Deoxygenating Reduction of CO$_2$ by [Cp*Al]$_4$ to Form a (Al$_3$O$_2$C)$_2$ Cluster Featuring Two Ketene Moieties

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ABSTRACT: Herein we report that the reaction of the low-valent aluminum(I) species [Cp*Al]$_4$ (Cp* = pentamethylcyclopentadienyl) with CO$_2$ exhibits complete cleavages of the C=O bonds. The deoxygenating reduction reaction of [Cp*Al]$_4$ with CO$_2$ at 120 °C afforded [(Cp*)$_3$Al$_3$O$_2$C(CO)]$_2$ (1), which featured two stacked (Al$_3$O$_2$C)$_2$ units and two C=C=O ketene moieties. Moreover, the isoelectronic analogues of diimine and isothiocyanate with CO$_2$ were also investigated, and the reactions of [Cp*Al]$_4$ with Dipp*-N=C=N-Dipp* and Dipp-C=N=S [Dipp* = 2,6-bis(diphenylmethyl)-4-tert-butylphenyl; Dipp = 2,6-diisopropylphenyl] afforded dialuminylimine (2) and tetrameric [Cp*AlS]$_4$ (3), respectively.

The CO$_2$ capture and subsequent cleavage of the strong C=O double bond are quite challenging; thus, the development of efficient methods for CO$_2$ activation and conversion is highly desirable.[1,2h,j] Transition metals can not only activate CO$_2$ but also perform as catalysts to convert CO$_2$ to CO or other useful reagents.[2] In comparison, p-block elements, such as frustrated Lewis pairs, can also mimic transition metals to activate small molecules and catalyze reactions.[3−5] Impressively, polar main-group ketone analogues or nonpolar multiple-bonded main-group species with intrinsic high reactivity can trap CO$_2$ and incorporate it into their skeleton.[6−9]

Aluminum, with the virtue of being relatively cheap, nontoxic, and abundant, has been extensively explored for synthetic chemistry.[10,11] Limited cases equipped with aluminum multiple bonds have been applied for the fixation of CO$_2$ to form aluminum-containing heterocyles (Figure 1a).[7c,d,12] Dialumene with an aluminum double bond performed a cycloaddition reaction with CO$_2$ to obtain the lactone I, which further converted to a carbonate-bridged species II.[7c,d] A mechanistic study revealed that the carbene-stabilized dialumanoxane with highly polarized Al−O bonds activates the C=O double bond of CO$_2$ to produce II. Moreover, the ionic species with a highly reactive Al−O and Al−N multiple bond reduces CO$_2$ to afford unprecedented carbonate compounds III and IV, respectively, via [2 + 2] cycloaddition reactions.[12a,c] Inspired by the remarkable reactivity of Cp-based aluminum(I) species,[13] we envisaged that it might activate CO$_2$. Herein, we report that the reduction of CO$_2$ (Figure 1b) and its isoelectronic analogues with [Cp*Al]$_4$[13a,b] forms 1−3, in which the unexpected product 1 features two stacked (Al$_3$O$_2$C)$_2$ units and two C=C=O ketene moieties.

