Cyclic (Alkyl)(Amino) Carbene-Assisted Reduction of Carbon Dioxide: Isolation of Crystalline Alkali Metal Clusters of Supported CO_2 Radical Anions and Dianions

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ABSTRACT: The reduction of the relatively inert carbon–oxygen bonds of CO_2 to access useful CO_2-derived organic products is one of the most important fundamental challenges in synthetic chemistry. Achieving this reduction using earth-abundant main group elements (MGEs) is especially arduous because of the difficulty in achieving strong inner-sphere reactions and bond activation events between CO_2 and the MGE. Herein we report the first successful chemical reduction of a zwitterionic carbene-CO_2 adduct by either one or two equivalents of light alkali metals to form isolable, room-temperature-stable crystalline clusters exhibiting remarkably diverse electronic and structural characteristics. The reduction of a CAAC-CO_2 adduct [CAAC–CO_2, **1**, CAAC = cyclic (alkyl)(amino) carbene] with one equivalent of lithium, sodium or potassium metal yields the monoanionic radicals $(THF)_3Li_2(CAAC{-}CO_2)_2$ (**2**), $(THF)_4Na_4(CAAC{-}CO_2)_4$ (**3**), or $(THF)_4K_4(CAAC{-}CO_2)_4$ (**4**). The reduction of **1** by two or more equivalents of lithium, sodium, or potassium yields the open-shell, dianionic clusters $(THF)_2Li_6(CAAC{-}CO_2)_3$ (**5**), $Li_{12}(CAAC{-}CO_2)_6$ (**6**), $Na_{12}(CAAC{-}CO_2)_6$ (**7**), and $K_{10}(CAAC{-}CO_2)_5$ (**8**). Each of the clusters was studied by a combination of X-ray crystallography, FTIR, UV-Vis, EPR and NMR spectroscopies, and theoretical calculations. The synthetic transformation described in this report results in the facile net reduction of CO_2 at room temperature by lithium, sodium, and potassium metal without the need for additional metallic promoters, catalysts, or reagents – a process which does not occur in the absence of carbene.

INTRODUCTION

Since the isolation of stable *N*-heterocyclic carbenes (NHCs) by Arduengo,[1] and cyclic (alkyl)(amino) carbenes (CAACs) by Bertrand,[2] these ligands have had a profound impact on synthetic chemistry.[3] Notably, the ambiphilic nature of stable singlet carbenes has allowed the development of a rich body of organic chemistry which is distinct from their utility in metal-based systems.[4] In such transformations, a common reaction step involves the carbene functioning as a neutral carbon nucleophile with the desired electrophilic substrate(s). A significant example of this class of reaction is the behavior of free carbenes in the presence of CO_2, where the carbene lone pair forms a covalent bond with the electrophilic carbon atom of CO_2. This results in the formation of highly stable zwitterionic adducts (i.e. *N,N'*-disubstituted imidazolium-2-carboxylates or, more generally, carbene-2-carboxylates). It is noteworthy that although CO_2 is estimated to be a comparable electrophile to benzaldehyde, similar electrophilic reactivity at CO_2 is generally thermodynamically unfavored.[5] These adducts have become an extremely important subclass of "masked" carbene due to their high air and moisture stability compared to the free carbene.[6] Indeed, a substantial number of imidazolium-2-carboxylate compounds are known, and their reactivity has been studied with organic nucleophiles (e.g. organosilanes, Figure 1A),[4a] organic electrophiles (e.g. epoxides, Figure 1B),[7] and organometallic complexes {e.g. $[Rh(COD)Cl]_2$, Figure 1C}.[6]

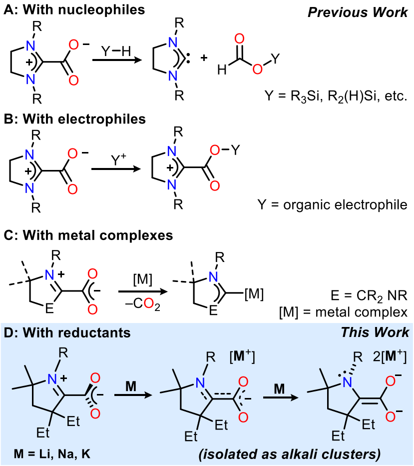


Figure 1. Known reactivity profile of carbene–CO_2 adducts (A) with nucleophiles, (B) with electrophiles, (C) with metal complexes. The reactivity with metallic electron donors (D) is hitherto unknown and the focus of the work presented in this report.

