $-C_6F_5$ ring. This specific arrangement also brings two free -C₆F₅ groups (one on each alane molecule) in close proximity to form a pi-stacking interaction with the shortest C17 to -C₆F₅ plane distance of 3.316(2) Å. In addition, the Al---F interaction is rather strong, as reflected by short Al-..F distances of 1.962(1) and 1.983(5) Å and the elongation of the involving C-F bonds (1.423(2) and 1.447(5) Å), when compared to an average of other C-F bond lengths (ca. 1.340 Å). Overall, our observation is consistent with what Krossing et al. reported on a similar Lewis acidic alane Al[OC(CF₃)₃]₃.³⁷ From their computational results, the fluoride ion affinities (FIA) of $Al[OC(CF_3)_3]_3$ and $Al(C_6F_5)_3$ are almost identical (537 and 530 KJ mol⁻¹, respectively). According to the calculated geometry of Al[OC(CF₃)₃]₃,



Fig. 1 X-ray structure (50% thermal displacement) of $[Al(C_6F_5)_3]_2$. Selected interatomic distances (Å) and angles (°): Al1---F16 1.962(1), Al2---F1 1.983(5), F16-C20 1.423(2), F1-C2 1.447(5), Al1-C1 1.984(2), Al2-C19 1.982(2), C1-C2 1.366(3), C19-C20 1.371(2). (A) The highlighted double Al---F bridging; (B) the overall structure; (C) the highlighted 8-membered Al₂C₄F₂ heterocycle.

the Al center features intramolecular Al…F interactions with fluorine atoms on its pendent groups. The X-ray structure of PhF \rightarrow Al[OC(CF₃)₃]₃ revealed the Al…F distance to be 1.864(2) Å, which is about 0.1 Å shorter than that observed for the unsolvated alane, while the C_{Ph}–F distance of 1.447(3) Å is nearly identical for both Al complexes.

Previous reports on the unsolvated Al(C₆F₅)₃ always emphasized its thermal and shock sensitivity,^{1,14} as an explosion was reported in an attempt to sublime the crude etherate, prepared from the reaction of AlCl3 and 3 equivalents of C6F5MgBr in ether, or in an attempt to prepare the unsolvated $Al(C_6F_5)_3$ by heating a mixture of B(C₆F₅)₃ and AlEt₃ to 70 °C.³⁸ This observation actually resembles the explosive nature of LiC₆F₅ at above -20 °C, which was due to the exothermic elimination of LiF to form the tetrafluorobenzyne species.³⁹ We speculate that the thermal and shock sensitivity of the unsolvated $Al(C_6F_5)_3$ might be due to a similar decomposition pathway, which is indeed indicative of the dimeric structure. A closer look at the X-ray structure reveals that the endocyclic (with respect to the Al₂C₄F₂ ring) C=C bond lengths (1.366(3) and 1.371(2) Å) are shorter than those of the exocyclic ones, which gave us hints on the possible pathway for the rearrangement



Scheme 1 Possible thermal decomposition pathway of $[Al(C_6F_5)_3]_2$.

of the dimer towards elimination of [Al]F, in the form of $(C_6F_5)_2AlF$ (Fig. S9†), and tetrafluorobenzyne shown in Scheme 1.

Complexation of Al(C₆F₅)₃ with ferrocene

Next, we examined the complexation between $Al(C_6F_5)_3$ and ferrocene (Cp₂Fe). In their recent communication Agapie et al.⁴⁰ utilized $B(C_6F_5)_3$ and ferrocene, which showed no interaction between them, as a FLP system for dioxygen reduction. We envisioned that, since ferrocene is more electron rich than benzene or toluene, it should form a stable and/or isolable adduct with the alane. Indeed, upon mixing equimolar $Al(C_6F_5)_3$ and ferrocene, we observed an immediate change of yellow colour of ferrocene to red. The downfield shift of the Cp ¹H NMR signal from 4.05 to 4.24 ppm also indicates the interaction between $Al(C_6F_5)_3$ and ferrocene, as well as the partial removal of the electron density from the ferrocene as a result of this interaction. Deep red crystals of the resulting complex were obtained by laying hexanes onto a 1,2-dichlorobenzene solution of this mixture. The X-ray structure reveals the 1:1 adduct formation, via the η^1 -coordination of the alane onto C1 of the Cp ring (Fig. 2A). The C1-Al1 distance is 2.214(2), which is shorter than the value (2.366(2) Å) reported for the Al(C₆F₅)₃·toluene adduct.²⁹ Further evidence of the strong inter-

