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**Toward the Development of Aluminum Cluster-Containing Materials for Propulsion Applications**

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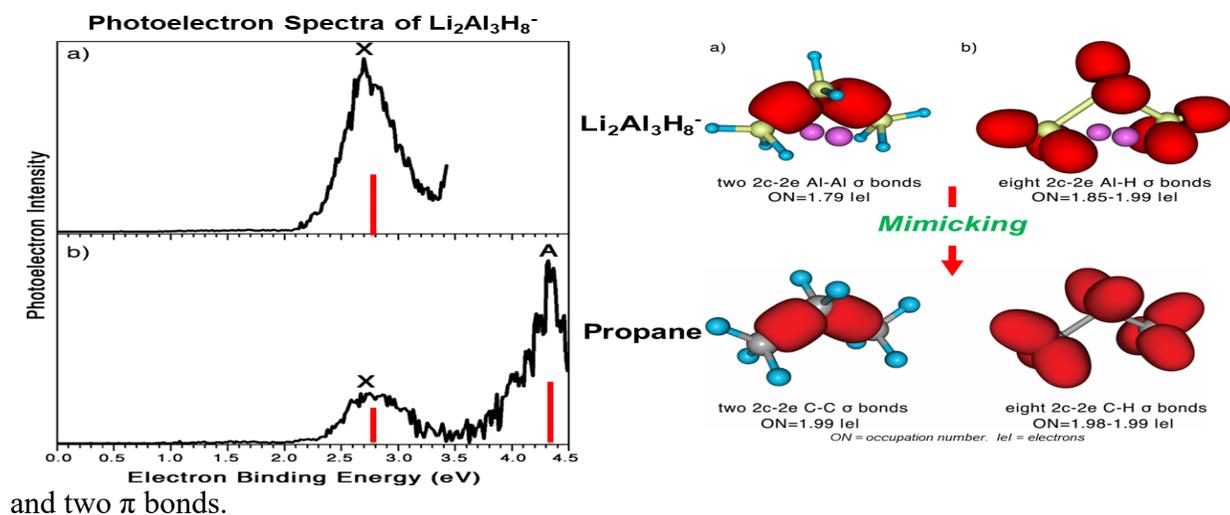
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<b>14. ABSTRACT</b> This work contributed toward the development of aluminum cluster-containing materials for propulsion applications. To accomplish this, we conducted numerous experiments in the gas phase on aluminum-containing cluster anions, using negative ion photoelectron spectroscopy as our primary experimental tool. Along with mass spectrometry to identify and isolate (massselect) the cluster anions of interest, we also developed several novel ion sources. Once formed, we often directed the cluster anions of interest through an ion-neutral reactivity cell to generate reaction products, which were then subjected to anion photoelectron spectroscopic studies in order to characterize their electronic structures. Both the spectroscopic and the reactivity studies were closely supported by complementary calculations.					
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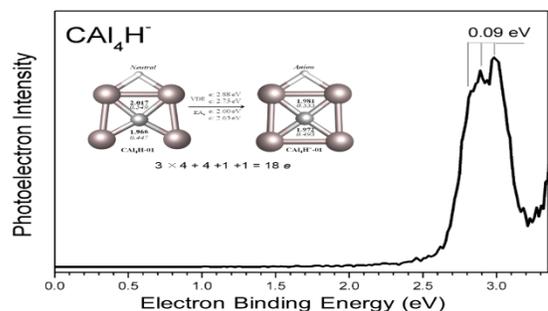
As a result of work completed during AFOSR grant (FA9550-15-1-0259), we published 23 papers, all of which were credited to it. Below, we highlight selected results from that work.

