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Structurally simple complexes of CO_2[†]

† Dedicated to Professor Osvald Knop on the occasion of his 92nd birthday.

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Introduction

In the past 10 years complex issues concerning energy and pollution have arisen, issues which will remain daunting challenges for the foreseeable future. Limits on the reserves of traditional hydrocarbons have been identified, but new technologies have also allowed access to huge new sources of fossil fuels. Thus, although finite, there is still a sufficient amount of fuel to drive human enterprise for several hundred years. Coupled with this ready access to additional fuel reserves and rampant industrial growth, is the ever-increasing carbon dioxide level in the earth's atmosphere.[1] Atmospheric carbon dioxide levels are now the highest ever measured.[2] The final effects are still unknown, however, it is clear that climate change and ocean acidification are already occurring.

The properties and reactivity of carbon dioxide have been of interest to scientists for decades. Carbon dioxide capture from flue gas emissions has been long sought as a means to offset the massive amounts of this gas accumulating in the atmosphere. There are, however, still many hurdles to overcome before such technologies are industrially viable.[3] CO_2 capture from ambient air for the same purposes is also currently receiving attention, although it has been predicted to be more costly.[4] In addition to carbon capture, the electrochemistry of CO_2 is of particular interest, as the ability to efficiently reduce CO_2 to fuels or feedstocks would clearly be invaluable for sustainability and energy purposes.[5]

CO_2 is a superficially simple molecule but its chemistry is quite complex. It is a triatomic molecule possessing two short, and equivalent, carbon-oxygen bonds (1.1602(8) Å)[6] arranged in a linear fashion about the central carbon atom. This arrangement leads to a nonpolar molecule. Together the molecular geometry and electron distribution produce a molecular quadrupole that accounts for most of the physical and chemical behaviors of carbon dioxide in the solid, liquid and gas phases. Figure 1A depicts a Lewis structure of CO_2 with the anticipated charge distribution based upon Pauling electronegativity differences. Figure 1B shows the electrostatic potential of CO_2 plotted on the total electron density isosurface (0.002 a.u.) at the PBE1PBE/aug-cc-pVTZ level of theory. It is clear from these diagrams that electrophilic attack will occur primarily at the oxygen atoms, whereas the carbon atom will typically be subject to nucleophilic attack.
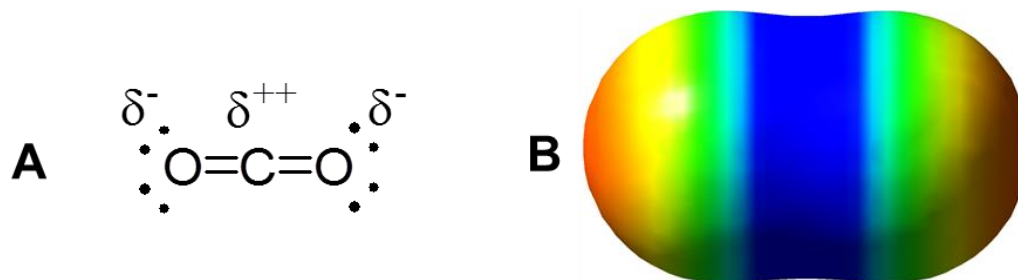
Figure 1: (A) The Lewis structure of CO_2 showing the anticipated charge distribution and (B) the electrostatic potential of CO_2 plotted on the total electron density isosurface (0.002 a.u.) at the PBE1PBE/aug-cc-pVTZ level of theory.

The formation of a strong covalent bond between the Lewis acidic carbon atom of CO_2 and a donor atom of a Lewis base leads to the most common examples of CO_2 complexes found in the literature. Carbamates, formed through the reaction of CO_2 with amines, an interaction taken advantage of in the field of CO_2 capture technology, are one such example. In contrast, examples of weakly bonded complexes of CO_2 are relatively few. The ability to bind CO_2 through the formation of low-energy, easily-broken, bonds could prove invaluable in a variety of contexts. For example, weaker bonds to CO_2 would greatly decrease the cost of the energy-intensive sorbent-regeneration step common to most carbon capture technologies. Furthermore, exploration of this field could lead to the discovery of novel CO_2 chemistry. Reduction of complexed carbon dioxide might generate chemical feedstocks for the preparation of value-added products, particularly transportation fuels or fuel precursors. Implementation on a large scale could help to drastically reduce CO_2 concentrations in the atmosphere.

