Activation of Carbon Dioxide by 9-Carbene-9-Borafluorene Monoanion: Carbon Monoxide-Releasing Transformation of Trioxaborinanone to Luminescent Dioxaborinanone

Kelsie E. Wentz, Andrew Molino, Lucas A. Freeman, Diane A. Dickie, David J. D. Wilson,* Robert J. Gilliard, Jr.*

ABSTRACT: The first structurally characterized example of a trioxaborinanone (**2**) is produced by the reaction of a 9-carbene-9-borafluorene monoanion and carbon dioxide. When compound **2** is heated or irradiated with UV light, one equivalent of carbon monoxide (CO) is released, and a luminescent dioxaborinanone (**3**) is formed. Notably, carbon monoxide-releasing molecules (CORMs) are of interest for their ability to deliver a specific amount of CO. Due to the turn-on fluorescence observed as a result of the conversion to **3**, CORM **2** serves as a means to optically observe CO loss "by eye" under thermal or photochemical conditions.

Given the overabundance of greenhouse gases such as carbon dioxide (CO_2) in the Earth's atmosphere, scientists have been interested in understanding the chemical transformations of these small molecules and their modification into higher-value chemical feedstocks.[1] Although the complete conversion of CO_2 into desirable materials is quite complex, a key first step is the activation of their inert chemical bonds. Because of the high thermodynamic stability of CO_2, reactive species are often required to break their strong bonds. Transition metal complexes have been widely used for the activation of these small molecules, but some of these elements remain costly and susceptible to potential supply chain issues (e.g., precious metals).[2] Therefore, researchers are interested in designing inexpensive main-group compounds that can activate inert gases. However, due to the inherent disposition of energetically accessible molecular orbitals, the synthesis of suitable main-group compounds that interact with small molecules remains an ongoing challenge.[3]

Owing to its ability to exist as both a strong electrophile or nucleophile, boron has been an element of choice for several small molecule activation studies.[4] Most germane to this report, Braunschweig recently reported that nonpolar B=B double bonds can activate CO_2 to form novel dibora-β-lactones and diboraoxetanones.[5] In contrast, a dibora-cumulene with partial triple bond character reacts with CO_2 to form a dioxaborinanone (Figure 1a).[6] Although these examples represent significant strides in main-group chemistry, studies of boryl anions activating small molecules are still limited.[4a]

Due to the reduced, electron-rich nature of 9-carbene-9-borafluorene monoanions that were recently isolated by our laboratory,[7] we hypothesized they would be a suitable platform for small molecule activation chemistry. Herein, we report the reaction of the 9-CAAC-9-borafluorene monoanion with CO_2 (CAAC = (2,6-diisopropylphenyl)-4,4-diethyl-2,2-dimethyl-pyrrolidin-5-ylidene)[8] (Figure 1b). Notably, the activation of CO_2 produces the first example of a trioxaborinanone, which is air-stable in the solid-state. Thermolysis or photolysis of trioxaborinanone results in CO release to yield a luminescent

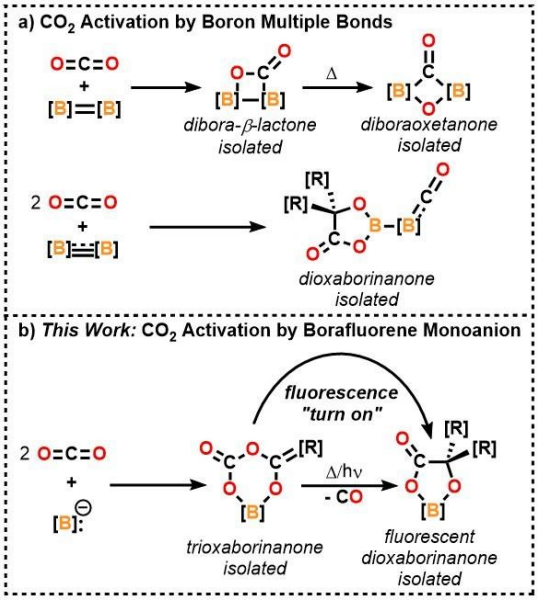


Figure 1. a) Activation of CO_2 by nonpolar double multiple bonds; b) *This Work*: synthesis of trioxaborinanone by borafluorene monoanion activation of CO_2, and elimination of CO to form the fluorescent dioxaborinanone.

