

# CO<sub>2</sub> Fixation and Catalytic Reduction by a Neutral Aluminium Double bond

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**Abstract:** CO<sub>2</sub> fixation and reduction to value added products is of utmost importance in the battle against rising CO<sub>2</sub> levels in the Earth's atmosphere. Herein we present the use of an organoaluminium complex containing a formal aluminium double bond (dialumene), and thus an alkene equivalent, for the fixation and reduction of CO<sub>2</sub>. The CO<sub>2</sub> fixation complex undergoes further reactivity in either the absence or presence of additional CO<sub>2</sub>, resulting in the first dialuminium carbonyl and carbonate complexes, respectively. Dialumene (**1**) can also be used in the catalytic reduction of CO<sub>2</sub>, providing selective formation of a formic acid equivalent via the dialuminium carbonate complex rather than a conventional aluminium-hydride based cycle. Not only are the CO<sub>2</sub> reduction products of interest for C<sub>1</sub> added value products, but the novel organoaluminium complexes isolated represent a significant step forward in the isolation of reactive intermediates proposed in many industrially relevant catalytic processes.

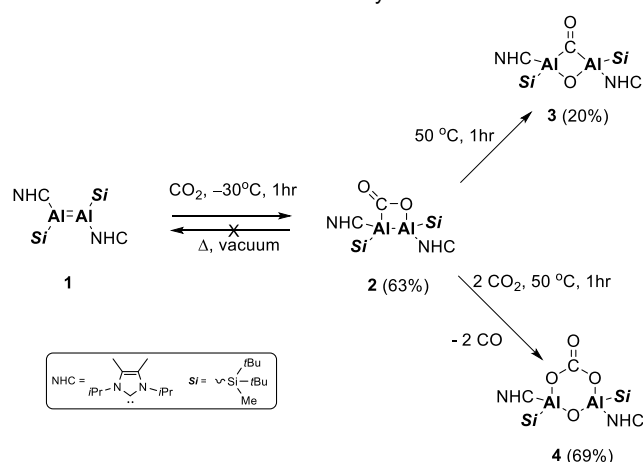
With worldwide increasing energy demands and subsequent rising carbon dioxide (CO<sub>2</sub>) emissions, alternate energy production methods are required as well as the development of new methods for the sequestration and utilization of CO<sub>2</sub>.<sup>[1,2]</sup> In this regard, use of CO<sub>2</sub> to form C<sub>1</sub> feedstocks for the production of value-added products has been a rapidly expanding area of research.<sup>[3]</sup> Conversion of CO<sub>2</sub> to carbon monoxide (CO), methanol, formic acid, and cyclic/polycarbonates has been shown to be possible by several homogeneous catalytic systems.<sup>[4-6]</sup> Whilst transition metals have dominated this field, the development of main group complexes that can act as transition metals<sup>[7,8]</sup> has begun to emerge as a cheaper and more environmentally benign alternative for CO<sub>2</sub> activation. 'Frustrated Lewis pairs' (FLPs)<sup>[9-11]</sup> and polar main group multiple bonds have proven to be efficient methods for CO<sub>2</sub> activation.<sup>[12,13]</sup>

In terms of non-polar multiply-bonded main group compounds, CO<sub>2</sub> activation has been shown to proceed by an initial [2+2]-cycloaddition for diborenes<sup>[14]</sup> and disilenes.<sup>[15,16]</sup> The resulting E-E-C-O (E = B or Si) 4-membered rings were found to be thermally unstable and undergo C-O cleavage-based reactivity.