Many of the complexes containing weak bonds to CO_2 come from the realm of coordination chemistry. Most of the known coordination chemistry of *carbon* involves carbon donating a pair of electrons to a Lewis acid, generating a complex through dative bond formation, as is prevalent in the field of *N*-heterocyclic carbenes (NHCs).[7] Examples of coordination complexes wherein a carbon atom accepts the lone pair of electrons rather than donating it are rare in comparison.[8,9] In the case of carbon dioxide, true coordination complexes to a 'naked' CO_2 fragment are nearly unheard of. These simplest adducts of CO_2 are of particular interest and will be discussed in the final section of this review, but a variety of other complexes of CO_2 featuring diverse binding modes and reactivity will also be examined.

Structurally characterized examples of inclusion complexes of CO_2, wherein the CO_2 is physically adsorbed onto a porous material, will be described first. These are some of the weakest known 'complexes' of CO_2. The CO_2 generally remains in its linear, unactivated, form (Scheme 1A) which sets these examples apart from all the others. Carbamate salts, both zwitterionic (Scheme 1B) and otherwise (Scheme 1C), will be discussed next, as examples of strongly bonded CO_2 complexes. These are the largest class of compounds and, as stated earlier, are heavily involved in current CO_2 capture and sequestration technologies. Also surveyed are the large numbers of insertion complexes of CO_2 that have been prepared (Scheme 1D). These are typically formed through insertion into metal-nitrogen bonds, although a variety of other examples have been uncovered with widely varying CO_2 binding modes. Similar to this latter class of complexes are those not derived through a formal insertion reaction, but that still result in the formation of a structurally similar CO_2 complex (Scheme 1E). The most common examples in this category are complexes derived from frustrated Lewis pair (FLP) chemistry. Common to these base-CO_2 complexes are the presence of other stabilizing interactions, most often between the oxygen atoms of CO_2 and a nearby Lewis acid. Complexes lacking such interactions (Scheme 1F), or with few such interactions, are of particular interest, as mentioned earlier, and include imidazol-2-carboxylates (*N*-heterocyclic carbene adducts of CO_2) as well as a few other examples that lie outside NHC chemistry.

The first structurally characterized complex of carbon dioxide bound to a transition metal was reported by Aresta et al. in 1975.[10] These authors prepared $[Ni(CO_2)(PCy_3)] \cdot 0.75\ C_7H_8$ (Cy = cyclohexyl) and using X-ray crystallography showed the carbon dioxide to be coordinated to the nickel center in an η^2-fashion, through the carbon and one oxygen atom of the markedly bent CO_2. Since that time, many coordination complexes of metals with this type of bonding to CO_2