Although these molecules are isolable under ambient conditions, adduct formation is known to be reversible, which allows the zwitterion to either directly transfer the carbene to metal centers[6, 8] or regenerate a free carbene *in situ*.[9] These properties imbue carbene-carboxylates with a distinct predisposition toward energy-relevant applications in CO_2 reduction/conversion chemistry, and a number of such studies have been reported focused on functionalizing or selectively transferring the carboxylate motif.[4a, 9b, 10] In contrast to the established body of synthetic chemistry that is known for NHC–CO_2 compounds, drastically less is known about isostructural CAAC–CO_2 species.[8a, 9b, 11] This is especially surprising considering the recent surge in interest concerning the reactivity of CAACs with a wide array of small molecules.[3a, 3f, 4b, 11-12] Furthermore, last year we published the first evidence that carbene–CO_2 adducts display redox activity in the absence of other reagents.[9b]

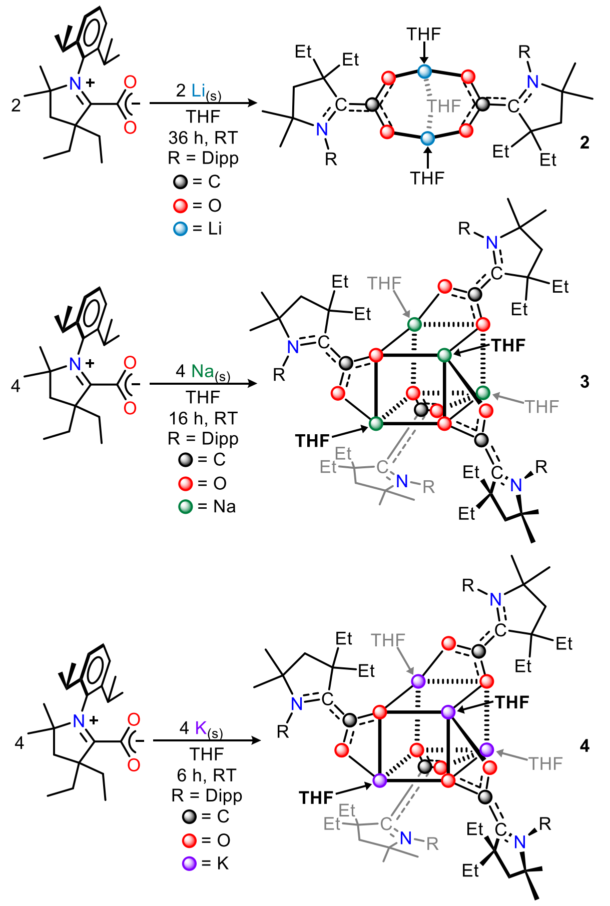
In this initial report, we electrochemically reduced a CAAC–CO_2 adduct under both argon and CO_2 saturation conditions, and found evidence of reductive chemistry centered around the CAAC–CO_2 species at reduction potentials where CO_2 is inert. Most importantly, reduction of CAAC–CO_2 under argon saturation showed that the CAAC–CO_2 adduct is not only able to readily accept electrons, but that this electron transfer is a reversible redox couple on the CV timescale at −2.15 V (vs. Fc^+/Fc). However, in spectroelectrochemical studies we observed that CO and carbonate were produced, indicating that a net reductive disproportionation reaction was occurring. Herein we report the results of our investigation of the ability of CAAC–CO_2 zwitterions to undergo chemical reduction by alkali metals. The syntheses, solid-state structures, and computational studies of crystalline, reduced CAAC–CO_2 species indicate that the CAAC ligand acts as an organic mediator to stabilize the controlled one- and two-electron reduction of carbon dioxide. These reactions occur readily at temperatures as low as −39 °C, and a remarkable array of *both* singly- and doubly-reduced CAAC–CO_2 complexes have been synthesized: $(THF)_3Li_2(CAAC–CO_2)_2$ (**2**), $(THF)_4Na_4(CAAC–CO_2)_4$ (**3**), and $(THF)_4K_4(CAAC–CO_2)_4$ (**4**), $(THF)_2Li_6(CAAC–CO_2)_3$ (**5**), $Li_{12}(CAAC–CO_2)_6$ (**6**), $Na_{12}(CAAC–CO_2)_6$ (**7**), and $K_{10}(CAAC–CO_2)_5$ (**8**). Compounds **2**-**8** were isolated as structurally diverse organoalkali metal clusters, and the reduced organic core exhibited high stability and solubility in both polar and non-polar solvents. The net reaction that occurs is the carboxylation of a carbene at RT and 1 atm of pressure, followed by the stepwise reduction of this CAAC-carboxylate to a CAAC-diolate dianion at RT using two electrons from alkali metals. In contrast to established CO_2 reduction reactions using organic nucleophiles and alkali elements to reduce CO_2, the reactions reported herein are the first examples of a reductive synthetic protocol which results in cleavage of CO_2 π-bonds without using carbanions,[13] organometallic reagents, or catalysts.

