

## Group 13 Multiple Bonds: Synthesis and Reactivity Towards CO<sub>2</sub>

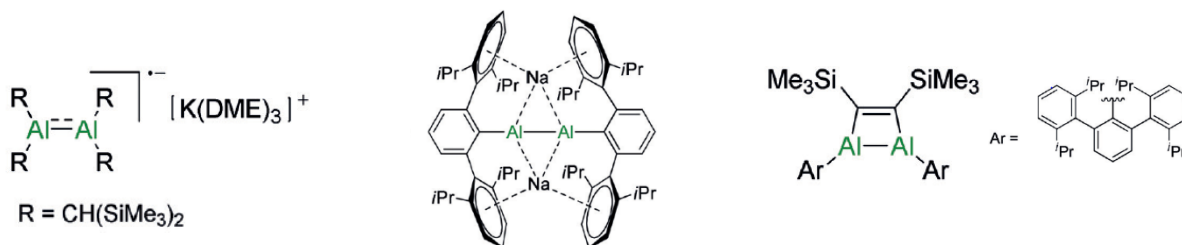
Kelly Gullett

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Finding new and efficient ways of activating small molecules has been at the crux of synthetic inorganic and organometallic chemistry for many decades.<sup>1</sup> Whether it be C-H activation or the reduction of abundant atmospheric molecules, such as N<sub>2</sub> and CO<sub>2</sub>, small molecule activation has been ubiquitously explored.<sup>1</sup> One way of accomplishing these types of reactions has been through the use of main group metals. In the last 20 years, dimeric, multiply-bonded heavy main group metal complexes have been shown to act in a similar nature to monomeric transition metals.<sup>2</sup>

Despite the progress in the synthesis of multiply bonded main group compounds<sup>2,3</sup>, there remains a dearth of understanding of lighter main group elements of group 13, especially aluminum. Aluminum, the most abundant metal on earth,<sup>4</sup> is highly reactive, recyclable, and relatively cheap. All of these qualities make aluminum an excellent synthetic target for potential catalysts.<sup>4</sup> Aluminum is naturally found in the 3+ oxidation state and the corresponding complexes have been widely used as Lewis acids in organic reactions; however, there is much less known about the more difficult to isolate Al-Al multiply bonded species and their reactivity towards small molecules.<sup>8</sup> Historically there have been three categories used to characterize multiple bonds in dimeric aluminum complexes; monoanionic, dianionic, and cyclic masked dialumenes.<sup>4</sup>



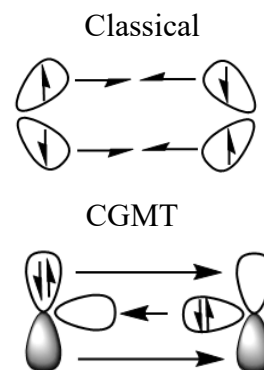
**Figure 1.** examples of monoanionic<sup>5</sup>, dianionic<sup>6</sup> and cyclic masked dialumene<sup>7</sup>

It was not until September of 2017 that the first neutrally charged Al-Al double bond containing structure was reported by Inoue and coworkers,<sup>8</sup> then followed by a more in depth look into the compounds reactivity towards CO<sub>2</sub>.<sup>9</sup> In the same month, Braunschweig and coworkers reported the first heterodiatom Group 13 multiple bond, formed between boron and aluminum, and its resulting reactivity towards CO<sub>2</sub>.<sup>10</sup> These two discoveries have shed light on how lighter main group element chemistry is understood and utilized for small molecule activation.

Inoue and coworkers accomplished the task of producing the first neutral species that contained an Al-Al double bond by working backwards from DFT calculations.<sup>8</sup> The group used computational tools to determine what set of ligands would optimize their chances of achieving a stable Al-Al double bond. A combination of N-Heterocyclic Carbene (NHC) and alkyl silyl ligands were chosen for their tunable steric bulk and sigma donating character; these qualities add to both the kinetic and thermodynamic stability of the system.<sup>8</sup> Once the ligands were chosen, the compound was synthesized through a halogen exchange of the NHC stabilized aluminum trihydride to an aluminum trihalide (x= Br or I), followed by a salt metathesis reaction to install

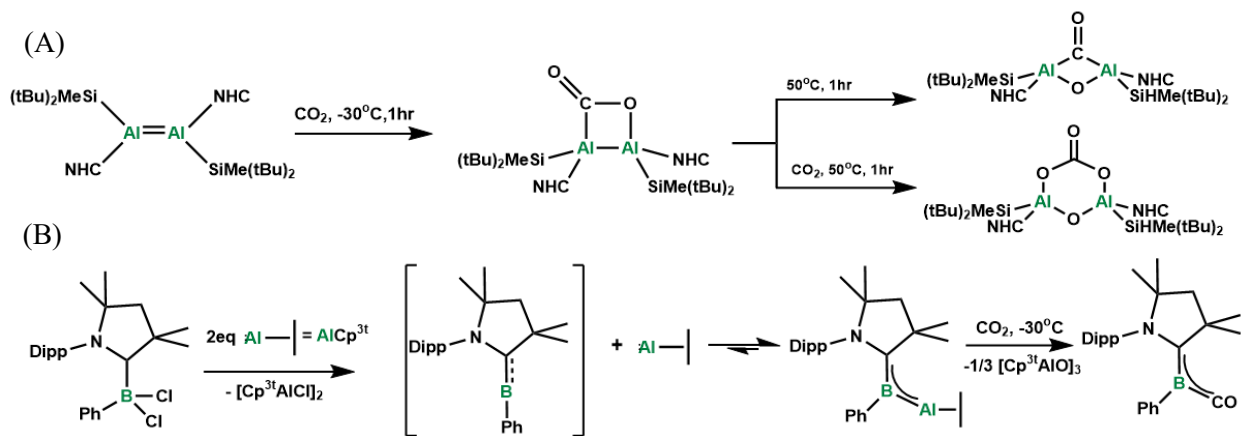
one alkyl silyl ligand.<sup>8</sup> The Al species then underwent reductive dehalogenation to achieve the Al=Al containing compound in 53% yield.<sup>8</sup>