A toluene solution of [Cp*Al]$_4$ was exposed to 1 bar of CO$_2$ and heated at 120 °C for 1 h (Scheme 1). After workup, 1 was obtained as a white powder in 57% yield. In the ^{1}H NMR spectrum, two new resonances belong to the Cp* groups of 1 at 1.99 and 2.03 ppm, indicating a distinguishable Cp* group.
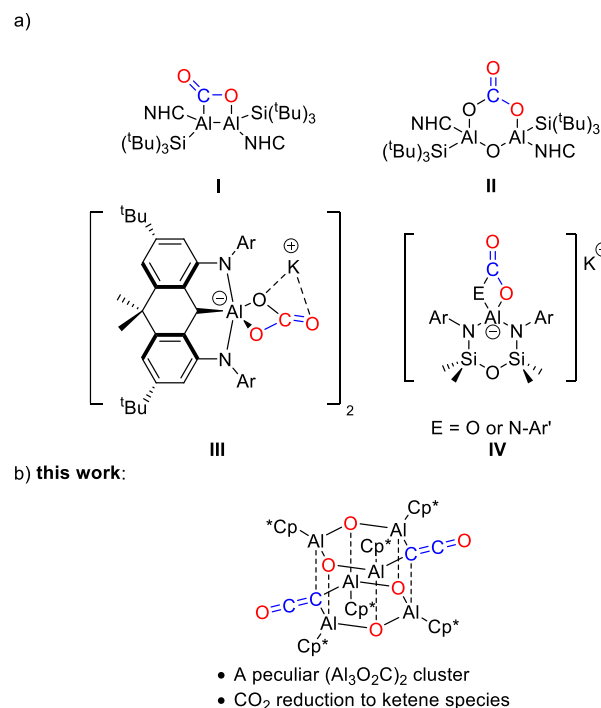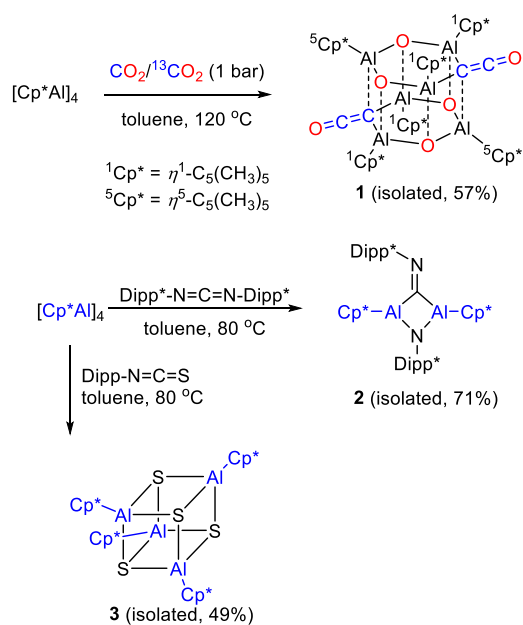
a)

b) **this work:**

- A peculiar (Al$_3$O$_2$C)$_2$ cluster
- CO$_2$ reduction to ketene species

Figure 1. (a) Examples of CO$_2$ activation by reactive aluminum-containing species. (b) Present work.

Scheme 1. Reactions of $[Cp*Al]_4$ with CO_2 ($^{13}CO_2$) as Well as Reactions with the Isoelectronic Analogues of CO_2

$[Cp*Al]_4$ $\xrightarrow[\text{toluene, 120 °C}]{CO_2/^{13}CO_2 \ (1 \ \text{bar})}$

$^1Cp* = \eta^1\text{-}C_5(CH_3)_5$
$^5Cp* = \eta^5\text{-}C_5(CH_3)_5$

1 (isolated, 57%)

$[Cp*Al]_4$ $\xrightarrow[\text{toluene, 80 °C}]{\text{Dipp*-N=C=N-Dipp*}}$

Cp*−Al   Al−Cp*

2 (isolated, 71%)

$\downarrow$ Dipp-N=C=S
toluene, 80 °C

3 (isolated, 49%)

Single crystals of **1** were obtained from a 1:10 mixture of a hexane/toluene solution. X-ray diffraction analysis of **1** revealed two symmetrical six-membered stacked rings, which comprised two heterocyclic Al_3O_2C units and two appended C=C=O ketene moieties (Figure 2). The six-membered Al_3O_2C ring in **1** is closed to a planar geometry (the sum of internal angles is 716.97°). The Cp* groups show η^1- and η^5-coordination modes with the four-coordinated Al1/Al1′ and Al2/Al2′ atoms, respectively. The slightly shorter Al1−O1 bond length in the four-membered Al_2O_2 ring is 1.8126(18) Å, compared with the Al1′−O1 bond of 1.8714(17) Å. The Al1−C18 bond lengths in the Al_3O_2C ring [1.9783(18) Å] are significantly shorter than the Al2′−C18 bond length [2.251(3) Å].[14] The C18−C17−O2 angle [176.5(3)°] is nearly straight with the double-bond characteristics of the C18−C17 [1.304(4) Å] and C17−O2 [1.169(4) Å] distances, definitely confirming the formation of the ketene (C=C=O) functional group.[15] Consistent with the X-ray crystallographic results, ^{13}C-isotopic-labeling experiments using $^{13}CO_2$ were carried out and verified formation of the ketene groups of **1**-$^{13}CO_2$. In the ^{13}C NMR spectrum of **1**-$^{13}CO_2$, a set of new resonances were observed at 153.0 ppm as a doublet ($^1J_{C13−C13}$ = 90.7 Hz) and 186.2 ppm as a broad singlet, which were assigned to ketene (^{13}C=^{13}C=O) moieties (Figures S1 and S2). To our best knowledge, the formation of ketene derivatives by a deoxygenating reduction of CO_2 without any catalyst is only reported using electrochemical reduction.[16]