RESULTS AND DISCUSSION

We selected the (${}^{\text{diethyl}}$CAAC)-2-carboxylate zwitterion, **1**, as the subject of this synthetic investigation due to the improved solubility and ease of preparation compared to the spirocyclic (${}^{\text{cyclohexyl}}$CAAC)-2-carboxylate we previously reported.[9b] Compound **1** possesses an isostructural CAAC-carboxylate core geometry in the solid-state molecular structure (Figure S1) along with nearly identical electronic properties.

Our initial studies focused on the isolation and structural characterization of the chemical reduction products resulting from the reaction of **1** with Li, Na, and K. Upon the addition of one equivalent of metal shavings (or KC_8 in the case of **4**) to a vigorously stirring solution of **1**, an immediate coloring of the mixture was observed (Li, Na, or K reducing agent yielded bright red, orange, or red colors, respectively). With vigorous stirring under inert conditions, the time necessary for complete consumption of the metal shavings scaled with the relative activity of the alkali metals (Li: 36 h; Na: 16 h; K: 6 h). The isolation of the products of these reactions via recrystallization from saturated THF or THF/hexane solutions at −39 °C yielded single crystals suitable for X-ray diffraction studies. The crystallographically determined structures of the monoanionic products $(THF)_3Li_2(CAAC–CO_2)_2$ (**2**), $(THF)_4Na_4(CAAC–CO_2)_4$ (**3**), and $(THF)_4K_4(CAAC–CO_2)_4$ (**4**) (Scheme 1, Dipp = 2,6-diisopropylphenyl) revealed a series of ion-contacted clusters incorporating the respective alkali metal cations in a CAAC–CO_2:M ratio of 1:1 (M = Li, Na, or K).

Scheme 1. Synthesis of singly-reduced CAAC–CO_2 compounds 2-4.



In all three cases, precise control of reaction stoichiometry and times were critical, as reactions were frequently complicated by the presence of either residual CAAC–CO_2 starting material which co-crystallizes with the desired products, or overreduction to a doubly-reduced complex.

Single crystals of compounds **2**-**4** suitable for X-ray diffraction studies were grown from saturated solutions of the complexes in either THF (**3**) or saturated THF/hexane mixtures (**2**, **4**). Interestingly, the CAAC–CO_2 core is completely planar in each singly-reduced species, which matches the predictions of our previously reported DFT calculations.[9b] The N2–C2 bonds [1.3802(12), 1.385(3), and 1.384(6) Å for **2**-**4** respectively] and C1–O bonds [1.2732(12) Å, **2**; 1.286(3) Å, **3**; 1.276(6), **4**] in each species are significantly longer than that of the neutral zwitterion [C1–N2 = 1.282(5) Å, C1–O1 = 1.236(5) Å]. Concomitantly, there is a substantial contraction of the C1–C2 bond from 1.516(5) Å in **1** to 1.4533(13) Å, 1.458(3) Å, and 1.451(7) Å in **2**-**4**, respectively. These changes are consistent with the addition of one electron from the alkali metal into a π-symmetric molecular orbital, increasing the bonding character between C1 and C2, and decreasing the bond order of the C2–N1, C1–O1, and C1–O2 bonds. Notably, the CAAC nitrogen atom remains planar in its geometry, indicating that the $N_{\text{non-bonding}}$ electrons are still involved in a π-symmetric interaction with the C2 center. The cumulative effects of these bonding metrics explain the observed planarity across the CAAC–CO_2 core.