have been reported (Nb,[11] Mo,[12] Fe,[13] Re[14]), including the recent examples of Beck,[15] Carden[16] and Kim[17] where the reactivity of such complexes is now being explored. Also now known are two forms of η^1-coordination, with CO_2 bound to the metal through carbon or through oxygen in an end-on fashion. Examples of the former include reported coordination complexes of Rh[18] and Ru[19] while the latter is much less common, having been structurally confirmed by Castro-Rodriguez et al. in 2004 for a unique uranium complex.[20] Unusual coordination modes to metals have been described over the years,[21–23] as have CO_2 bridged dimers/clusters of both homo-[24] and hetero-metal centers.[25,26] Insertion products of CO_2 into Metal–X bonds[27] have been reported as have additions of CO_2 to Metal–X coordinated atoms.[28] Because of the large number and wide scope of the products that have been described, metal–CO_2 complexes, have, for the most part, not been included in this review. A recent article in Chemical Reviews on the biochemical and chemical catalysis of CO_2 fixation discusses many of the metal–CO_2 complexes that have been reported to be catalytically active.[29]
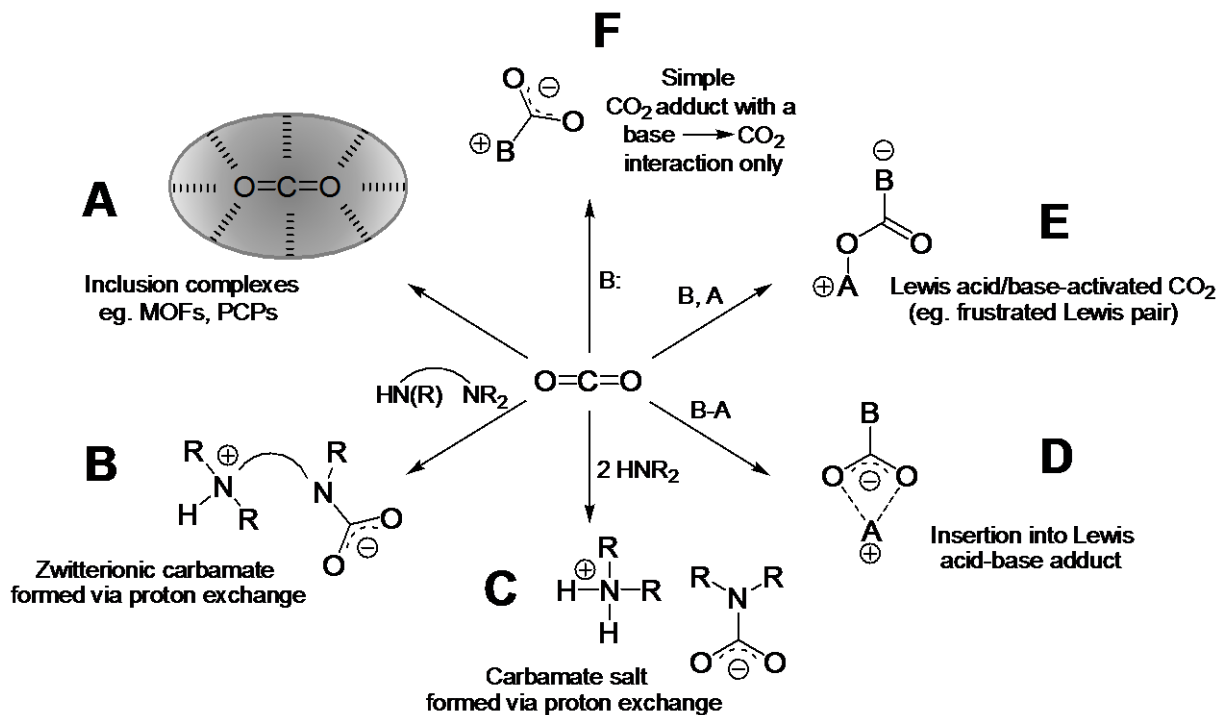
Scheme 1: General structures of some of the types of CO_2 complexes discussed in this review. (A) Inclusion complexes of CO_2 in porous materials. (B) Zwitterionic carbamates produced from the reaction of CO_2 with polyamines. (C) Carbamate salts produced from reaction of CO_2 with two equivalents of an amine. (D) Insertion products of CO_2 into acid-base adducts (*e.g.*, metal complexes). (E) Lewis acid/base activated CO_2, such as frustrated Lewis pair complexes. (F) Simple base-CO_2 adducts, wherein the base-CO_2 bond is the only interaction formed. Bonding modes are variable, particularly for CO_2 insertion products (bottom right). B = Lewis basic species, A = Lewis acidic species, R = any side chain, including hydrogen.

1. Inclusion Complexes of CO_2

The physical adsorption of carbon dioxide and other gases into porous materials, which can occur without drastically altering the original structure, has been extensively studied for potential applications in separation technologies. The incorporation of CO_2-reactive fragments (*e.g.*, amino groups), coupled with their inherently high-surface area, has allowed MOFs and porous coordination polymers (PCPs) to be designed with very high gas-loading capacities. Characterization of inclusion compounds using techniques such as X-ray crystallography has offered insight into their structure and behaviour. In the early 1980s, Gies *et al.* crystallographically characterized two forms of melanophlogite (a naturally occurring silicate mineral), which were determined to include methane, nitrogen and CO_2 as guest molecules using mass spectrometry.[30,31] Later Hirotsu *et al.* reported the crystal structure of a macrocyclic heterocyclophane with CO_2 incorporated into its hydrophobic core.[32] These were the first structurally characterized CO_2 inclusion complexes.