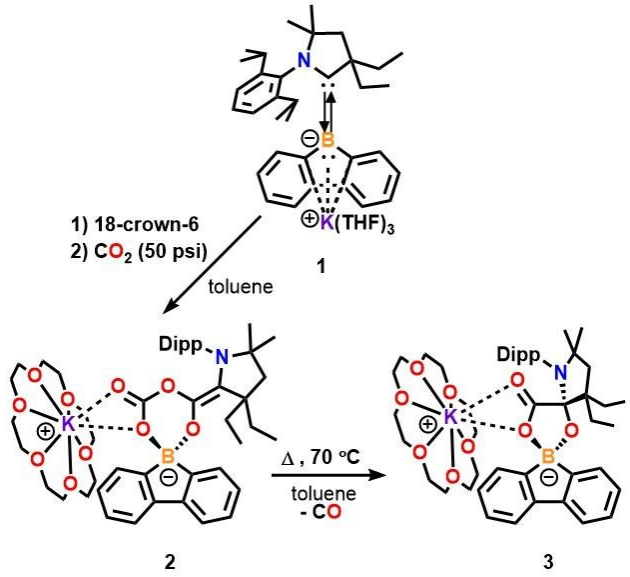
dioxaborinanone, which is stable in open air in solution. Carbon monoxide is essential physiologically as a messenger for various neurological pathways, however, it is fatal if inhaled in high concentrations.[9] Accordingly, materials that can deliver specific amounts of CO in a controlled manner [e.g., carbon monoxide-releasing molecules (CORMs)] have gained significant attention for anti-inflammatory therapies and other medicinal applications.[10] Furthermore, the majority of CORMs are transition metal-based and acyclic,[11] while metal-free heterocyclic CORMs remain exceptionally rare.[9, 12] Thus, the new trioxaborinanone-based CO-releasing process features a unique heterocycle to heterocycle transformation where CO loss can be optically observed.

We began our studies by pressurizing a THF solution of CAAC-borafluorene monoanion (**1**) to 50 psi with CO_2 and an immediate color change from deep red to yellow was observed. A crude ^1H NMR spectrum of the solid obtained from the reaction showed the formation of a complex mixture of intractable products. However, when 18-crown-6 was added to a solution of **1** before pressurizing with CO_2, the 6-membered trioxaborinanone (**2**) was cleanly isolated as a colorless solid in 71% yield (Scheme 1). Compound **2** was characterized by a distinct $^{11}B\{^1H\}$ NMR chemical shift at 8.0 ppm and a C=O stretching band at 1693 cm^{-1} in the infrared spectrum.

The mechanism for the formation of **2** was investigated using density functional theory. The addition of electron-rich boron in **1** to the carbon center of CO_2 forms borylcarboxylate adduct **Int1a** (Figure 2). The nature of the formation of **Int1a**, described by **TS1a**, was further examined using energy decomposition analysis in conjunction with the natural orbitals for chemical valence method (EDA-NOCV). The boron center in **TS1a** adopts sp^3 hybridization. The highest occupied fragment orbital describes a lone-pair centered at boron, with the complimentary π* lowest occupied fragment orbital on bent CO_2. The resultant NOCV identifies charge-transfer from boron to the carbon atom of CO_2, indicating the initial adduct formation proceeds via nucleophilic addition (Figure 3). The CO_2 adduct undergoes a concerted migration from boron to the carbene carbon, forming *β*-lactone intermediate **Int1b**. The concerted [2+2] cycloaddition of CO_2 to the $B–C^{carbene}$ bond of **1** was found to be energetically inaccessible ($\Delta G^{\ddagger}$=+216.4 kJ mol^{-1}). Dissociation of the $B–C^{carbene}$ bond in **Int1b** yields **Int1c** possessing a nucleophilic site at the singly coordinated oxygen. **Int1c** readily undergoes nucleophilic addition with CO_2 (**Int1d**) and subsequent intramolecular cyclization to form **2** (ΔG_{rxn} = -68.2 kJ mol^{-1}).

Heating a solution of **2** in toluene to 70 °C for 18 hours results in CO release and the air-stable 5-membered dioxaborinanone (**3**) was obtained in 80% isolated yield (Scheme 1). The azolium carboxylate (CAAC-CO_2)[13] also forms in minor amounts but can be easily separated from the mixture (mechanism, vide infra). Monitoring the reaction in C_6D_6 (70 °C) or THF-d_8 (60 °C) by ^1H NMR indicates that **2** completely converts to **3** in 2 hrs which was observable by the disappearance of methine environments at 3.61 and 3.36 ppm (**2**) and growth of new peaks at 4.16 and 3.89 ppm (**3**) (Figure S7-S8). Photolysis of **2** under UV light also promotes CO release to form **3** and CAAC-CO_2, albeit with additional unidentified species as side products. An $^{11}B\{^1H\}$ NMR chemical shift at 11.8 ppm, in addition to a C=O stretching band at 1690 cm^{-1} in the infrared spectrum were consistent with compound **3**.