The discovery of new aluminum compounds and clusters and the characterization of their bonding has been a unifying theme in this work. While our primary experimental tool in these studies was anion photoelectron spectroscopy, our partnerships with the theorists: Alexandrova, Boldyrev, Hooper, and Kandalam, were also indispensable. Consider for example our discovery of a three-member aluminum-aluminum chain within the cluster anion,  $\text{Li}_2\text{Al}_3\text{H}_8^-$ . Metal-metal bonded chains had been thought to be rare among Group 13 elements. Just as important, the  $(\text{Al}_3\text{H}_8)^{3-}$  moiety within  $\text{Li}_2\text{Al}_3\text{H}_8^-$  was also found to mimic both the propane and the trisilane molecules.

In addition to aluminum atom chains, where each aluminum atom is bound to its neighbor by a single bond, we also found an  $\text{Al}=\text{Al}$  double bond within the  $\text{Al}_2\text{H}_4^{2-}$  moiety of the  $\text{LiAl}_2\text{H}_4^-$  cluster anion. The  $\text{Al}_2\text{H}_4^{2-}$  dianion is both isoelectronic and isostructural to  $\text{Si}_2\text{H}_4$ . The synthesis of  $\text{Al}=\text{Al}$  double bonds had been elusive for decades. Even more exciting is our recent discovery of an  $\text{Al}\equiv\text{Al}$  triple bond in the cluster anion,  $\text{Na}_3\text{Al}_2^-$ . This is the first classical  $\text{Al}\equiv\text{Al}$  triple bond ever to be observed, where the term, “classical”, denotes a triple bond composed of one  $\sigma$  bond