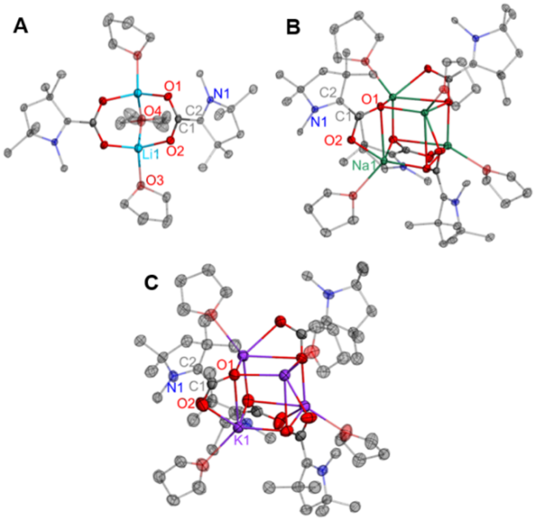


Figure 2. Solid state molecular structures of **2** (A), **3** (B), and **4** (C). All H atoms and carbon atoms not directly attached to the CAAC core ring are omitted for clarity. Selected bond lengths (Å) and angles (deg): **2**: O1–C1: 1.2732(12); O2–C1: 1.2778(12); C1–C2: 1.4533(13); N1–C2: 1.3802(12); O1–C1–O2: 123.71(9); O1–C1–C2: 119.84(9); O2–C1–C2: 116.45(9); N1–C2–C1: 124.85(9); N1–C2–C3: 110.81(8). **3**: O1–C1: 1.286(3); O2–C1: 1.266(3); C1–C2: 1.458(3); N1–C2: 1.385(3); O2–C1–O1: 122.9(2); O2–C1–C2: 118.7(2); O1–C1–C2: 118.3(2); N1–C2–C1: 124.7(2); N1–C2–C3: 109.7(2). **4**: O1–C1: 1.276(6); O2–C1: 1.265(7); C1–C2: 1.451(7); N1–C2: 1.384(6); O2–C1–O1: 123.0(5); O2–C1–C2: 119.1(5); O1–C1–C2: 117.9(5); N1–C2–C1: 123.3(5); N1–C2–C3: 110.2(4).

In order to further probe the electronic structure of the reduced CAAC–CO_2 species, CW X-band EPR data were collected for compounds **2**-**4** in toluene solutions at RT (Figure 3). In spite of the differences in their solid-state molecular structures, the EPR spectra were all nearly identical exhibiting weak splitting by two ^{13}C nuclei, with little to no observable ^{14}N interactions.

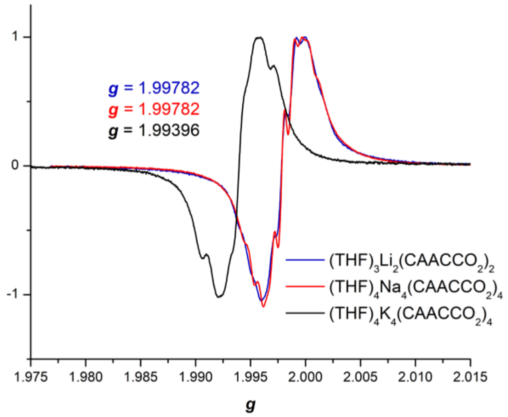


Figure 3. Continuous Wave X-band EPR spectra of **2**-**4** taken on a 250 μM toluene solution at RT.

Theoretical calculations were carried out for **2**-**4**, and were geometries optimized with the HF-3c method that is appropriate for large molecular systems.[14] All calculations were inclusive of THF solvation.[15] Geometries are consistent with SC-XRD studies, with the CAAC nitrogen remaining planar in all three singly-reduced compounds. The N1-C2, C1-C2 and C1-O bond distances displayed the general trend of increasing with the size of the alkali metal. This same trend was observed in the dihedral angle of the N1-C2-C1-O1 intersecting planes; 5.9°, 2.3° and 2.5° for compounds **2**-**4**, respectively.

Molecular orbitals (MO) at the ROB3LYP-D3(BJ)/def2-SVP level of theory indicate that for **2**-**4** the singly occupied MO (SOMO) largely resides on the bonded carbon atoms from the carbene and CO2 units. The LUMO is concentrated on the Dipp substituents. Plots of the SOMO are illustrated in Figure 4. Analysis of the spin density (see ESI Table S3, Figure S24) indicates that the largest contribution is from the carbene $^{\text{CAAC}}$C (0.239 – 0.170 e-), followed by $^{\text{CAAC}}$N (0.093 – 0.041 e-), $^{\text{CO2}}$O (0.038 – 0.017 e-), and $^{\text{CO2}}$C (0.036 – 0.018 e-).