Scheme 1. Reaction of 1 with CO_2 yields the 6-membered trioxaborinanone (2). Heating a solution of 2 releases CO and produces the 5-membered dioxaborinanone (3).



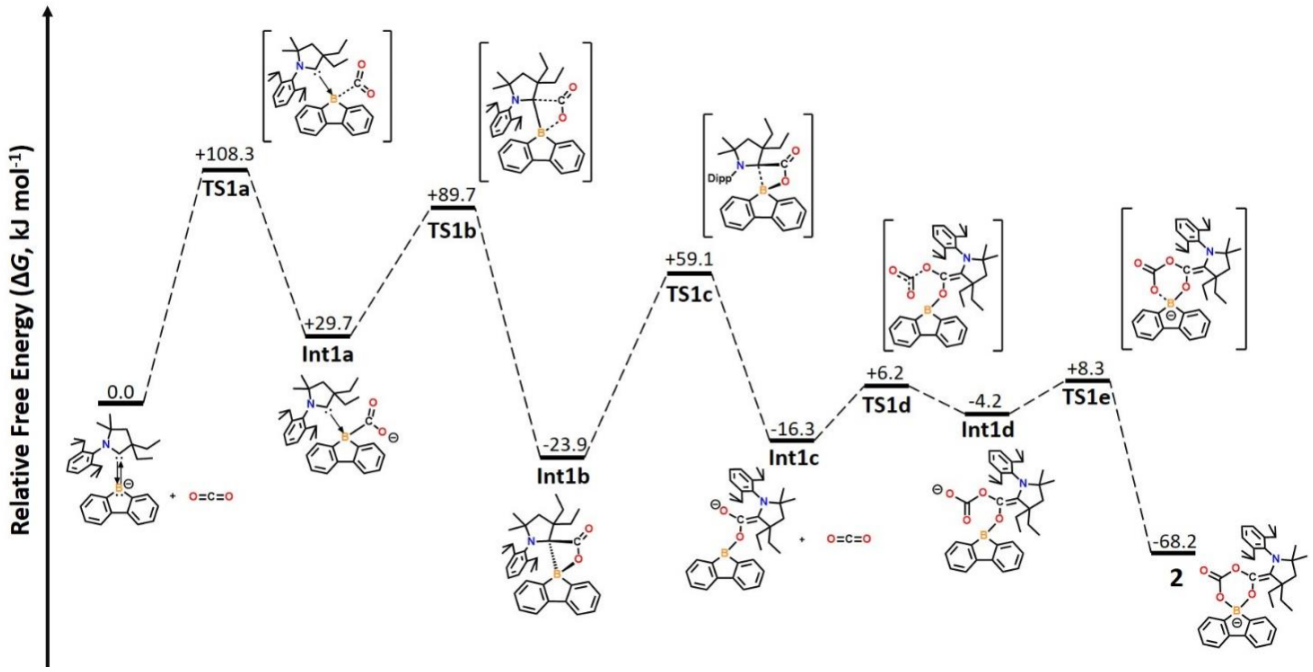


Figure 2. Calculated relative free energies (ΔG, kJ mol^{-1}) for the reaction of **1** with CO_2 to form **2** at the B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP (SMD, Toluene) level of theory. All thermochemical values computed at 298.15 K and 3.4 atm.

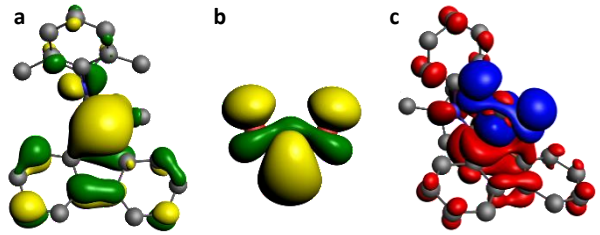
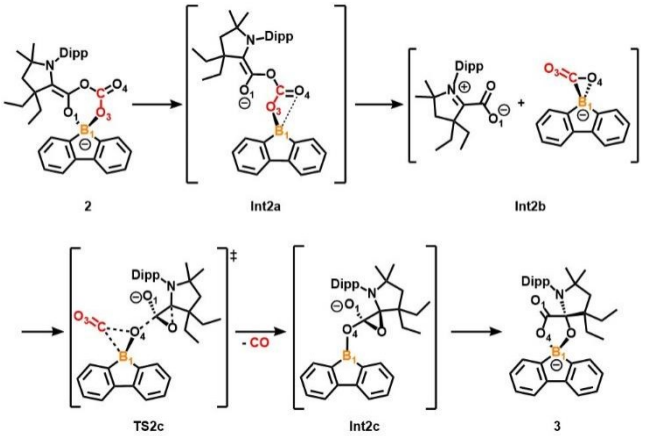