Alternatively, Braunschweig and coworkers used the idea of singlet fragment dimerization supported by the Carter-Goddard-Malrieu-Trinquier model to construct the first Group 13 heterodiatomic multiple bond.<sup>10</sup> The CGMT model theorizes that as you move down a row in the periodic table it is more energetically favorable for the metal atom to maintain its singlet character than to excite to a triplet state, then forming the double bond, as is common with the lighter main group elements.<sup>11,12</sup> To synthesize this complex, two singlet fragments are generated in order to dimerize, forming the pi bond. The boron half of the molecule was synthesized using a cyclic alkyl amino carbene (CAAC) ligand, chosen for its steric protection and sigma donating characteristics.<sup>10</sup> A monomeric Al complex supported by a Cp\* derivative, Cp<sup>3t</sup> (3t=1,3,4-tri(*tert*-butyl)-cyclopentadienyl), was used as both the singlet containing aluminum source, and a reducing agent that would work to form the boron singlet fragment in situ.<sup>10</sup> Once generated, the B and Al fragments then dimerize to form the first B-Al multiple bond in 58% yield.<sup>10</sup>



**Figure 2.** triplet vs singlet fragments

Both strategies, reductive dehalogenation and singlet fragment dimerization, have been often employed to achieve main group multiple bonds for heavier metals in rows 13-16.<sup>3,10</sup> However, the two aforementioned structures serve as the first examples of these synthetic strategies being successfully utilized to form lighter group 13 element multiple bonds. In order to confirm the multiple bond nature of these systems, the groups characterized the structures crystallographically and through computational studies. Computational studies suggest the bond order of the Al-Al bond is two;<sup>9</sup> however, for the B-Al structure, the calculations and bond distances determined by the crystal structure suggest a delocalized pi bond across the Al-B-C<sub>ipso</sub> atoms, giving the B-Al bond a bond order closer to 1.5.<sup>10</sup> After characterizing the new structures, both groups went on to test the reactivity of their systems with CO<sub>2</sub>.



**Figure 3.** (A) CO<sub>2</sub> activation by Al=Al bond (B) synthesis of B-Al bond followed by reactivity towards CO<sub>2</sub>

The reactivity of Inoue's and Braunschweig's systems toward CO<sub>2</sub> initially follow a similar mechanism, with a [2+2] cycloaddition of CO<sub>2</sub> to the Al-Al and B-Al pi bonds, respectively.<sup>9,10</sup> Upon cycloaddition a significant divergence in reactivity is observed between the two complexes. Inoue's complex was shown to isomerize to form a planar, four membered Al-CO-Al-O ring or react with another equivalent of CO<sub>2</sub> to form a six membered ring with a bridging oxygen and bridging carbonate moiety.<sup>9</sup> These intermediates have been crystallographically characterized, and studies into their formation are ongoing. Alternatively, Braunschweig's system is believed to proceed through cleavage of the B-Al bond, inserting the CO<sub>2</sub> moiety between the metals.<sup>10</sup> Then the system may react with another equivalent of CO<sub>2</sub> through cycloaddition, followed by elimination of [Cp<sup>3t</sup>Al(CO<sub>3</sub>)], which can then trimerize to form [Cp<sup>3t</sup>AlO]<sub>3</sub>.<sup>10</sup> This mechanism has been explored exclusively through DFT; the isolated and characterized products of the reaction of [(CAAC)PhB=AlCp3t] and CO<sub>2</sub> are [Cp<sup>3t</sup>AlO]<sub>3</sub> and [(CAAC)PhBCO].<sup>10</sup>

These two papers represent just a small fraction of the exciting new aluminum chemistry that has been recently discovered. Now that the first Al-Al double bond and the first heterodiatomic Group 13 multiple bond have been successfully synthesized, main group chemists can now focus on the catalytic properties these systems may hold. The computational calculations performed in these papers show that each system has the capability to react with a variety of small molecules.<sup>9,10</sup> Now that it is confirmed that NHC and CAAC type ligands can support this bonding scheme, it is possible for more Group 13 multiple bonds to be synthesized and designed to activate specific small molecules. As precious transition metals and heavier main group metals become scarce it is important to look towards Earth's most abundant metal to discover all it has to offer.

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