Donor-stabilised bis(silylene)<sup>[17]</sup> and a disilicon(0) species<sup>[18]</sup> showed that CO<sub>2</sub> binding and subsequent C-O cleavage resulted in carbonate formation. Whereas, reaction of a digermene with CO<sub>2</sub>,<sup>[19]</sup> which is also thought to contain some multiple bond character, resulted in oxygen abstraction and concomitant formation of CO. Examples of C-O cleavage has also been observed in *f*-element chemistry, in particular for U(III) complexes, where CO<sub>2</sub> cleavage to CO and O has been noted to occur at room temperature.<sup>[20,21]</sup>

Whilst the reactivity of group 14<sup>[22]</sup> and boron multiple bonds<sup>[23]</sup> is rather well established, aluminium multiple bond chemistry is still in its infancy.<sup>[24]</sup> Even though aluminium is the most abundant metal found within the Earth's crust, and the high industrial use of Al(III) related catalysts<sup>[25,26]</sup> research into low oxidation state and/or low coordinate Al(I) complexes is somewhat often overlooked due to the synthetic challenges in isolating such reactive species. Despite this, recent advances in Al(I) chemistry have shown that not only can Al react as an electrophile and undergo oxidative addition reactions<sup>[27]</sup> but also as a nucleophile and thus challenging traditional conceptions of aluminium's chemical behaviour.<sup>[28, 29]</sup>

Recently our group succeeded in isolating the first neutral dialumene (**1**) species, a compound with a formal Al=Al double bond.<sup>[30]</sup> This highly reactive species, with a significantly low HOMO-LUMO gap (2.24 eV), showed varied reactivity towards C-C multiple bonds. Thus, highlighting its ability to undergo multiple reaction pathways, as both [2+2]-cycloaddition and C-H activation products were observed. With this in mind, our attention turned to more challenging substrates. Herein, we report the use of **1** for the fixation and selective reduction of CO<sub>2</sub>, both of which can be achieved in a stoichiometric and catalytic fashion.



**Scheme 1.** CO<sub>2</sub> fixation and stoichiometric reduction mediated by dialumene (**1**).

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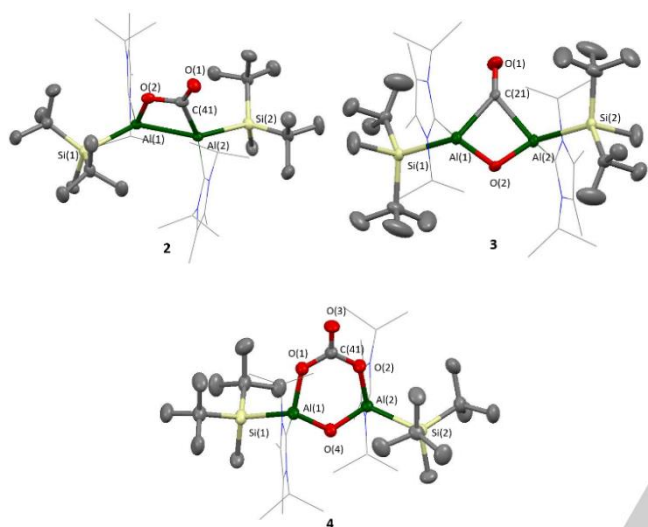
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## COMMUNICATION

Reaction of a toluene solution of dialumene (**1**) with 1 atm of CO<sub>2</sub> at -78 °C (Scheme 1), and subsequent warming to -30 °C resulted in the loss of the deep purple colour associated with **1** and formation of a yellow solution with concomitant yellow precipitate. Removal of all solvent and extraction with THF allowed for isolation of a yellow powder (**2**) in almost quantitative yields. Single crystal X-ray analysis revealed that CO<sub>2</sub> fixation had occurred *via* formal [2+2]-cycloaddition to the Al=Al double bond (Figure 1).