Figure 3. Plots of the reactant fragment orbitals for **TS1a** (a) and (b). Plot of the deformation density $\Delta\rho_{(1)}$ (c) indicating charge flow between NOCVs for **TS1a** and the associated contribution to the total orbital interaction, $\Delta E_{(1)}$ = -176 kJ mol^{-1}, $\nu_{(1)}$ = ± 0.849. Eigenvalue $\nu_{(1)}$ quantifies the amount of transferred electron density (red: charge depletion, blue: charge accumulation), isosurface = 0.001. Hydrogen atoms and terminal methyl groups omitted for clarity.

Spirocyclic **2** can be considered among carbon monoxide-releasing molecules (CORMs) that are important for their ability to deliver specific amounts of CO, reducing the risk of CO poisoning.[10b, 10c] To confirm the release of CO from **2,** gas chromatography studies with a flame ionization detector (GC-FID) were performed with argon as the carrier gas. The GC instrument was first injected with pure CO gas and the retention time was determined to be 3.5 min, and subsequently with an aliquot of the reaction headspace to which a peak at t_r = 3.5 min was observed (Figure S12).

Theoretical methods were used to gain insight into the decarbonylation mechanism of **2** (Scheme 2). In order to avoid any mechanism bias, a systematic investigation was conducted with relaxed scans for the heterolytic dissociation of each bond in the central carbonate ring (Figure S15). These calculations indicated that dissociation of B1-O1 (**Int2a**) was most favored energetically (ΔG = +115 kJ mol^{-1}). Acyclic **Int2a** features an sp^2 hybridized boron and a weak electrostatic interaction with the carbonyl oxygen (B1-O4, 2.71 Å). A subsequent transition state was located for the dissociation of **Int2a** ($\Delta G^{\ddagger}$ = +28 kJ mol^{-1}) forming reactive intermediate complex **Int2b** (ΔG = +74 kJ mol^{-1}), composed of zwitterionic CAAC-CO$_2$ and a bora-α-lactone anion. This step is consistent with the experimentally observed CAAC-CO$_2$ intermediate. Intrinsic reaction coordinate calculations reveal the bora-α-lactone intermediate is formed via the inversion of boron-oxygen bond B1-O3 with the carbonyl oxygen (O4). Nucleophilic addition of the endocyclic oxygen of bora-α-lactone to the electron-deficient carbon center of CAAC-CO$_2$ via **TS2c** ($\Delta G^{\ddagger}$ = +27 kJ mol^{-1})

Scheme 2. Proposed mechanism for the thermal decarbonylation of 2.



releases CO in a concerted step, forming epoxide **Int2c**. The strained epoxide intermediate is relieved through intramolecular cyclization to form the 5-membered dioxaborinanone **3** (ΔG_{rxn} = -33 kJ mol^{-1}). While decarbonylation reactions are common across the chemical literature, most examples describe exocyclic CO release from transition metal complexes,[11c, 11d] main-group compounds,[3c, 14] or unsaturated cyclic hydrocarbons.[12a] In the case of thermal decarbonylation, the mechanism for CO release is exclusively cheletropic elimination, while photolytic decarbonylation proceeds via a Norrish Type I reaction.[15] Rare examples of heterocyclic decarbonylation, and more specifically CO extrusion from cyclic esters, typically require high temperature thermolytic fragmentation pathways.[16] Thus, compound **2** is a rare example, or perhaps even the first example, of a metal-free spirocyclic CORM that releases endocyclic-CO under relatively mild conditions.