To gain a better understanding of the mechanism, density functional theory (DFT) calculations were performed at the B3LYP-D3/def2-SVP level of theory (Figure 3).[17] In the initial step of activation, the monomer Cp*Al derives from tetrameric $[Cp*Al]_4$ to overcome the dissociation energy barrier and interacts with the π orbitals of CO_2 via a transition state of **TS1** to yield **Int1** with a AlCO three-membered unit. An additional Al atom of Cp*Al coordinating with the O atom of **Int1** breaks the C−O bond, resulting in the formation of **Int2**. In addition to the approach to the ring-opening species **Int2**, **Int1** may undergo decarboxylation to dissociate CO, which is also
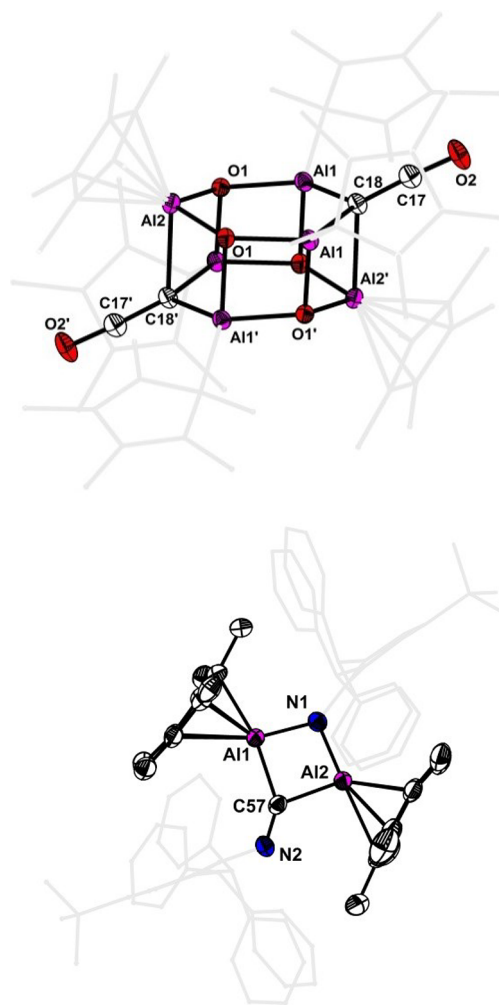

Figure 2. Molecular structures of **1** and **2** (H atoms are omitted for clarity; the Dipp* and Cp* substituents are depicted as wireframes for simplicity).

supported by a ^{13}C-isotopic-labeling experiment between $[Cp*Al]_4$ and $^{13}CO_2$. In a J. Young NMR tube, $^{13}CO_2$ was introduced to a C_6D_6 solution of **1**, and the tube was sealed and allowed to heat at 120 °C for 1 h. The resulting products were characterized by NMR spectroscopy. In the ^{13}C NMR spectrum, a signal for the extra $^{13}CO^{18}$ appeared at 184.5 ppm and two resonances for $[Cp*AlO]_4^{19}$ were observed at 11.6 and 112.9 ppm, corresponding to the decarbonylation products (Figure S1). In line with the ^{13}C-isotopic-labeling experiment, DFT calculations estimated that the decarbonylation of **Int1** has a low energy barrier of 19.8 kcal/mol to obtain ^{13}CO and the monomer Cp*Al=O of $[Cp*AlO]_4$ (Figure S7).

