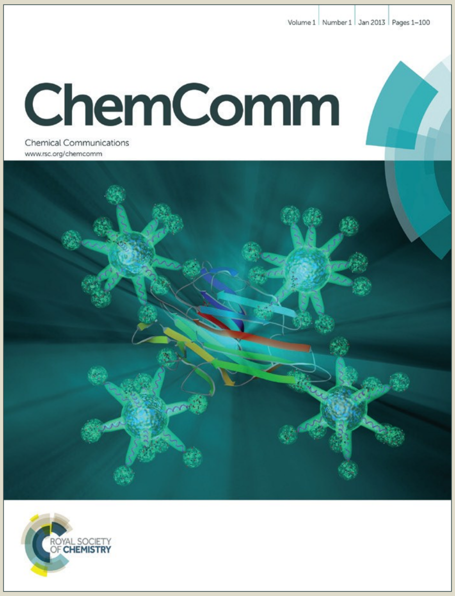
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ARTICLE TYPE

Cationic Aluminum Hydride Complexes: Reactions of Carbene-Alane Adducts with Trityl-Borate

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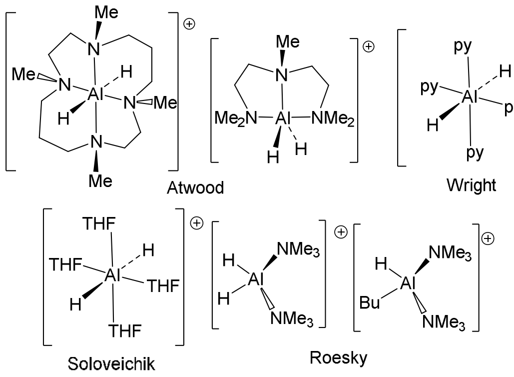
Reaction of (Idipp)AlH$_3$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in toluene affords the dimeric aluminum dication [((Idipp)AlH(μ-H))$_2$][B(C$_6$F$_5$)$_4$]$_2$ 2. In contrast, the reaction of (IBn)AlH$_3$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in bromobenzene gives a redistribution product, the salt of a monomeric dication [(IBn)$_2$AlH][B(C$_6$F$_5$)$_4$]$_2$ 4.

Aluminum hydrides are important reagents in organic, inorganic and materials chemistry. Indeed, such species are used in a variety of roles including reagents for reductions[1-6] and in inorganic synthesis.[7-8] Applications as components in materials chemistry and in particular, hydrogen storage materials[9-11] have also garnered attention. From a coordination chemistry perspective, aluminum-hydride derivatives exhibit a range of geometries resulting from the low steric demand of hydride and the ability of aluminum to accommodate coordination numbers ranging from three to six. The majority of reported aluminum hydride species are either neutral or anionic while, in contrast, cationic aluminum-hydride species are less common. A matrix isolation study at 4 K described a [AlH]•$^+$ radical cation which was studied by EPR spectroscopy.[12-13] The first fully characterized Al-hydride cations [H$_2$Al((MeNCH$_2$CH$_2$N(Me)CH$_2$CH$_2$CH$_2$)$_2$)][AlH$_4$] and [H$_2$Al(MeN(CH$_2$CH$_2$NMe$_2$)$_2$)][AlH$_4$] (Scheme 1) were prepared and reported by Atwood and coworkers in 1991.[14-15] These species exhibited six- and five-coordinate aluminum centers, respectively. In 1994, Soloveichik and coworkers described the structure of the salt [AlH$_2$(C$_4$H$_8$O)$_4$][(C$_5$H$_5$)$_3$Yb(Na)Yb(C$_5$H$_5$)$_3$] (Scheme 1) which contained a six-coordinate aluminum-dihydride cation.[16] In 2004, we employed an aluminum complex of a phosphinimine-amine ligand to generate salts of the aluminum-hydride cation [(*i*Pr$_2$C$_6$H$_3$N)C(Me)CHPPh$_2$(NC$_6$H$_3$*i*Pr$_2$)AlH][B(C$_6$F$_5$)$_4$].[17] Roesky and coworkers exploited a bulky non-coordinating anion to isolate the salts [H$_2$Al(NMe$_3$)$_2$]$_2$[(AlH)$_8$(CCH$_2$*t*Bu)$_6$] and [H(*n*Bu)Al(NMe$_3$)$_2$][(AlH)$_7$(AlNMe$_3$)(CCH$_2$*t*Bu)$_6$] (Scheme 1) in 2005.[18] These latter compounds are examples of four-coordinate aluminum hydride cations. Most recently, Wright and coworkers described the structure of [(1,4-H-pyrid-1-yl)$_4$Al][(pyridine)$_4$AlH$_2$], which was formed from the reaction of (*t*BuO)AlH$_2$ and pyridine.[19] In this manuscript, we describe two reactions of carbene-alane adducts with trityl cation affording the first dimeric four-coordinate and monomeric three-coordinate aluminum hydride dications.