action came from the distorted tetrahedral geometry at the Al center with a sum of the C–Al–C angles $\Sigma_{C-Al-C} = 338.63(6)^{\circ}$ for the $Al(C_6F_5)_3$ unit. Interestingly, the attachment of Al also renders the corresponding C(Cp) atom to be pyrimidalized, which perturbs the aromaticity of the Cp ring. A large alternation of the bond distance of the complexed Cp was observed. For the C1-C2-C3-C4-C5 ring, the C-C bond distances are 1.464(2), 1.414(2), 1.426(2), 1.418(2) and 1.465(2) Å. Last but not least, the proton attached to the same C1 was refined without constraint or restraint, which yields a short C1–H1 distance of 0.90(2) Å (the regular C_{cp} –H distance for other protons using the riding mode is set at 1.000 Å). This proton carries a partial positive charge, as it bends out of the Cp plane towards the iron center, forming a Fe… $H^{\delta+}$ distance of 2.56(2) Å. In comparison, the alane-toluene complex features an Al-C (toluene) distance of 2.366(2) Å and an angle of 96.1°, which results in the elongation of the related C-H bond length, but with only slight perturbation of the phenyl ring. In the alaneferrocene complex, we observed a shorter Al1-C1 contact of 2.214(2) Å and a larger angle of 99.44(6)°. As a result, this interaction leads to quite considerable alternation of the Cp ring and contraction of the C1–H1 distance due to the Fe \cdots H^{δ +} interaction. It is also worth noting that the stabilization and shuffling of protons via the iron center have been proposed in the metathesis involving 1,2-disubstituted stannylated ferrocene derivatives and boron halides, which usually yields a mixture of 1,2-, 1,3- and 1,1'-products.41-45

To further confirm the conclusion that ferrocene is a stronger donor than toluene toward the alane drawn from the SC-XRD analysis, a separate NMR scale experiment was performed. After dissolving an equimolar amount of $Al(C_6F_5)_3$. (toluene)_{0.5} adduct and ferrocene in C_6D_5Br , a similar red colour solution was obtained. ¹H NMR analysis indicates the replacement of toluene by ferrocene according to the signal at 4.23 ppm. This solution was then heated at 100 °C for 3 days to give a dark green solution (Fig. 2C) and the ¹H NMR signal



Fig. 2 (A) X-ray structure (50% thermal displacement) of Cp₂Fe·Al(C₆F₅)₃. Selected interatomic distances (Å) and angles (°): C1-H1 0.90(2), Fe1…H1 2.56(2), Al1-C1 2.214(2), Al1-C11 1.985(2), Al1-C17 1.998(2), Al1-C23 1.994(2), Σ_{C-AL-C} 338.63(6), C1-C2 1.464(2), C2-C3 1.414(2), C3-C4 1.426(2), C4-C5 1.418(2), C1-C5 1.465(2). Cent_{cp}-C1-H1 11.8(12), Cent_{cp}-C1-Al 99.44(6). (B) Color of ferrocene and Cp₂Fe·Al(C₆F₅)₃; (C) after heating at 100 °C for 3 days.



Fig. 3 Overlay of UV-Vis spectra of Cp₂Fe (yellow), Cp₂Fe-Al(C₆F₅)₃ (red) and a mixture of Cp₂Fe and Al(C₆F₅)₃ after being heated at 100 °C for 3 days (green).