Subsequently, Al−O bond formation in **Int2** occurs and leads to the ring-expanding product **Int3** with a Al_2CO_2 five-membered ring. An additional monomer Cp*Al inserts into the C−O single bond of **Int3** to produce the key intermediate **Int4**, which could potentially be regarded as a carbene species via completely reductive cleavages of the C=O double bonds. Because of the high electrophilicity of the dialuminum-substituted carbene center in **Int4**, the carbonylation of **Int4** with CO leads to monoketene **Int5**, which is exergonic in energy by 102.7 kcal/mol. Notably, a handful of carbenes react with CO to afford stable ketenes, which require the strong π-
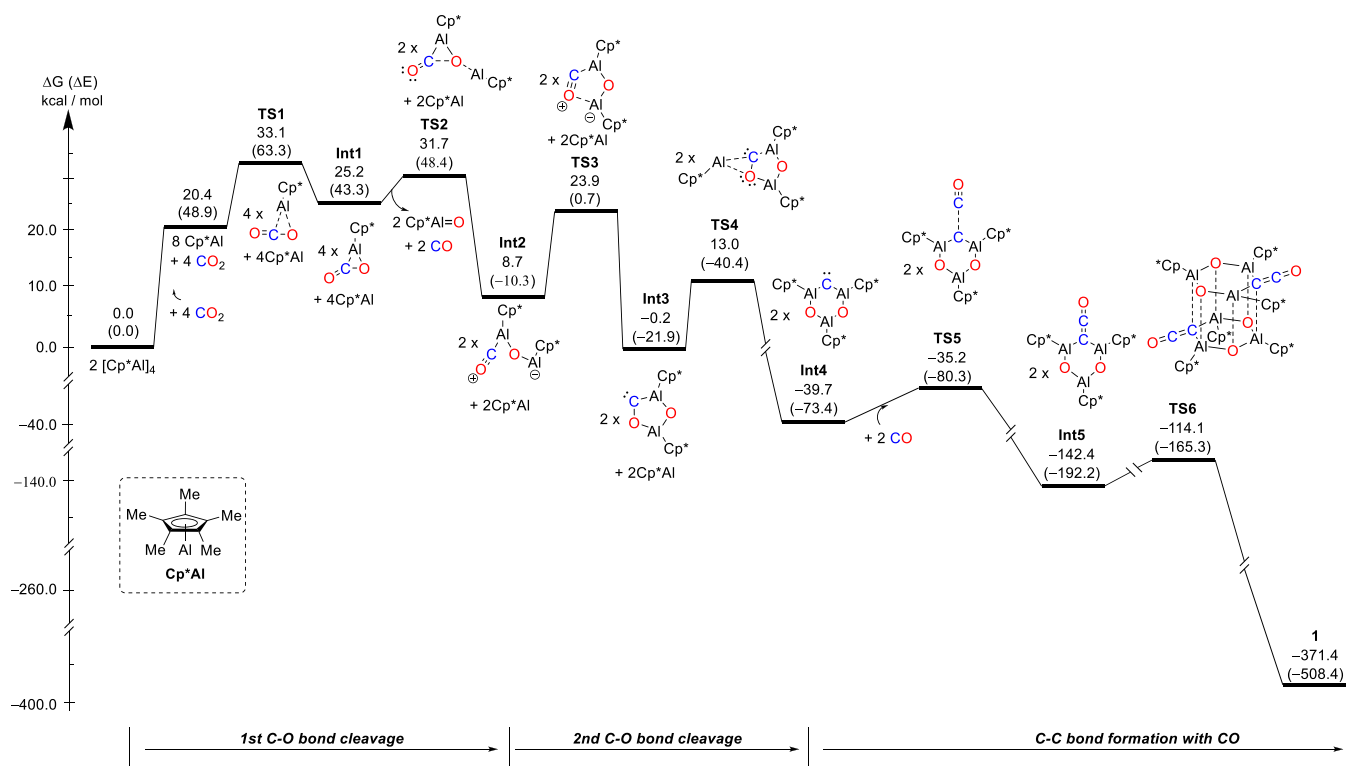
Figure 3. Computed relative energy (*E*) and free energy (*G*) profiles (kcal/mol) for the formation of **1** at the B3LYP-D3/def2-SVP level of theory.

withdrawing capability of carbenes.[15a,e,20] Finally, dimerization of **Int5** tends to form the bis-**Int5** species **1**.