The known carbene-alane adduct (Idipp)AlH$_3$ **1**, was prepared via literature methods.[20] Reaction of species **1** with one equivalent of [Ph$_3$C][B(C$_6$F$_5$)$_4$] at room temperature in toluene resulted in the immediate precipitation/crystallization of a new species **2** (Scheme 2). The formation of **2** proceeds via hydride abstraction from **1**, liberating Ph$_3$CH, followed by subsequent dimerization and crystallization. Although this avenue of reactivity is not widely exploited in aluminum-hydride chemistry, it is known in the literature to generate both aluminum[17] and transition metal alkyl cations.[21-22] The formation of **2** represents, to our knowledge, the first dimeric aluminum-hydride dication salt.

Scheme 1 Structurally characterized aluminum-hydride cations.



The complete insolubility of this product in all organic solvents in which it was stable precluded spectroscopic characterization, however compound **2** was characterized by single crystal X-ray diffraction (Figure 1). Solution of the structure via direct methods revealed that the asymmetric unit contains a single Al center and a [B(C$_6$F$_5$)$_4$]$^-$ anion, and structure refinement confirmed the molecular structure of **2** to be that of the centrosymmetric dimeric dication salt, [((Idipp)AlH(μ-H))$_2$][B(C$_6$F$_5$)$_4$]$_2$. The Al center adopts a pseudo-tetrahedral geometry featuring coordinate bonds to the carbene, a terminal hydride, and two bridging hydrides. The angles about Al range from 102.1(8)° to 128.5(9)° and the Al-C bond length is 1.964(3) Å. The terminal Al-hydride bond length refined to 1.50(2) Å and the bridging Al-H distances were determined to be 1.66(2) Å and 1.71(2) Å. The resulting Al···Al distance in the cation of **2** is 2.584(2) Å, a value greater than the sum of the covalent radii of the two atoms.[23] The structure of the cation **2** is reminiscent of the neutral dimeric Al(II) species reported by Jones and coworkers,[24] which features an Al-Al single bond (2.6375(8) Å, and terminal Al–H distances of 1.56(2) Å and 1.53(2) Å). Similarly, the compound $[(iPr_2N(CNDipp)_2AlH)]_2$[24] exhibited an Al···Al distance of 2.675(1) Å with terminal Al–H distances of 1.53(2) Å. The observation of a shorter Al···Al distance in **2** in comparison to that in Al(II) species is consistent with the higher oxidation state of the Al centers in **2** prompting shorter Al-H_{bridge} bonds thus drawing the Al atoms closer together.

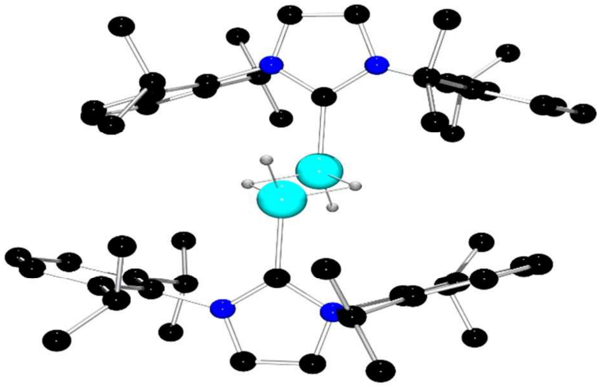
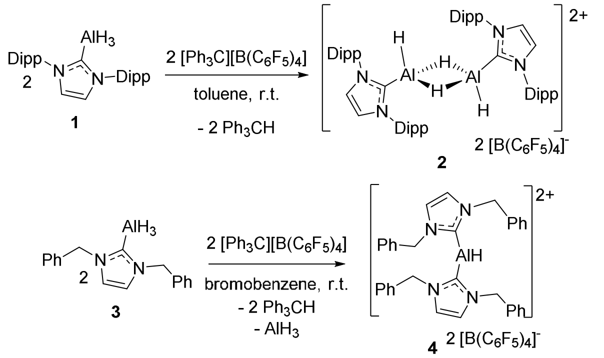