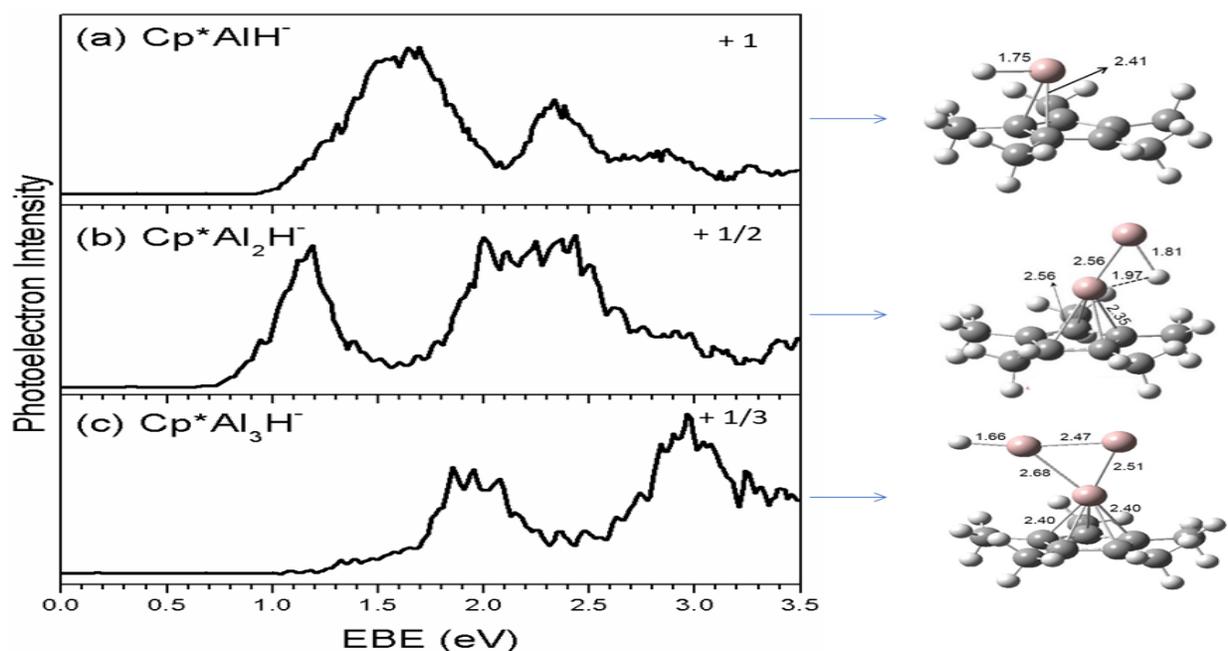


We have also formed and characterized the hydrogenated, planar tetra-coordinate carbon (ptC) cluster species,  $\text{CAI}_4\text{H}$ , and its anion,  $\text{CAI}_4\text{H}^-$ . This was the first report of a hydrogenated ptC species. The hydrogen atom was shown to bridge an Al-Al bond, rather than bonding to a single aluminum atom. Surprisingly, the covalently bonded hydrogen atom does not disturb the ptC  $\text{CAI}_4^{2-}$  core in the  $\text{CAI}_4\text{H}^-$  anion. Instead, it functions as part of the core to fulfill the 18-electron rule by contributing its electron. This work showed that the ptC  $\text{CAI}_4^{2-}$  unit is extremely robust, even when a part of a covalently bonded system.

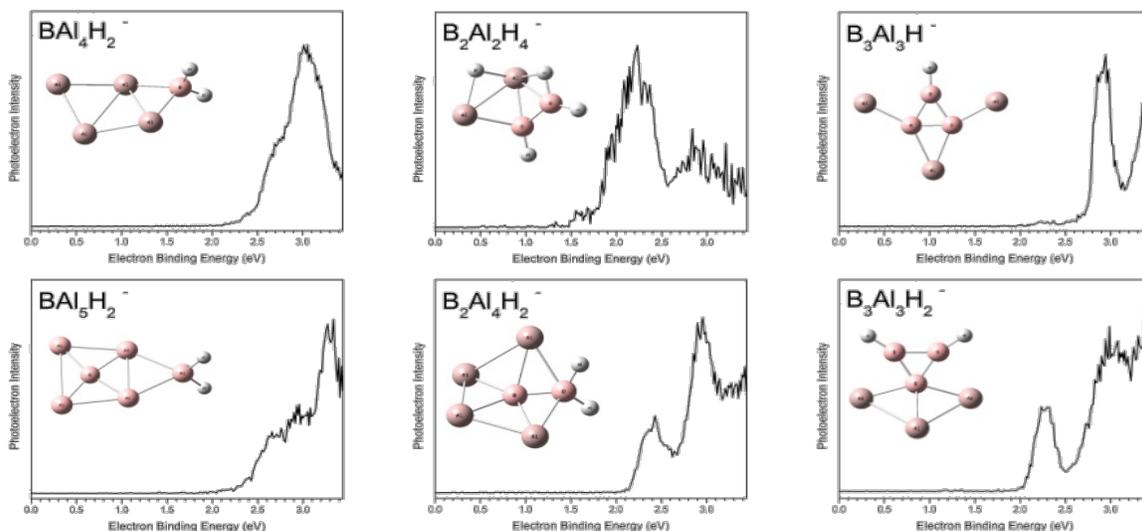


Low oxidation state aluminum-containing molecules and clusters are inherently energetic and thus have significant potential as propellants. We have made and studied several of them. Low oxidation state aluminum hydride anions,  $\text{Al}_n\text{H}_m^-$ , which were generated in a pulsed super-arc discharge source, proved to be versatile reagents for preparing other low oxidation state molecules and clusters. For example, the anion,  $\text{Cp}^*\text{Al}_n\text{H}^-$ , was formed by reacting aluminum hydride anions,  $\text{Al}_n\text{H}_m^-$ , with  $\text{Cp}^*\text{H}$  in a reaction cell downstream from the source, after which the  $\text{Cp}^*\text{Al}_n\text{H}^-$  anions were mass-selected and photodetached. Complementary calculations then predicted the main features of the resulting anion photoelectron spectrum as well as the geometric structures of the anions. Agreement validated the computations and provided confidence in the computed structures.