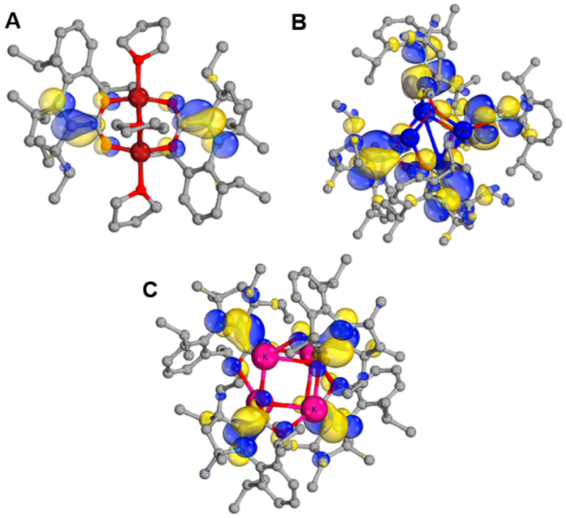
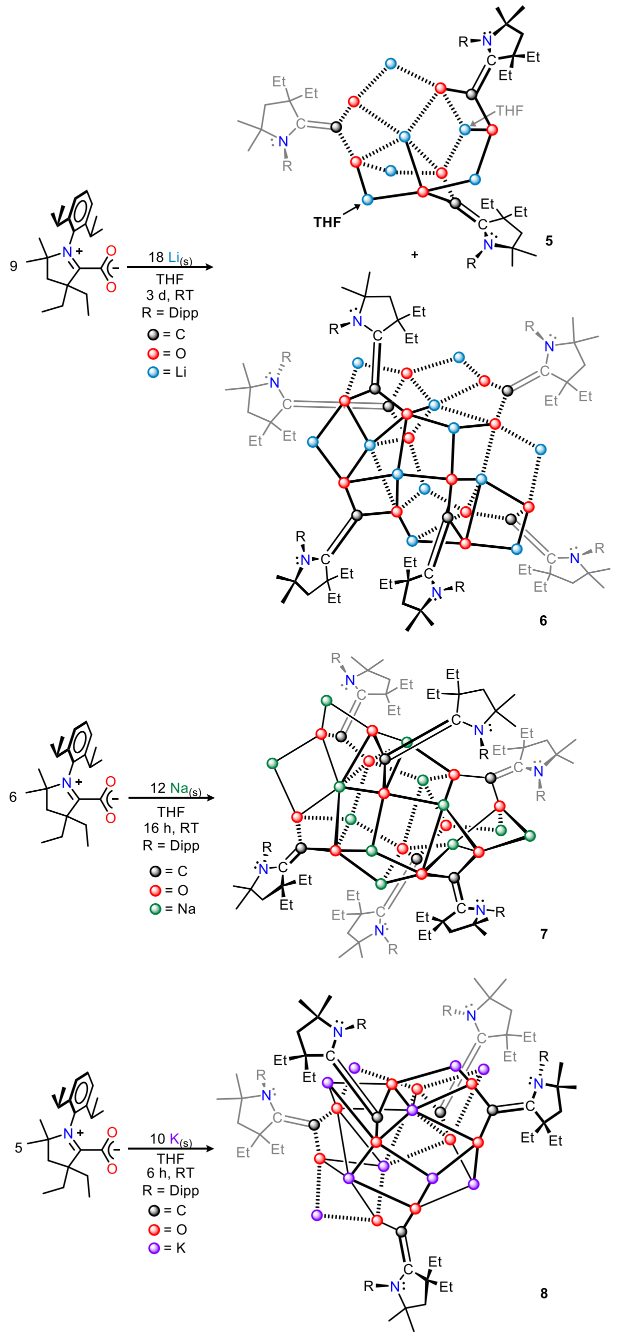


Figure 4. Plots of the SOMOs of **2** (A), **3** (B), and-**4** (C). H atoms (and THF for **3** and **4**) omitted for clarity.