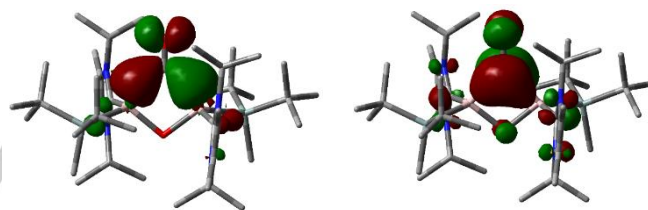
**Figure 1.** Molecular structures of compounds **2-4** in the solid state with thermal ellipsoids set at the 50% probability level. Hydrogen atoms and co-crystallised solvent molecules are omitted for clarity and NHC ligands are depicted in wireframe for simplicity. Selected bond lengths (Å) and angles (°): Compound **2** Al(1)-Al(2) 2.5848(16), Al(1)-Si(1) 2.5150(16), Al(2)-Si(2) 2.5039(16); Compound **3** Al(1)-Al(1') 2.730(1), Al(1)-O(2) 1.707(5), Al(1)-C(21) 2.166(6), C(21)-O(1) 1.194(8), Al(1)-C(1) 2.069(2), Al(1)-C(21)-Al(1') 78.2(2), Al(1)-O(2)-Al(1') 106.7(3); Compound **4** Al(1)-O(1) 1.796(3), Al(1)-O(4) 1.720(3) Al(1)-C(1) 2.074(3), C(41)-O(1) 1.315(4), C(41)-O(3) 1.217(4), C(41)-O(2) 1.324(4), Al(2)-O(2) 1.798(2), Al(2)-O(4) 1.713(3), Al(2)-C(21) 2.068(3), Al(1)-Si(1) 2.4781(15), Al(2)-Si(2) 2.4971(16), O(1)-C(41)-O(2) 117.4(3), Al(1)-O(4)-Al(2) 120.54(14).

The resulting planar 4-membered Al-Al-C-O ring is structurally analogous to the related diboron and disilicon compounds.<sup>[14, 16]</sup> Retention of the carbonyl moiety exocyclic to the ring, was confirmed by IR spectroscopy (1640 cm<sup>-1</sup>) which is in good agreement with the calculated value (1658 cm<sup>-1</sup>). As expected, the Al-Al distance is longer than that of **1** (2.5848(16) Å vs 2.3943(16) Å, respectively) indicating loss of double bond character, and is now in the range of a typical Al-Al single bond (2.53-2.75 Å).<sup>[24]</sup> Compound **2** is relatively stable in the solid state (mp. 135 °C) and can be stored at room temperature in an inert atmosphere for at least 1 month without any signs of decomposition. Monitoring a solution (C<sub>6</sub>D<sub>6</sub> or THF-d<sub>8</sub>) of **2** at room temperature, however, resulted in the loss of the yellow colour of **2** after 18 hrs to form a dark orange solution. The NMR spectra showed the emergence of a new species, with a downfield signal in the <sup>13</sup>C NMR spectrum at δ 276.0 ppm, similar to that reported by Braunschweig and co-workers for the carbonyl-bridged diboron complex.<sup>[14]</sup> Repetition of this reaction at 50 °C

(Scheme 1), resulted in a dark red solution within 1 hr after which subsequent work up and crystallisation provided **3** in 20% yield. X-ray crystallographic analysis revealed **3** (Figure 1) to contain a bridging carbonyl and oxo unit.

The central Al-CO-Al-O core in **3** is completely planar, with the NHC and silyl groups *trans*-orientated to the ring. Compound **3** represents the first dialuminacarbonyl compound and a rare example of a central M(μ-CO)(μ-O)M bridging motif.<sup>[14,31,32]</sup> The retention of the carbonyl group is confirmed upon comparison of structural data. The C=O bond length is 1.194(8) Å which fits well with average μ-CO bridging motifs (1.17-1.22 Å), and the notable downfield shift in <sup>13</sup>C NMR is also similar to those reported for M(μ-CO)(μ-O)M cores (M = B (δ 278.7 ppm) and Fe (δ 289.8 ppm)). The IR stretch was found to be at 1630 cm<sup>-1</sup>, which is lower than expected with typical μ-CO stretches found >1700 cm<sup>-1</sup> and a matrix isolation of Al<sub>2</sub>CO was reported at 1737 cm<sup>-1</sup>.<sup>[33]</sup> A short Al-Al interatomic distance was also noted (2.730(1) Å), which is within range of Al-Al single bonds.<sup>[24]</sup>