Other low oxidation state, aluminum-containing cluster anions that we have formed and studied include  $\text{LAlH}^-$  and  $\text{LAl}_n^-$  ( $n = 2-4$ ), where the ligand, L, is  $\text{HN}[\text{Si}(\text{Me})_3]_2$  (HMDS). Again, these were formed by reacting aluminum hydride cluster anions,  $\text{Al}_n\text{H}_m^-$ , with ligands in a reaction cell located downstream.

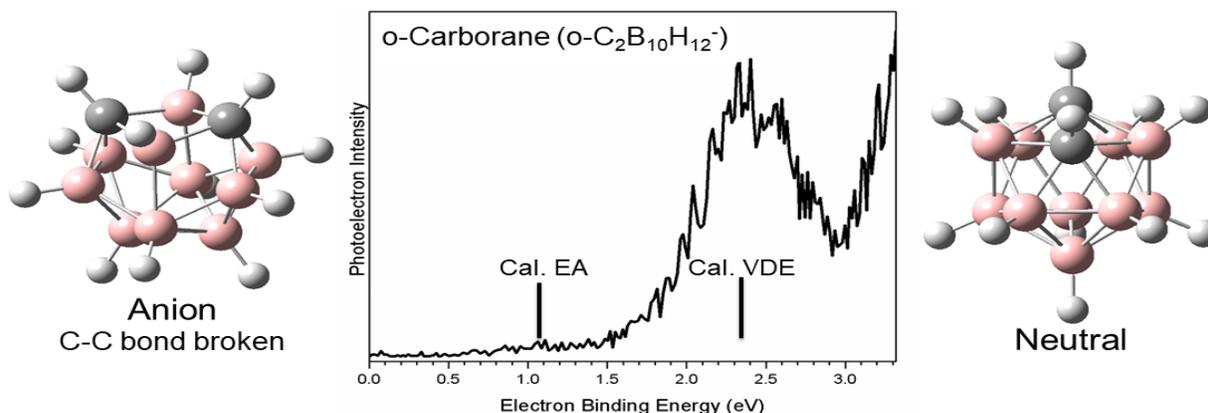
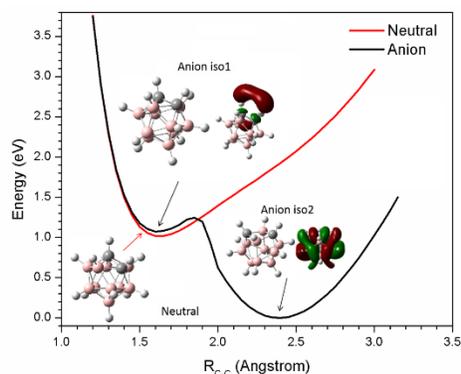


The substitution of boron atoms for some of the aluminum atoms in aluminum hydrides leads to dramatically different structures, i.e., the boro-alanes. While aluminum hydrides, i.e., alanes, burn thoroughly to  $\text{Al}_2\text{O}_3$ , boranes do not burn well to  $\text{B}_2\text{O}_3$ , getting caught instead in the famous HOBO kinetic trap. Our experiments found that boron bypassed the HOBO trap when part of a boro-alane.

