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Cationic aluminum hydride complexes: reactions of carbene–alane adducts with trityl-borate†

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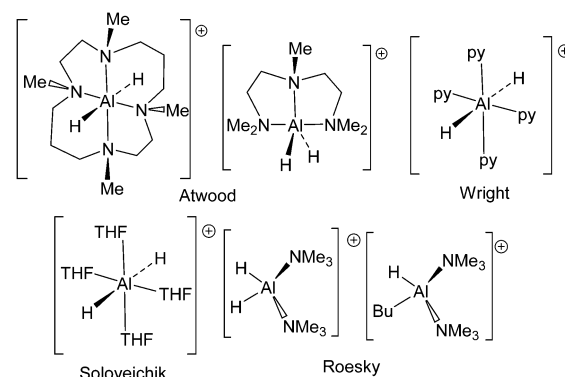
Reaction of (Idipp)AlH₃ with [Ph₃C][B(C₆F₅)₄] in toluene affords the dimeric aluminum dication [(Idipp)AlH(μ-H)]₂[B(C₆F₅)₄]₂ **2**. In contrast, the reaction of (IBn)AlH₃ with [Ph₃C][B(C₆F₅)₄] in bromobenzene gives a redistribution product, the salt of a monomeric dication [(IBn)₂AlH][B(C₆F₅)₄]₂ **4**.

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 [H₂Al(MeNCH₂CH₂N(Me)CH₂CH₂CH₂)₂][AlH₄]⁺ and [H₂Al(MeN(CH₂CH₂NMe₂)₂)][AlH₄]⁺ (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 [AlH₂(C₄H₈O)₄][[(C₅H₅)₃Yb(Na)Yb(C₅H₅)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 [(iPr₂C₆H₃N)C(Me)CHPPH₂(NC₆H₅iPr₂)AlH][B(C₆F₅)₄]⁺.¹⁷ Roesky and coworkers exploited a bulky non-coordinating anion to isolate the salts [H₂Al(NMe₃)₂]₂[(AlH)₈(CCH₂tBu)₆] and

[H(*n*Bu)Al(NMe₃)₂][(AlH)₇(AlNMe₃)(CCH₂tBu)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)₄Al]–[(pyridine)₄AlH₂]⁺, which was formed from the reaction of (*t*BuO)AlH₂ 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)AlH₃ **1**, was prepared *via* literature methods.²⁰ Reaction of species **1** with one equivalent of [Ph₃C][B(C₆F₅)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 and crystallization. Although this avenue of reactivity is not widely exploited in aluminum-hydride chemistry, it is known in the literature to generate both aluminum¹⁷ and transition metal alkyl cations.^{21,22} The formation of **2** represents, to our knowledge, the first dimeric aluminum-hydride dication salt.

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



Scheme 1 Structurally characterized aluminum-hydride cations.

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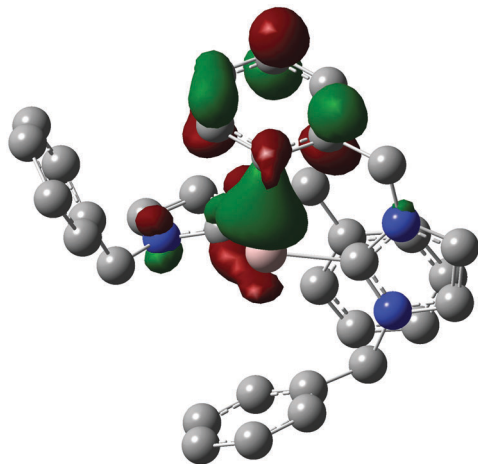


Fig. 3 Lowest unoccupied molecular orbital (LUMO) plot for the dication of **4**.

the IR active band at 1963 cm^{-1} arises from a normal mode comprising almost exclusively the Al–H stretch (see ESI†). Based on natural population analysis (NPA),^{27,28} the Al atom of compound **4** bears a natural atomic charge of +1.50 (see ESI,† Fig. S11 and Table S2). An NPA analysis reported for a similar dicationic hydrido boron complex prepared by Ong and co-workers²⁹ suggested that their boron complex was stabilized by redistribution 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 (Fig. 3) is mainly located on the Al atom but 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.³⁰ 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 ESI,† Fig. S12 and 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 $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{Al}(\text{C}_6\text{F}_5)_2$ ^{31,32} and $(\text{C}_6\text{H}_{10})\text{Al}(\text{C}_6\text{F}_5)_3$.³³ 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.

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 $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ 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 .

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.

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