DFT calculations were performed at the B97d/Def2SVP/W06 level of theory on **3**. The calculated structure is in good agreement with experimental parameters, including the IR stretch for the C=O (1640 cm<sup>-1</sup>). The calculated orbitals suggest that one of the degenerate π\* orbitals of the CO unit is effectively occupied, with the other being the LUMO (Figure 2). Thus, the bridging unit can best viewed as a CO<sup>2-</sup> anion which also accounts for the lower wavenumber observed. The Al-O bonds in the bridging oxo unit were found by NBO analysis to be highly polarized, almost ionic in character ([7%]Al(1)-O(2)[93%]). Despite the short Al-Al distance observed, no evidence of an Al-Al bond was found in the orbital analysis.



**Figure 2.** HOMO (-2.17 eV, left) and LUMO (-1.18 eV, right) of **3** (isovalue 0.04)

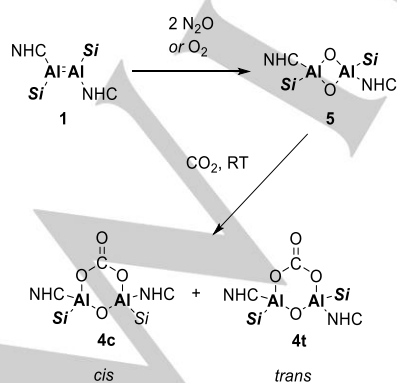
Heating a C<sub>6</sub>D<sub>6</sub> solution of **1** under an atmosphere of CO<sub>2</sub> resulted in the initial formation of **2** followed by formation of a colourless solution, rather than the expected red solution for the formation of **3**. Inspection of the resulting <sup>13</sup>C NMR spectrum revealed new signals at δ154.4 ppm and δ184.4 ppm indicating likely carbonate and CO formation, respectively. Crystallographic analysis, revealed compound **4** to consist of a six-membered ring containing a bridging carbonate group and oxygen between the two aluminium centres, reminiscent of the cyclic silicon structures reported.<sup>[17,18]</sup> The C=O bond (1.217(4) Å) is longer than in **2** and **3**, and the C-O single bonds were found to be 1.32 Å (average) indicating a degree of delocalisation across the CO<sub>3</sub> unit. This along with the notably long Al-OCO<sub>2</sub> bond lengths (1.797 Å average) indicates a high degree of polarisation across the Al-O bond, and likely contributes to the lower than expected C=O (1670 cm<sup>-1</sup>) IR stretch.

## COMMUNICATION

Mechanistic insights into the formation of compounds **3** and **4** were sought both experimentally and computationally. As noted previously both compounds are formed via the initial [2+2]-cycloaddition product (**2**). This compound can either undergo isomerisation, to form carbonyl species **3**, or undergo oxygen abstraction and de-carboxylation to form carbonate species **4** in the absence or presence of further CO<sub>2</sub>, respectively (Scheme 1). Computational studies indicated an overall exothermic isomerisation of **2** to **3** (Fig. S36), the C-O cleavage step is endergonic (+24.9 kcal mol<sup>-1</sup>) but this is offset by the recombination of CO and formation of the 4-membered ring (-42.4 kcal mol<sup>-1</sup>). Attempts to confirm this mechanism experimentally focused on the isolation of a Al<sub>2</sub>O 3-membered ring (Compound A, Fig. S36). Exposure of **1** to approximately 1 atmosphere of either O<sub>2</sub> or N<sub>2</sub>O at -78 °C and gradual warming to room temperature, resulted in the formation of a colourless solution indicating loss of the double bond character of **1**. Upon inspection of the corresponding <sup>1</sup>H NMR spectra, the same symmetrical single species was observed to have formed in both cases (Compound **5**, Scheme 2). Compound **5** was identified as a cyclic dialumanoxane [(NHC)(Si)Al(μ-O)]<sub>2</sub> (Fig. S12), formed by the oxidative addition of oxygen to dialumene (**1**).