Scheme 2 Proposed pathway for the oxidation of ferrocene through electronic interaction with the alane.

of Cp became broader and also shifted to a downfield region of 11.4 ppm (Fig. S7†), all of which are a typical indication of gradual oxidation of ferrocene. The presence of the Cp_2Fe^+ cation was also evidenced by the emergence of a LMCT band at around 630 nm from the UV-Vis absorption measurement (Fig. 3). The ¹⁹F NMR spectrum (Fig. S8†) indicates the generation of a complex mixture of aluminum-based species, presumably due to the decomposition of the transient aluminum based radical anion (Scheme 2). Indeed, the attempts on isolation of the boron based radical anion also proved futile.^{46–48}

Conclusions

In summary, we report the crystal structure of the unsolvated $Al(C_6F_5)_3$, which features the dimeric structure with the double Al...F interactions between the Al and the ortho-F of the adjacent molecules. This finding indicates that, due to the high FIA of the monomeric $Al(C_6F_5)_3$, even in non-coordinating solvents such as hexanes, it seeks for additional stabilization through its pendent -C₆F₅ group. In practice, when comparing the Lewis acidity of the alane, the dimeric structure should be considered. In addition, the thermal and shock sensitivity of the unsolvated $Al(C_6F_5)_3$ might have originated from its dimeric structure, which favors the exothermic elimination of [Al]F and formation of tetrafluorobenzyne, in a fashion similar to the LiC₆F₅ decomposition. The complexation between $Al(C_6F_5)_3$ and ferrocene results in the formation of the stable adduct $Cp_2Fe \cdot Al(C_6F_5)_3$, which is in contrast to $B(C_6F_5)_3$. Electronic interaction between the alane and ferrocene rendering oxidation of ferrocene also occurred in such a system, albeit with the decomposition of the aluminum based radical anion.

Experimental

Materials, reagents, and methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an inert gas (Ar or N_2)-filled glovebox. NMR-scale reactions were conducted in Teflon-valve-sealed J. Young-type NMR tubes. HPLC-grade organic solvents were first sparged extensively with nitrogen during the filling of 20 L solvent reservoirs and then dried by passage through activated alumina (for Et₂O, THF, and CH₂Cl₂) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. Benzene- d_6 , bromobenzene- d_5 , and cyclohexane- d_{12} were dried over a sodium/potassium alloy and vacuum-distilled or filtered, whereas CD₂Cl₂ and CDCl₃ were distilled over CaH₂ and then stored over activated Davison 4 Å molecular sieves. NMR spectra were recorded on Varian Inova 400 MHz (FT 400 MHz, ¹H; 100 MHz, ¹³C; 376 MHz, ¹⁹F) and 500 MHz spectrometers. Chemical shifts for all spectra were referenced to internal solvent resonances and were reported in parts per million relative to SiMe₄, whereas ¹⁹F NMR spectra were referenced to external CFCl₃. EPR spectra were recorded on a Bruker ESP-300 spectrometer. UV-Vis spectra were recorded on a Varian Cary 500 UV-Vis-NIR spectrometer. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ.

Triethylaluminum and ferrocene were purchased from Sigma-Aldrich Chemical Co. and used as received. Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was obtained as a research gift from Boulder Scientific Co. and further purified by double sublimation under vacuum. Other commercial reagents were purchased from Sigma-Aldrich and used as received. Literature procedures were employed or modified for the preparation of the following compounds or adducts: $Al(C_6F_5)_3$ and $Al(C_6F_5)_3$ (toluene)_{0.5}.¹⁻³ (*Extra caution should be exercised when handling these materials, especially the unsolvated alane, due to its thermal and shock sensitivity!*)

X-ray diffraction intensities were collected on a Bruker SMART APEX CCD Diffractometer using CuK α (1.54178 Å) or MoK α (0.71073 Å) radiation at 100 or 120 K. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least squares on F^2 for all reflections.⁴⁹ All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions expect the H1 (at distorted position due to the attack of Al) in adduct [Cp₂Fe·Al(C₆F₅)₃]. Hydrogen H1 was found on the difference density map and refined without restraint or constraint. Crystallographic data for the structures of [Al(C₆F₅)₃]₂ (CCDC 1429349) and [Cp₂Fe·Al(C₆F₅)₃] (CCDC 1429350) have been deposited with the Cambridge Crystallographic Data Center as supplementary publications.