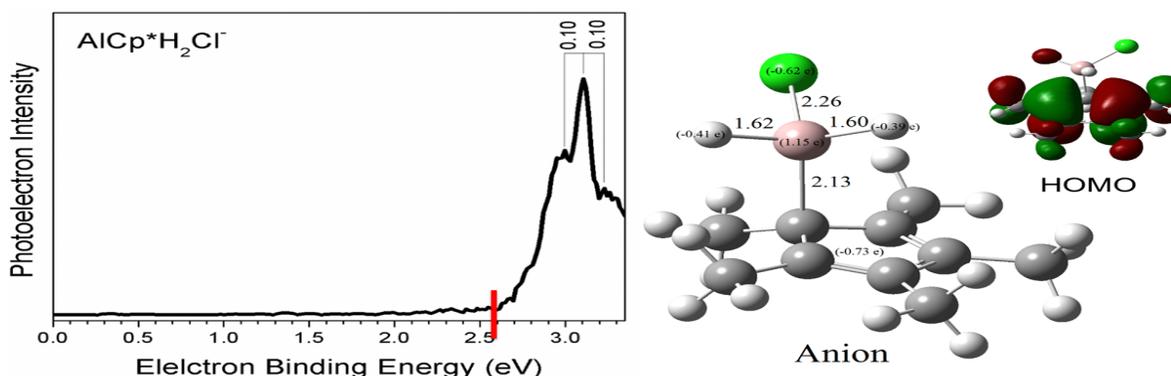


We have also generated over eighty carbon aluminum hydride cluster anions (carbo-alanes), i.e.,  $C_xAl_yH_z^-$ , and measured their anion photoelectron spectra. Many of these spectra show strong similarities to their isoelectronic analogs among the aluminum hydride cluster anions, i.e.,  $Al_{x+y}H_{x+z}^-$ . We suspect that the carbo-alanes follow the same electron counting rules as the alanes, i.e., the aluminum hydrides. Both carbo-alanes and boro-alanes may have applications as propellants.

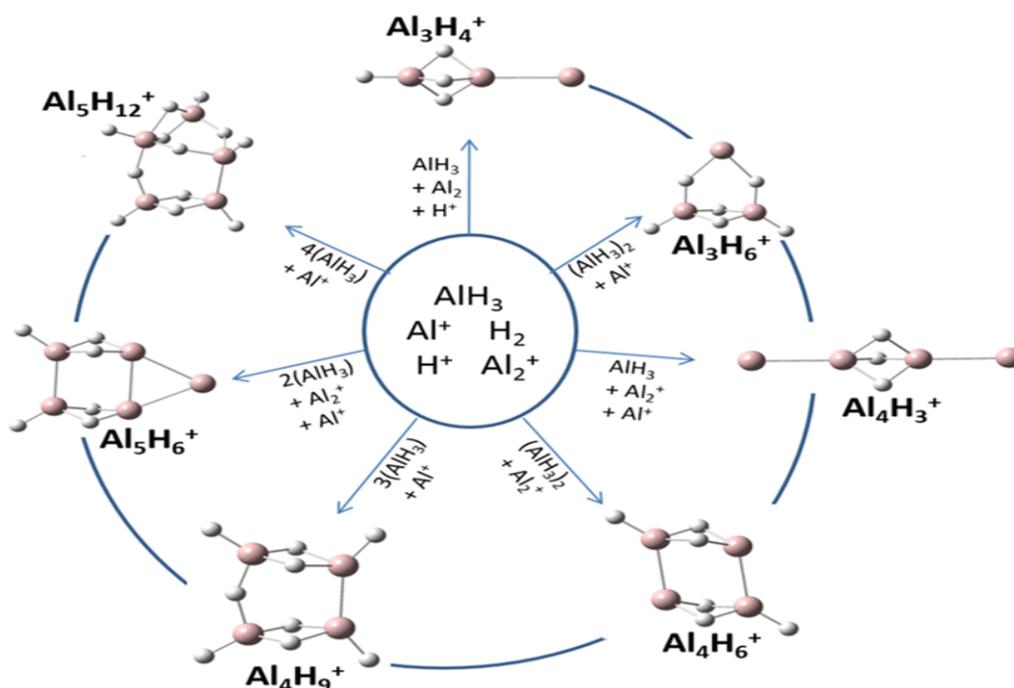
Carboranes, boranes, alanes, carbo-alanes, and boro-alanes all share significant similarities in their bonding. Among these, o-dicarbododecaborane (o-carborane) is especially interesting. While its electron affinity had been reported to be negative, i.e., -2.2 eV, we were able to make its parent anion and measure its photoelectron spectrum. The explanation of this apparent paradox lies in the existence of a second, lower energy anionic isomer, shown as Anion iso2 in the accompanying figure. Anion iso2 had stabilized itself by cleaving its C-C bond.