Since then, the number of known CO_2 inclusion complexes has increased markedly. The manner in which the gas is actually adsorbed varies from system to system, both in terms of the placement and the nature of the moieties anchoring the CO_2. For example, CO_2 can adsorb in the central 'hole' of a large cyclic molecule, giving structures which often form channels when stacked in the solid state. Alternatively, CO_2 may adsorb inside a 'cage'-like molecule (*e.g.*, carcerands or hemicarcerands). Adsorption into the space generated *between* molecules in the solid-state is also quite common. Of course, there are many systems that have been shown to physically adsorb carbon dioxide (and other gases) without having been structurally characterized. These will not be discussed here as many other reviews are available on the topic.[33-36]

Adsorption of CO_2 into a framework generated by octahedral manganese(III) atoms bridged by formate ions has been reported.[37] The crystal structure reveals the formation of C–H⋯O hydrogen bonds between carbon dioxide and the hydrogen atom of the formate, a factor likely driving the adsorption. In fact, several other CO_2 inclusion complexes of metal formates feature such interactions.[38] Hydrogen bonds to CO_2 were again observed in a rhodium(II) benzoate-pyrazine complex, formulated as $[Rh^{II}_2(O_2CPh)_4(pyz)]_n$. The complex undergoes a monoclinic to triclinic phase transition upon absorption of CO_2,[39] and the crystal structure of the CO_2-absorbed complex has been determined (Figure 2).[40] The CO_2 molecules are located within a cage formed by aromatic rings belonging to four separate molecules of the dirhodium complex. The oxygen atoms of CO_2 hydrogen bond with specific hydrogen atoms of the phenyl rings forming the cage. In this particular case, interactions of CO_2 with the π-orbitals of the aromatic rings are also thought to help stabilize the structure. In fact, π-type interactions are another recurring feature in complexes of this type.[41-43] In one study investigating a porous calcium sulfonyldibenzoate framework, they have been deemed key for its selective adsorption of CO_2.[44]
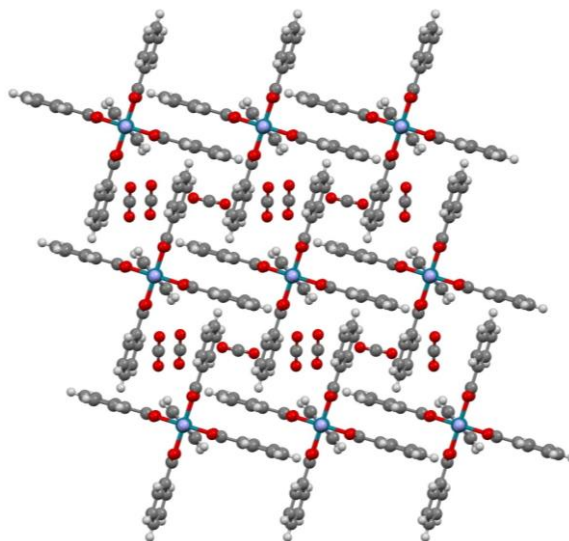
Figure 2: Packing of the molecules in the solid state structure of the rhodium(II) benzoate-pyrazine : 2 CO_2 complex [IKURIP][45] synthesized by Takamizawa *et al*.[39] (Diagram prepared using Mercury CSD 3.3.1[46]).

As alluded to earlier, in the majority of these complexes, the adsorption of CO_2 is accompanied by changes in the unit cell and crystal system (monoclinic to triclinic in both of the cases mentioned above). Crystal-to-crystal transformations are rare but have been observed in other complexes of this type.[47,48] The greater flexibility of these frameworks are thought to have advantages over their more rigid analogues in terms of molecular recognition, separation and sensing applications.[49] In one such system, a *tert*-butylcalix[4]arene bridged by NH groups, the formation of C–H···O interactions (2.47-3.17 Å) between the sorbent and CO_2 was deemed necessary for its adsorption.[50] However, in the case of another complex featuring a Cu(II) pyridine-based framework and generally shorter C–H···O bonds (2.46-2.59 Å), complete desorption of carbon dioxide was described as very difficult,[51] illustrating the very strong stabilizing effect H-bonds can have and the necessity of striking an appropriate balance. The presence of H-bonds, with the oxygen atoms of CO_2 acting as acceptors, are common features in the structures of many other MOFs and inclusion complexes of CO_2, and certainly contribute to the adsorption capacity and stability of these materials.[52,53]