The addition of two or more eq of metal to a THF suspension of **1** gave gradual conversion (Li: 3 d, Na: 16 h, K: 6 h) to deeply colored, strongly absorbing, homogeneous mixtures containing new reduced species. Completely drying this solution under reduced pressure, followed by extraction and recrystallization in hexanes produced single crystals suitable for X-ray diffraction studies. These revealed the respective solid-state structures of the doubly-reduced complexes $(THF)_2Li_6(CAAC{-}CO_2)_3$ (**5**), $Li_{12}(CAAC{-}CO_2)_6$ (**6**), $Na_{12}(CAAC{-}CO_2)_6$ (**7**), $K_{10}(CAAC{-}CO_2)_5$ (**8**) in high yields (Li: 70%;[16] Na: 86%; K: 96%), which were observed to be highly stable, crystalline, analytically pure solids at room temperature under inert atmosphere (Scheme 2).

Scheme 2. Synthesis of doubly-reduced CAAC–CO_2 compounds 5-8.



Notably, when lithium metal is used, the complete removal of THF from the crude reaction residue proved difficult. Even after multiple triturations with hexanes and prolonged drying under reduced pressure, a sticky red-orange semi-solid was obtained. Upon recrystallization of the highly soluble, red-orange bulk material from hexanes, two distinguishable crystalline species – one dark red and one bright yellow – were observed which crystallized from the same solution (Figure 4A). Surprisingly, similar behavior was not observed when Na or K was used, for which only one crystalline product was obtained in multiple trials [Figure 4B (Na) and 4C (K)].

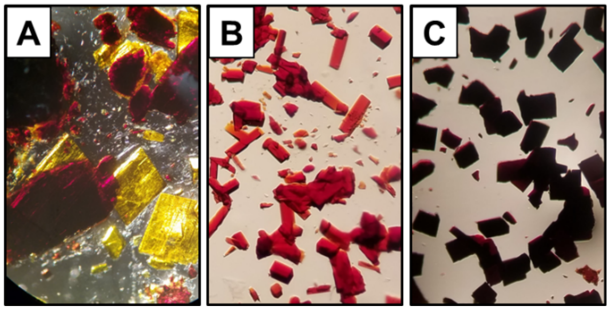


Figure 5. Digital image of the mixture of compounds **5** (red crystals) and **6** (yellow crystals) (A), **7** (B), and **8** (C) viewed at 40x magnification on an optical microscope.

From the mixture of crystals obtained from the Li reduction, two different dilithiated CAAC–CO_2 clusters (**5**, Figure 6A; **6**, Figure 6B) were structurally characterized. Despite exhibiting drastically different crystal habits and colors, both compounds contained an equal ratio of lithium ions to CAAC–CO_2 units (2:1). However, the size of the cluster varies. Compound **5** contains half the number of $Li_2(CAAC{-}CO_2)$ units as compound **6**. Also, compound **5** is the only doubly reduced species in this study which exhibited THF coordination in the solid-state. Combustion microanalysis performed on a bulk sample of this mixture matched the calculated CHN content for **5**, suggesting this is the major species present in the bulk material.

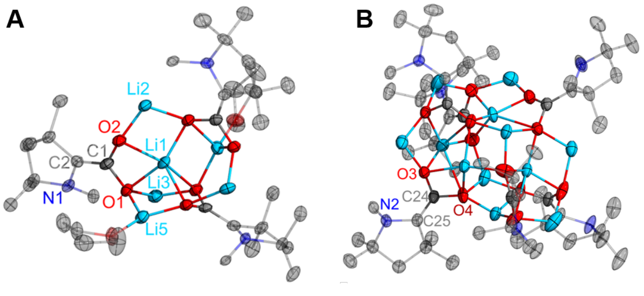


Figure 6. A) Solid state molecular structure of **5** (A) and **6** (B). All H atoms and carbon atoms not directly attached to the CAAC core ring are omitted for clarity. Selected bond lengths (Å) and angles (deg): **5**: O1–C1: 1.354(7); O2–C1: 1.332(7); C1–C2: 1.379(8); N1–C2: 1.463(7); O2–C1–O1: 114.1(5); O1–C1–C2: 121.2(5); O2–C1–C2: 124.6(5); C1–C2–N1: 120.0(5); N1–C2–C3: 109.6(5). **6**: O1–C1: 1.365(2); O2–C1: 1.360(2); C1–C2: 1.343(3); N1–C2: 1.452(2); O2–C1–O1: 114.20(15); C2–C1–O1: 120.63(16); C2–C1–O2: 125.16(16); C1–C2–N1: 121.20(16); N1–C2–C3: 110.58(15).