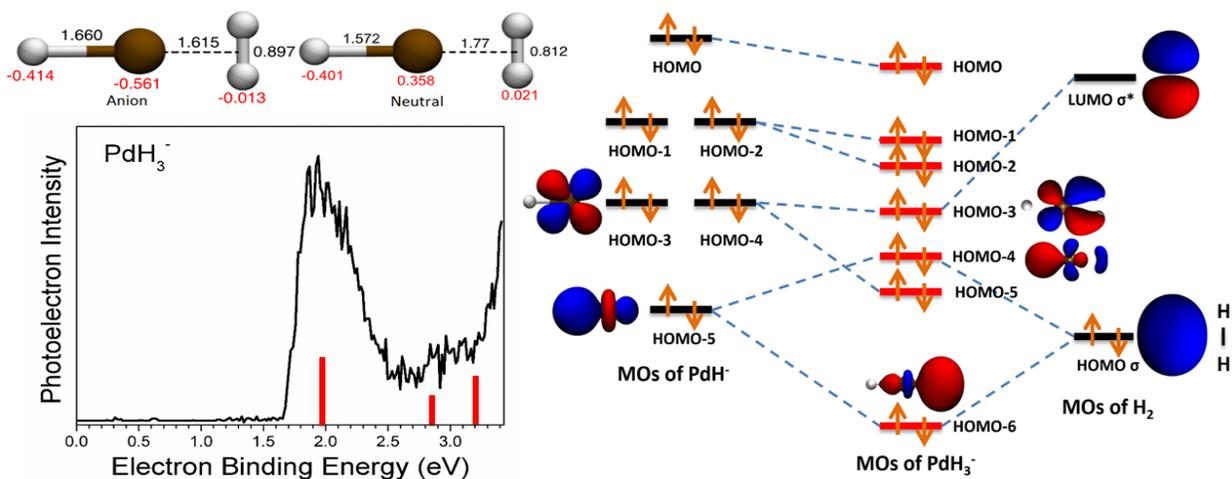
Owing to their high stabilities, tetra-coordinated aluminum anions, such as  $\text{AlH}_4^-$  and  $\text{AlCl}_4^-$ , have been widely used as building blocks both in solid salts and ionic liquids. We have prepared and characterized the new tetra-coordinated aluminum cluster anion,  $\text{AlCp}^*\text{ClH}_2^-$ . Being both asymmetric and larger in size than  $\text{AlH}_4^-$  and  $\text{AlCl}_4^-$ ,  $\text{AlCp}^*\text{ClH}_2^-$  may be promising as an anionic component of ionic liquids.



We also studied aluminum hydride cluster cations, discovering numerous magic numbers among the observed stoichiometries. The computed structures of these aluminum hydride cluster cations and their possible genesis from available building blocks are shown below.



We characterized the anion,  $\text{PdH}_3^-$  as  $\text{PdH}\cdots\text{H}_2$ , with the bond length of its  $\text{H}_2$  ligand considerably elongated relative to that of free  $\text{H}_2$ . Molecular orbital analysis of  $\text{PdH}^-$ ,  $\text{H}_2$  and  $\text{PdH}_3^-$  revealed that back-donation from a d-type orbital in  $\text{PdH}^-$  to the  $\sigma^*$  orbital of  $\text{H}_2$  had caused the H-H elongation. At  $\sim 90$  kJ/mol, the binding energy of  $\text{H}_2$  to  $\text{PdH}^-$  was quite high, i.e., even higher than that between CO and Pd.



We also discovered two extraordinarily novel, mixed-metal hydride cluster anions,  $\text{PtZnH}_5^-$  and  $\text{PtMgH}_5^-$ . Both exhibit  $\sigma$ -aromatic bonding character and planar pentagonal coordination between the  $\eta^5\text{-H}_5$  moiety and the Pt atom.