It is noteworthy that dioxaborinanone **3** emits blue light under UV excitation. Therefore, compound **2** is an especially unique CORM with the ability to deliver CO under both thermal or photochemical conditions with a simultaneous optical response (i.e., fluorescence turn-on due to the formation of **3**). The lowest energy transition for **3** in THF was observed at 318 nm, with a red-shifted emission maximum at 352 nm (Figure S11). In order to quantify luminescence, an absolute quantum yield was determined for **3** ($\Phi_{solution}$ = 21%). Theoretical modelling of the electronic excitations for **3** at the CAM-B3LYP-D3(BJ)/def2-TZVP(-f) (CPCM, THF) level of theory identifies the lowest energy transition to be a mixed HOMO→LUMO (44%) and HOMO-1→LUMO (34%) configuration. These transitions describe π→π* transitions centered on the borafluorene moiety with minor charge-transfer character from CAAC to borafluorene (Figure S17).

In the solid state, both **2** and **3** feature unique structures with spirocyclic cores containing boron and oxygen heteroatoms (Figure 4). Although spirocyclic molecules have received great attention in drug discovery for their three-dimensionality, spirocycles featuring heteroatoms have historically been less explored.[17] Remarkably, compound **3** possesses two spiro-centers bound to the same heterocycle moiety. In addition, **3** adopts an unusual structure by which the oxidized carbene carbon forms a spirocycle, representing one of only a few examples.[6, 18]

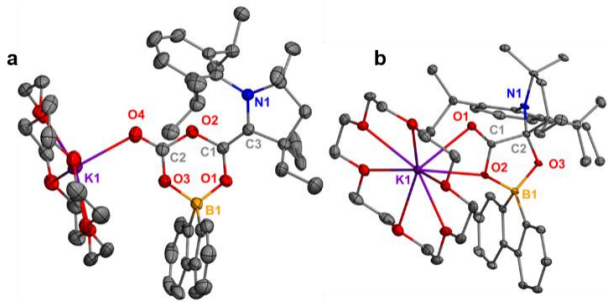


Figure 4. Molecular structures of **2** (a) and **3** (b). Hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50% probability. Selected bond lengths [Å]: **2**: B1–O1 1.478(4), B1–O3 1.535(3), C1–O1 1.350(3), C1–O2 1.410(3), C2–O2 1.351(3), C2–O3 1.298(3), C2–O4 1.210(3), C1–C3 1.340(4); **3**: B1–O2 1.5429(18), B1–O3 1.4746(17), C1–O1 1.2223(17), C1–O2 1.3113(16), C1–C2 1.5517(18), C2–O3 1.3945(16).

The 5-membered ring of **3** is planar, while the 6-membered ring of **2** is puckered. The B1–O1 and B1–O3 bond lengths of **2** are 1.478(4) Å and 1.535(3) Å respectively and are close to the sum of the covalent radii (R(B–O) = 1.50 Å)[19] for a single bond. In the 6-membered ring of **2** the endocyclic C–O

bond lengths range from 1.298(3) to 1.410(3) Å while the length of the exocyclic C2–O4 bond is significantly shorter [1.210(3) Å] and indicative of double bond character. In compound **3**, the B–O bond lengths [1.5429(18) Å and 1.4746(17) Å] are comparable to those of **2**.

In conclusion, we report the first structurally authenticated example of a trioxaborinanone (**2**), which was synthesized from the activation of CO_2 by the 9-CAAC-9-borafluorene monoanion. Notably, compound **2** functions as a carbon monoxide-releasing molecule when heated or irradiated with UV light and forms the luminescent dioxaborinanone (**3**) via loss of CO. Thus, a fluorescent response can be observed optically upon CO release. Remarkably compound **2** represents a new metal-free, heterocyclic CORM that does not require the use of toxic CO gas in the synthesis. Both **2** and **3** are stable under aerobic conditions in the solid-state, and **3** is even stable in solution. Furthermore, theoretical mechanistic studies reveal that the reactivity of 9-CAAC-9-borafluorene monoanion with CO_2 proceeds via a nucleophile addition pathway, which is unique compared to known single-electron transfer mechanisms for 9-carbene-9-boryl anions.[7a, 20] Additional studies to investigate the reactivity of the 9-carbene-9-borafluorene monoanions with other small molecules are currently underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at http://pubs.acs.org. Experimental details, NMR spectra, computational details, and single-crystal X-ray diffraction data (PDF) Crystallographic data for **2** and **3** (CIF)

Accession Codes. CCDC 2166590 and 2166591 (for compounds **2** and **3**, respectively) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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SYNOPSIS TOC:

A reaction between a 9-carbene-9-borafluorene monoanion and carbon dioxide produces the first example of a trioxaborinanone. Remarkably, when heated or irradiated, the trioxaborinanone releases carbon monoxide and gives the luminescent dioxaborinanone.