As in the cases of the singly-reduced species, the structural features of the CAAC–CO_2 core yield information about the extent of reduction. Perhaps the most notable structural change between **2** and **5**/**6** is the pyramidal geometry of the CAAC nitrogen atom in the doubly-reduced complexes. This geometric change, along with a shortening of the C1–C2 bonds from 1.4533(13) Å in **2** to 1.379(8) Å (**5**) and 1.343(3) Å (**6**) clearly supports the existence of a nonbonding lone pair on the $\mathrm{N_{CAAC}}$ atom and a formal π-bond between C1 and C2. Moreover, the C1–O1 and C1–O2 bond lengths in **5** [1.354(7) Å, 1.332(7) Å] and **6** [1.365(2) Å, 1.360(2) Å] indicate C–O bond orders of 1. The only major structural differences between **5** and **6** are in the nature of the non-covalent ion contacts between the electron-rich π-system of the CAAC–CO_2 core and nearby lithium cations. Perturbations in the π-π* energy gap by these nearby charges presumably lead to the observed differences in the absorption of visible light by complexes **5** and **6** in the solid state.

Similar reactions conducted with sodium and potassium yielded highly pure single crystals suitable for X-ray diffraction studies from a saturated hexane extract of the crude product mixture. SC-XRD data collected on crystals of the Na and K products revealed the structures shown in Figure 7A and 7B.

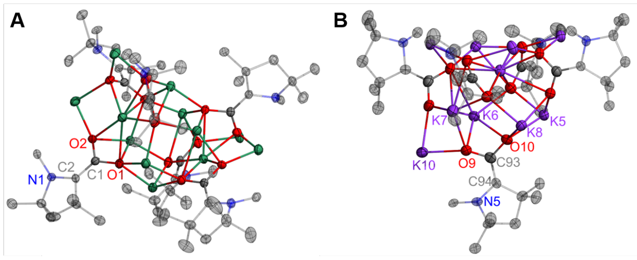
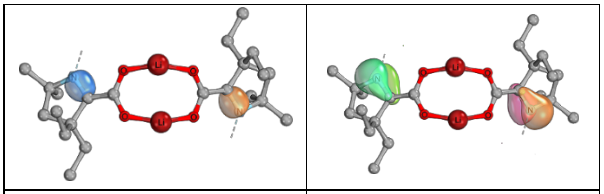


Figure 7. Solid state molecular structures of **7** (A) and **8** (B). All H atoms and all carbon atoms not directly attached to the CAAC core ring are omitted for clarity. All H atoms and carbon atoms not directly attached to the CAAC core ring are omitted for clarity. Selected bond lengths (Å) and angles (deg): **7**: O1–C1: 1.364(4); O2–C1: 1.336(4); C1–C2: 1.365(5); N1–C2: 1.452(4); O2–C1–O1: 113.4(3); O1–C1–C2: 124.0(3); C1–C2–N1: 122.9(3); N1–C2–C3: 107.9(3). **8**: O9–C93: 1.342(10); O10–C93: 1.304(9); C93–C94: 1.385(11); N5–C94: 1.455(9); O10–C93–O9: 115.8(7); O9–C93–C94: 120.0(7); C93–C94–N5: 119.5(6); N5–C94–C95: 108.7(6).

The solid-state molecular structure of **7** shows an oblong $Na_{12}(CO_2)_6$ core "capped" by six bound CAACs, which is pseudo-S_4 symmetric (S_4 axis containing Na2 and Na9). The ratio of Na ions to CAAC–CO_2 units (2:1) and the bond lengths across the CAAC–CO_2 core [N1–C2: 1.452(4) Å; C1-C2: 1.365(5) Å; O1-C1: 1.364(4) Å; O2-C1: 1.336(4) Å] indicate that each unit is doubly-reduced, analogous to **5** and **6**. This description is further supported by pyramidal geometries exhibited by all $^{\mathrm{CAAC}}$N atoms in the cluster. In the solid-state structure of **8**, a C_1-symmetric $K_{10}(CO_2)_5$ core was observed. All of the core structural features noted for complexes **5**-**7** were also observed in **8**, however all five Dipp substituents in this complex exhibited substantial K–(η^6-Dipp) interactions with externally oriented K ions. These interactions were present in **7** but weak, and not observed in **5** or **6**.

