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

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Reaction of (ldipp)AlH3 with [Ph3C][B(C6F5)4] in toluene affords the dimeric aluminum dication [[(ldipp)AlH(n-H)]2][B(C6F5)4]2. In contrast, the reaction of (Ibn)AlH2 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 reductions1–6 and in inorganic synthesis.7,8 Applications as components in materials chemistry and in particular, hydrogen storage materials9–11 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(MeNC2H4Me)3][AlH4] and [H2Al(Me(N(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][AlH2(NMe3)2][[AlH]2][AlH2(NMe3)](Scheme 1) which contained a six-coordinate aluminum-hydride cation.16 In 2004, we employed an aluminum complex of a phosphinimine–amine ligand to generate salts of the aluminum-hydride cation [[IP3C6H3N](C6H3NC6H3IP3)AlH][B(C6F5)4].17 Roesky and coworkers exploited a bulky non-coordinating anion to isolate the salts [H2Al(NMe3)2][[AlH]2][CCH2(Bu)6] and [H(n-Bu)Al(NMe3)2][[AlH]2][AlNMe3]2][CCH2(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]3Al][pyridine]3AlH2, which was formed from the reaction of (IBuO)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 (ldipp)AlH31, 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 from 1, liberating Ph3CH, 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 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 crystal X-ray diffraction23 and by 31P{1H} NMR spectroscopy (see ESI†).

Scheme 1 Structurally characterized aluminum-hydride cations.
crystal X-ray diffraction (Fig. 1). Solution of the structure via direct methods revealed that the asymmetric unit contains a single Al center and a $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, and structure refinement confirmed the molecular structure of 2 to be that of the centrosymmetric dimeric dication salt, $[[\text{dipp}]\text{AlH}(\mu-H)]_2[\text{B}(\text{C}_6\text{F}_5)_4]_2$. 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 structural data also reveals that one of the benzyl substituents on one of the IBn ligands is oriented orthogonal to each other, allowing the benzyl substituents to envelop the aluminum center. Two of the pendant 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 optimized geometry corresponded well with the crystallographically determined structure (non-hydrogen RMSD = 0.30 Å), and a frequency calculation confirmed that the electronic structure of 4 in 3.124(5) Å and 2.572(4) Å, respectively. 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

To probe the impact of altering the carbene, 1,3-dibenzylimidazol-2-ylidene (IBn) was allowed to react with (EtMe$_2$N)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$_6$D$_5$Br at 4.38 ppm corresponding to the aluminum-bound hydride center. 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. An X-ray crystallographic study of 3 (see ESI† Fig. S3) confirmed the formulation, revealing a Al–NHC bond length of 2.059(2) Å, which falls within the range of typical Al–NHC bonds (2.034–2.067 Å). Treatment of 3 with a stoichiometric amount of [Ph$_3$C][B(C$_6$F$_5$)$_4$] in C$_6$H$_5$Br at room temperature results in the formation of Ph$_3$CH and a new species 4 in 46% yield. The $^1$H NMR spectrum of 4 in C$_6$D$_5$Br 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. The solid state structure of 4 was unambiguously confirmed by X-ray crystallography. Compound 4 proved to be the dicaticonic borate salt [[IBn]$_2$AlH]$[\text{B}(\text{C}_6\text{F}_5)_4]_2$. The cation of this salt is a planar monohydrido aluminum dication containing two IBn ligands (Fig. 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 pendant 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.

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

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

Fig. 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 $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions, are omitted for clarity. Selected bond distances and angles: Al–Al$^1$ 2.584(2), Al–H$_{\text{bridge}}$ 1.71(2), Al–H$_{\text{term}}$ 1.50(2), Al–C$_{\text{left}}$ 1.964(3), H$_{\text{bridge}}$–Al–C$_{\text{left}}$ 104.1(8), H$_{\text{term}}$–Al–C$_{\text{left}}$ 128.5(9), H$_{\text{term}}$–Al–H$_{\text{bridge}}$ 114(1), H$_{\text{term}}$–Al–H$_{\text{bridge}}$' 117(1).

Fig. 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 $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions are omitted for clarity. Selected bond distances and angles: Al–C$_{\text{right}}$ 1.987(4), Al–C$_{\text{left}}$ 2.010(4), Al–H 1.431(5), C$_{\text{right}}$–Al–H 131(2), C$_{\text{left}}$–Al–H 114(2), C$_{\text{right}}$–Al–C$_{\text{left}}$ 113.6(2).
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 [Ph₆(C)(B(C,F₃)₃)] proceeds to generate a dimeric analog of 2 but that the lesser steric demands of IBr facilitate the redistribution affording 4 and liberation of AlH₃.

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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