Compound **5** is a centrosymmetric dimer featuring a planar Al<sub>2</sub>O<sub>2</sub> square core, these are structurally analogous to those obtained from the reactions of heavier group 13 dimetalenes (Ga and In) towards N<sub>2</sub>O.<sup>[34]</sup> Notably, this is a rare example of a discrete [RAIO]<sub>n</sub> type complex where n=2. Due to the highly polarised Al-O bond self-oligomerisation readily occurs and thus requires sterically demanding substituents to control aggregation. With the only other example of a [RAIO]<sub>2</sub> species requiring the use of the chelating β-diketiminato ligand.<sup>[35]</sup> NBO analysis confirmed the highly polarised bond ([9%]Al(1)-O(1)[91%]) and despite the short Al-Al distance (2.4812(12) Å), no such interaction between the two Al centres was found (Fig. S43).

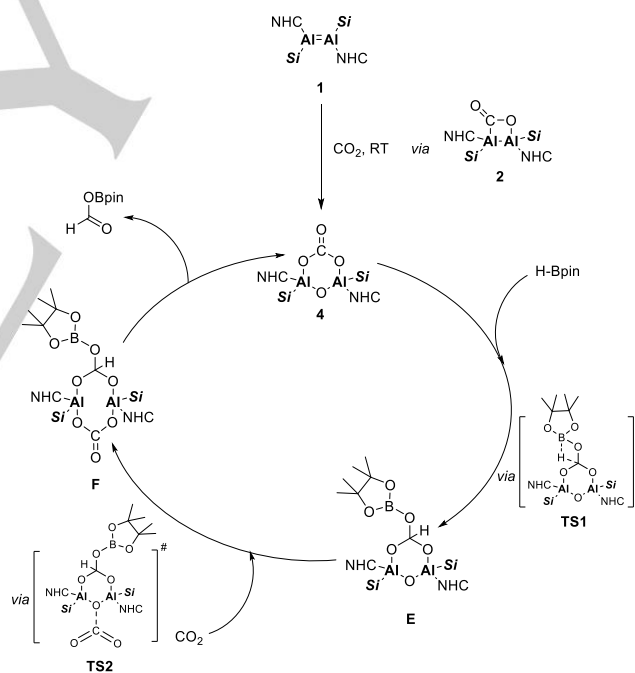
Whilst compound **5** was not implied as an intermediate in the formation of carbonate species (**4**), it is plausible that CO<sub>2</sub> could insert into the Al-O bond to yield such a species. Therefore, exposure of 1 atm of CO<sub>2</sub> to **5** was tested. The resulting <sup>1</sup>H NMR spectrum identified two similar species in an approximately 50:50 mixture, one of which was identified as compound **4**. Further inspection of the <sup>13</sup>C NMR data revealed the formation of both *cis* (**4c**) and *trans* (**4t**) isomers due to the characteristic carbonate signals (δ 158.45 and δ 154.81 ppm).



Scheme 2. Formation of compound **5** and stoichiometric reduction CO<sub>2</sub>

Computational studies on the formation of compound **4** via the two different routes, Route A via compound **2** (Fig. S37) and Route B via compound **5** (Fig. S38), were undertaken to provide further insight. Both routes were found to be overall exothermic processes (-77.3 kcal mol<sup>-1</sup> and -36.5 kcal mol<sup>-1</sup> for Routes A and B, respectively). Differences in the observed isomers of compound **4** can also be accounted for via these mechanisms; Route A proceeds through a series of 6- and 5-membered rings, Al(CO<sub>2</sub>)<sub>2</sub>Al (**B**) and Al(CO<sub>2</sub>)(O)Al (**C**), respectively. Whereas in Route B, the 4-membered ring is broken (Intermediate **D**, Fig. S38) allowing for recombination at either face of the Al center, thus accounting for the 50-50 geometric isomers.