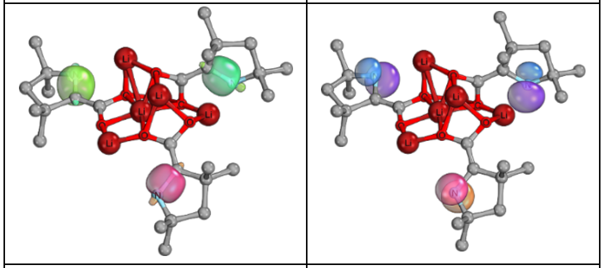
Notably, the products **5-8** were observed to be both NMR silent and EPR silent (at RT in perpendicular mode), indicating that there is significant population of an S=1 (*i.e.* non-Kramers') paramagnetic electronic state for all doubly reduced compounds. In order to gain insight into the electronic properties of **5-8**, theoretical calculations were carried out with HF-3c geometry optimizations of singlet electronic states. The multiplicity of the ground state was assessed with single-point RO-B3LYP-D3(BJ)/6-31+G(d) DFT calculations of singlet and triplet states at the singlet-state geometries; triplet states are lower in energy for compounds **5** (by 380 kJ/mol) and **7** (270 kJ/mol), with singlet states lower in energy for **6** (140 kJ/mol) and **8** (203 kJ/mol). While these are vertical rather than adiabatic energy differences, it is expected that compounds **5** and **7** would be likely to possess a triplet ground state.

The optimized geometries of **5-8** follow the trends observed of the crystal structures, with the optimized bond distances generally longer than from the crystal structures. In all doubly reduced species, the $\mathrm{N_{CAAC}}$ is pyramidal and the length of the C1-C2 bond shortens relative to the singly reduced counterparts. The pyramidal geometry of the $\mathrm{N_{CAAC}}$ suggests a non-bonding lone-pair on the nitrogen atom and a C1-C2 π-bond. Intrinsic bonding orbital (IBO) analysis supports this observation. The $\mathrm{N_{CAAC}}$ atom of the doubly-reduced species each possess a *p* lone pair and a *σ* N1-C2 bond. No *π*-bond is observed between N1-C2 of **5-8**, unlike the singly-reduced species **2-4** where the π-bond is present (Figure 8).



(**2**) N1-C2 *σ*-bond (N1 = 1.169; C2 = 0.813)

(**2**) N1-C2 *π*-bond (N1 = 1.603; C2 = 0.180)



(**5**) N1-C2 *σ*-bond (N1 = 1.147; C2 = 0.822)

(**5**) N1 *p* lone-pair (N1 = 1.866; C1 = 0.00)

Figure 8. Intrinsic bonding orbitals (IBOs) of **2** (top) and **5** (bottom), numbers in parentheses indicate the partial charge distribution of the IBO at the B3LYP-D3(BJ)/6-31+G(d)//HF-3c level of theory. Orbital iso-surfaces enclose 0.80 of the integrated electron densities of the orbital. Hydrogen atoms, Dipp and THF substituents omitted for clarity).

CONCLUSION

The synthetic protocols reported herein result in the carboxylation of a CAAC at RT and 1 atm of pressure, followed by the stepwise reduction of this CAAC-carboxylate to a an open-shell CAAC-diolate dianion at RT using two electrons from alkali metals. The reduced products were isolable as soluble, crystalline mono- and dianionic alkali-CAAC-CO_2 clusters with diverse electronic properties dependent on the nature of the cation and cluster topology. This report highlights novel methods for facile cleavage of CO_2 π-bonds, sheds light on the previously unknown redox behavior of carbene-carboxylates, and will facilitate the development of new chemistries using these compounds as simple and efficient electron-transfer platforms.

ASSOCIATED CONTENT

Supporting Information contains experimental procedures, NMR spectra, and computational studies. This material is available free of charge via the Internet at http://pubs.acs.org

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Author Contributions

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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16. The bulk mixture of 5 and 6 was analyzed as one product with a varying amount of THF, as discussed in the SI. As such, this yield is given with respect to the chemical formula of the bulk mixture as determined by combustion analysis.