To further examine the electronic structure of **1**, DFT calculations were performed at the M06-2X/Def2-TZVP level of theory (Table S22). The Wiberg bond index (WBI) values of the C18−Al1 and C18−Al2′ bonds are 0.34 and 0.27, respectively, which suggest these relatively weak bonds. The WBI values of the C17−C18 (1.72) and C17−O2 (1.94) bonds are larger than 1, indicating a double-bond character of these bonds. Compared with the covalent bonding of the C17−C18 and C18−Al1 bonds, there is no polarization and hybridization between the C18 and Al2′ atoms. Therefore, the bonding situation of C18 should be described as four chemical bonds (two C18−Al1 single bonds and one C17−C18 double bond) rather than a pentavalent C atom. The interactions between two $(Al_3O_2C)_2$ rings in **1** are possibly dominated by four O → Al donor−acceptor interactions.

In terms of the valence electron, diimine and isothiocyanate derivatives are formally isoelectronic with CO_2. We further explored the reduction reactions of $[Cp^*Al]_4$ with Dipp*-N═C═N-Dipp* and Dipp-N═C═S [Dipp* = 2,6-bis-(diphenylmethyl)-4-*tert*-butylphenyl; Dipp = 2,6-diisopropyl-phenyl]. A total of 2 equiv of Dipp*-N═C═N-Dipp* was added to a toluene solution of $[Cp^*Al]_4$, and the reaction mixture was heated at 80 °C for 2 h. After purification, **2** was obtained in 71% yield as light-green crystals.

The solid-state structure of **2** displays that two molecules of Cp*Al moieties insert into the C═N double bond of Dipp*-N═C═N-Dipp* to obtain a nearly planar Al_2CN four-membered ring (the sum of the internal angles is 359.96°), which is confirmed by an X-ray diffraction study. The Al−N (1.855−1.867 Å) and Al−C (2.009−2.044 Å) bond lengths get close to the typical Al−N and Al−C single bonds.[21,22] The C57−N2 [1.255(5) Å] bond length is consistent with the C═

N double-bond length. It is worth noting that only a limited number of dialuminylimines have been reported up to now.[7d,23] To better understand the mechanism for the formation of **2**, DFT calculations were performed and revealed that an intermediate **2-Int1** was generated *in situ* through a [2 + 1] cycloaddition reaction between monomer Cp*Al and Dipp*-N═C═N-Dipp* (Figure S7). Subsequently, **2-Int1** reacts with an additional Cp*Al to afford **2**.

Furthermore, reduction of the C═S double bond of Dipp-N═C═S with $[Cp^*Al]_4$ was also explored, which led to product **3** and Dipp-N≡C: (Figure S3). X-ray diffraction analysis revealed that **3** features a heavier heterocubane $[Al_4S_4]$ core (Figure S4). Although Braun et al. reported that **3** could be obtained by the reaction of $[Cp^*Al]_4$ with sulfur, its solid-state structure was disclosed for the first time.[19]

In summary, we have demonstrated that the first example of the unique $(Al_3O_2C)_2$ cluster **1** appended with C═C═O moieties was prepared via deoxygenating reduction of CO_2. Theoretical calculation indicated that complete cleavages of the C═O double bonds produced the dialuminum-substituted carbene, which subsequently fixed CO to form ketene species. Consistent with DFT calculations, the ^{13}C-labeled study revealed that the conversion of [13]CO_2 to [13]CO occurred. Furthermore, to investigate the reduction of isoelectronic analogues of CO_2, the reactions of $[Cp^*Al]_4$ with Dipp*-N═C═N-Dipp* and Dipp-N═C═S were explored, and it was found that they afforded heterocyclic **2** and heterocubane-type **3**, respectively.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at

https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01587.

Experimental procedures, spectroscopic data, X-ray crystallography, DFT calculations, and collected NMR spectra of compounds **1−3** (PDF)

Accession Codes

CCDC 2106648, 2106650, and 2128200 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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