Isolation of the unsolvated Al(C₆F₅)₃

In a glovebox, to a suspension of $B(C_6F_5)_3$ (512 mg, 1.00 mmol) in 10 mL of hexane was added neat AlEt₃ (0.137 mL, 1.00 mmol, 1.00 equiv.) in a 20 mL vial. The mixture gradually became clear after stirring for 10 min. The vial was capped tight and left undisturbed at room temperature for 2 days, after which X-ray quality crystals were developed. The crystals were collected by filtration, washed with hexane (2 mL) twice, and dried under vacuum, affording 400 mg of the product. Additional crop of 80 mg was obtained by reducing the mother liquor to 2 mL followed by crystallization at -30 °C (yield: 480 mg, 91%). ¹⁹F NMR (C₆D₁₂, 25 °C): δ -124.9 (br, 6F, *o*-F), -146.7 (br, 3F, *p*-F), -157.6 (br, 6F, *m*-F) ppm. ¹⁹F NMR (C₆D₆,

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25 °C): δ –122.7 (d, ³*J* = 17.7 Hz, 6F, *o*-F), –150.6 (pst, ³*J* = 19.9 Hz, 3F, *p*-F), –160.5 (m, 6F, *m*-F) ppm.

Isolation of Cp₂Fe·Al(C₆F₅)₃

In a glovebox, ferrocene (186 mg, 1.00 mmol) and Al(C₆F₅)₃ (528 mg, 1.00 mmol, 1.00 equiv.) were dissolved in 2 mL of 1,2-dichlorobenzene. The mixture was layered with 2 mL of hexanes and placed in a freezer at -30 °C. X-ray quality crystals were developed overnight. The crystals were collected by filtration, washed with hexanes (2 mL) twice, dried under vacuum, affording 600 mg of the product (yield: 84%). ¹H NMR (C₆D₅Br, 25 °C): δ 4.24 (br, 10H, Cp). ¹³C NMR (C₆D₅Br, 25 °C): δ 149.8, 142.3, 136.9, 111.4 (C₆F₅), 70.1 (Cp). ¹⁹F NMR (C₆D₅Br, 25 °C): δ –120.4 (d, ³*J* = 16.9 Hz, 6F, *o*-F), –149.3 (pst, ³*J* = 19.9 Hz, 3F, *p*-F), –159.4 (m, 6F, *m*-F) ppm. Elemental analysis for C₂₈H₁₀AlF₁₅Fe: calcd C 47.09, H 1.41; found C 46.95, H 1.49%.

NMR scale reaction of Cp_2Fe and $Al(C_6F_5)_3$ (toluene)_{0.5}

A Teflon-valve-sealed J. Young-type NMR tube was charged with ferrocene (10.0 mg, 0.025 mmol), $Al(C_6F_5)_3$ ·(toluene)_{0.5} (30.9 mg 0.025 mmol, 1.00 equiv.) and 0.7 mL of C_6D_5Br at ambient temperature. The mixture was allowed to react for 10 min before NMR analysis, which indicates the adduct formation between ferrocene and $Al(C_6F_5)_3$. The NMR tube was heated at 100 °C for 3 days. ¹H and ¹⁹F NMR spectra were recorded at different time intervals. The gradual color change from red to dark green also indicates the oxidation of ferrocene, which was also confirmed by UV-Vis absorption study.

Acknowledgements

This work was supported by the United States National Science Foundation (CHE-1507702). We thank Dr Roger A. Lalancette for the generous access to the SC-XRD facility at Rutgers-Newark for determining the structure of the alane–ferrocene adduct and Boulder Scientific Co. for the research gift of $B(C_6F_5)_3$.

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Published on 16 November 2015. Downloaded by Florida International University on 30/11/2015 17:10:51.

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