Figure 1 POV-ray depiction of the dication of **2**. C: black, N: blue, Al: teal , H: gray. All ligand-based H atoms, as well as the $[B(C_6F_5)_4]^-$ anions, are omitted for clarity. Selected bond distances and angles: Al-Al‘ 2.584(2), Al-H_{bridg} 1.71(2), 1.66(2), Al-H_{term} 1.50(2), Al-C 1.964(3), H_{bridg}-Al-C 102.1(8), H_{bridg}‘-Al-C 104.1(8), H_{term}- Al-C 128.5(9), H_{term}-Al-H_{bridg} 114(1), H_{term}-Al-H_{bridg}‘ 117(1).



Scheme 2 Synthesis of **2** and **4**.

To probe the impact of altering the carbene, 1,3-dibenzylimidazol-2-ylidene (IBn) was allowed to react with $(EtMe_2N)AlH_3$ in toluene, to readily afford $(IBn)AlH_3$ (**3**) in 72% yield after recrystallization. This species gives rise to a broad singlet resonance in ^{1}H NMR spectrum in C_6D_5Br at 4.38 ppm corresponding to the aluminum-bound hydride centers. The ^{27}Al NMR spectrum of **3** shows a broad singlet resonance at 108.7 ppm. These data are comparable to those seen for related NHC-alane adducts.[25-26] An X-ray crystallographic study of **3** (See SI, Figure S3) confirmed the formulation, revealing a Al-C_{NHC} bond length of 2.059(2) Å, which falls within the range of typical Al-C_{NHC} bonds (2.034-2.067 Å).[25-26]

Treatment of **3** with a stoichiometric amount of $[Ph_3C][B(C_6F_5)_4]$ in C_6H_5Br at room temperature results in the formation of Ph_3CH and a new species **4** in 46% yield. The ^{1}H NMR spectrum of **4** in C_6D_5Br shows resonances attributable to the IBn ligand but no signal was observed in the ^{27}Al NMR spectrum. The IR spectrum of **4** featured a signal at 1963 cm^{-1}, which is in the same region as observed for other cationic aluminum hydride species.[27] The solid state structure of **4** was unambiguously confirmed by X-ray crystallography. Compound **4** proved to be the dicationic borate salt $[(IBn)_2AlH][B(C_6F_5)_4]_2$. The cation of this salt is a planar monohydrido aluminum dication containing two IBn ligands (Figure 2). The planes of the two carbenes are oriented approximately orthogonal to each other, allowing the benzyl substituents to envelop the aluminum center. Two of the pendent arenes are positioned above and below the pseudo-trigonal coordination plane of the aluminum center. The sum of the angles about aluminum is 359° and the C-Al-C‘ angle is 113.6(2)°. The Al-C bond distances in **4** are 1.987(4) Å and 2.010(4) Å. The structural data also reveals that one of the benzyl substituents on one of the IBn ligands is oriented such that a C-C π-bond is positioned above with Al-C distances of 3.124(5) Å and 2.572(4) Å, respectively.

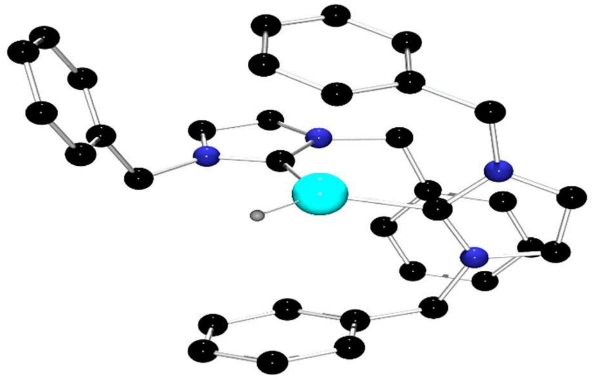


Figure 2 POV-ray depiction of the dication of **4**. C: black, N: blue, Al: teal, H: gray. All ligand-based H atoms as well as the $[B(C_6F_5)_4]$ anions are omitted for clarity. Selected bond distances and angles: Al-C_{right} 1.987(4), Al-C_{left} 2.010(4), Al-H 1.43(5),C_{right}-Al-H 131(2), C_{left}- Al-H 114(2), C_{right}-Al-C_{left} 113.6(2).