Our attention turned to the catalytic reduction of CO<sub>2</sub>. Attempts at hydrosilylation of CO<sub>2</sub> failed, and resulted in decomposition of **1**. Use of pinacol borane (HBpin), however, resulted in turnover. Close monitoring of the reaction through <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy, identified the formic acid derivative (OCHOBpin, 86%) after 1 week at room temperature. Use of higher temperatures (60 and 80 °C) allowed for lower catalyst loadings (5 mol%) and resulted in 80% consumption of HBpin within 3-4 hours and selective formation of the formic acid equivalent in NMR yields of 94% and 95%, respectively.



Scheme 3. Proposed Catalytic Cycle.

Mechanistic studies indicated the reaction proceeds via initial [2+2]-cycloaddition (**2**) as reaction of **1** with HBpin resulted in no reaction, and after 24 hrs at room temperature decomposition of **1** was observed. This suggests that formation of an aluminium hydride complex is unlikely and therefore catalysis is thought to proceed via the dialuminium carbonate compound (**4**). It was initially thought that **4** undergoes a σ-bond metathesis type reaction with HBpin to form OCHOBpin and dioxo species **5**. This non-hydridic route would also account for the

selectivity of the observed products, as OCHOBpin could easily insert back into a Al-Hydride based cycle resulting in hemi-acetal and methanol derivatives. Addition of 1 eq. of HBpin to **4t** resulted in the consumption of starting materials and a mixture of species, however no products that were identified in the catalysis were observed indicating that this stoichiometric reaction is not representative of the active catalytic cycle. Subsequent computational analysis found the conversion of **4** to **5** to be energetically uphill (+23.1 kcal mol<sup>-1</sup>) and therefore unfavourable. Further computational studies, taking into account the combined effect of CO<sub>2</sub> and HBpin, revealed a facile transformation (overall -13.4 kcal mol<sup>-1</sup>). Initial coordination of HBpin to the exocyclic oxygen of the carbonate fragment occurs followed by subsequent hydride transfer. This hydride transfer is proposed to be rate determining, as +22.2 kcal mol<sup>-1</sup> is required to reach the transition state (TS1, Scheme 3), this is subsequently offset by -26.6 kcal mol<sup>-1</sup> upon formation of the reduced carbonate (**E**). Next a concerted mechanism is proposed, in which CO<sub>2</sub> coordination at the opposite plane of Al---Al (TS2) causes reformation of carbonate moiety. The 8-membered ring (**F**) breaks down releasing the formic acid derivative and reforming compound **4** in an overall facile transformation (5.0 kcal mol<sup>-1</sup>).

In summary, we report CO<sub>2</sub> fixation by an aluminium-aluminium double bond which promotes both catalytic and stoichiometric reduction of CO<sub>2</sub> to value added C<sub>1</sub> products under mild conditions. Extension of this work to include catalytic turnover, provided facile transformation to a formic acid derivative under ambient conditions and represents one of the first examples of catalysis using a homonuclear main group multiple bond.

## Acknowledgements

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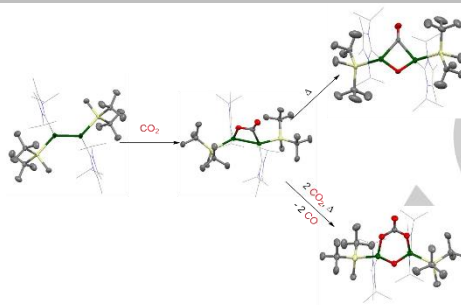
## COMMUNICATION

Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

CO<sub>2</sub> fixation by an aluminium-aluminium double bond promotes catalytic and stoichiometric reduction under mild conditions.



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