DFT calculations were performed at the B3LYP/6-311G(d,p) level of theory to gain further insight into the electronic structure of dication **4**. The optimized geometry corresponded well with the crystallographically determined structure (non-hydrogen RMSD = 0.30 Å), and a frequency calculation confirmed that that IR active band at 1963 cm^{-1} arises from a normal mode comprising almost exclusively the Al-H stretch (See SI). Based on natural population analysis (NPA),[28-29] the Al atom of compound **4** bears a natural atomic charge of +1.50 (See SI, Figure S11 & Table S2). An NPA analysis reported for the similar dicationic hydrido boron complex prepared by Ong and co-workers[30] suggested that their boron complex was stabilized by distribution of positive charge from the boron center onto the carbodicarbene supporting ligands. The lack of such charge redistribution in **4** suggests that it is stabilized by other effects. The LUMO of the dication (Figure 3) is mainly located on the Al atom and has significant contribution from the proximal arene ring. An electronic interaction between the Al center and the aromatic ring of the pendent benzyl group, inferred from the crystal structure of **4** in addition to the delocalized nature of the LUMO, was corroborated by the results of a natural bond orbital

(NBO) analysis.[31] Using second order perturbation theory, a donor acceptor interaction was identified between a bonding NBO on the pendent arene ring and an empty lone pair NBO on the Al center. The Al-based NBO has essentially pure $3p_z$ character and the bonding NBO, localized between the two carbon atoms of the arene ring that are closest to the metal center, has π-symmetry and is oriented such that it overlaps with the Al-based NBO (See SI, Figure S12 & Table S3). This interaction may impart stabilization on the complex, accounting for its unexpected stability. For instance, NMR spectroscopy revealed no evidence of degradation of a sample of **4** that had been stored in an inert atmosphere for over a month. The Al-arene interaction in **4** is reminiscent of the olefin-Al interaction described for $CH_2=C(CH_3)CH_2CH_2CH_2Al(C_6F_5)_2$[32-33] and $(C_6H_{10})Al(C_6F_5)_3$,[34] The equivalence between the benzyl groups of **4** observed in the solution state NMR spectrum suggest that this interaction is fluxional, at least on the NMR time scale. The transient nature of the interaction, coupled with the fact that the distance separating the Al center and the nearest carbon of the arene ring is greater than the sum of their van der Waals radii, leads us to formulate the species as a 3-coordinate aluminum complex.

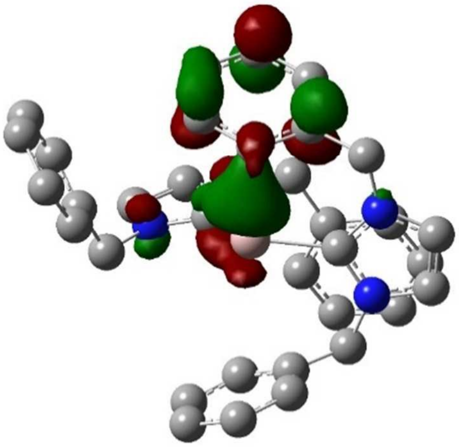


Figure 3. Lowest unoccupied molecular orbital (LUMO) plot for the dication of **4**.

Although redistribution reactions are common in aluminum chemistry, the formation of **4** is a rare example of such a redistribution involving a carbene ligand. One can speculate that the reaction of **3** with $[Ph_3C][B(C_6F_5)_4]$ proceeds to generate a dimeric analog of **2** but that the lesser steric demands of IBn facilitate the redistribution affording **4** and liberation of AlH_3.

Conclusions

The above reactions of NHC-alane adducts with trityl borate were shown to generate the dimeric aluminum-hydride dicationic salt **2** as well as the monomeric three-coordinate aluminum-hydride salt **4**. These observations represent the first dicationic aluminum-hydride salts to be characterized. The differing nature of these species illustrates the influence of carbene substituents on the aggregation of aluminum-hydrides.

Notes and references

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[a] These authors contributed equally.

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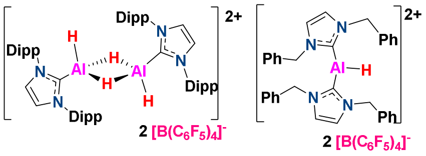
TOC Graphic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