Crystallographically characterized examples of porous materials that do not contain metals, but do include adsorbed CO_2, are quite rare in comparison to their metal-containing cousins. The earliest reported examples have already been mentioned at the beginning of this section. In 2002, an inclusion complex of CO_2 and decamethylcucurbit[5]uril (a macrocyclic *N*-heterocycle-containing compound) was reported,[54] and a few years later so too was a complex of *tert*-butylcalix[4]arene, *t*BC, and CO_2 (Figure 3).[55] The latter was obtained in two forms with 1:1 and 2:1 CO_2:*t*BC loadings. The 2:1 compound was observed to release its second CO_2 molecule over time. That CO_2 molecule was found to be located in the interstitial space between the arene molecules, while the first, disordered, CO_2 molecule was localized inside the cavity. Its increased stability relative to the second CO_2 molecule is presumably due to C–H···O hydrogen bonds formed with the *tert*-butyl groups, however, π-orbital stabilizing interactions of the type previously mentioned might contribute as well.
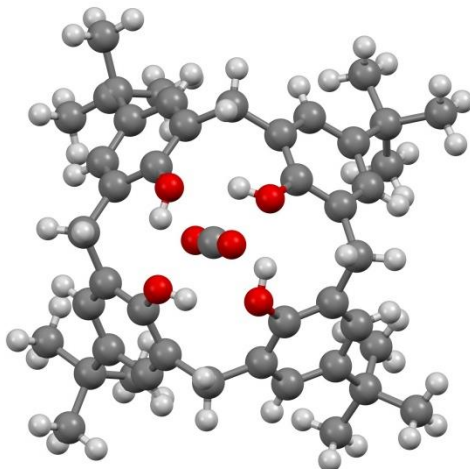
Figure 3: Structure of *p-tert*-butylcalix[4]arene with one molecule of CO_2 adsorbed in the central cavity [MOVMEQ].[45] Disorder of the CO_2 and one of the *t*-butyl groups has been removed for clarity by showing only the main contributor. In the study by Udachin *et al.*[55] additional CO_2 was also adsorbed between the molecules in the 1:2 complex. (Diagram prepared using Mercury CSD 3.3.1[46]).

Decamethylcucurbit[5]uril likely interacts with the carbon atom of CO_2 via partially delocalized lone pairs on its nitrogen atoms. Interactions such as these have been observed in other CO_2 complexes of nitrogen-containing porous materials,[56-59] and some have been studied computationally.[60] The stabilizing effect of nitrogen is not surprising considering the known reactivity of CO_2 towards basic nitrogen atoms, primary and secondary amines in particular, which will be discussed in the next section. Interactions between the carbon atom of CO_2 with oxygen atoms of host-guest complexes are also common,[56,61,62] as are similar interactions with halogen atoms.[63]

End-on (η^1) coordination of carbon dioxide directly to the nickel center of a MOF, nickel(II) dihydroxyterephthalate, has been observed.[64] This coordination-mode is exceedingly rare, having first been observed in 2004 in a uranium complex.[20] In the nickel case, an interaction with a neighbouring oxygen atom of a terephthalate ion to the carbon atom of CO_2 likely aids in its stabilization. The O–C–O angle, which is 162(3)°, deviates significantly from linearity. Coordination of a CO_2 oxygen atom to a lithium ion in a MOF has also been suggested, though not through direct observation of the bond *via* X-ray crystallography.[65]

The development of porous materials for CO_2 adsorption certainly has application in CO_2 capture as well as separation technologies. However, in terms of facilitating a transformation of CO_2, the energy barrier associated with bending the molecule is not overcome in the generation of these complexes. Reaction of physically adsorbed CO_2 within a porous material would likely prove to be a significant challenge, mainly due to the potential for side-reactions occurring with the host material. Any such alteration would, of course, likely lead to desorption of the guest molecule.

2. Carbamates

It has long been known that CO_2 can undergo nucleophilic attack by amines.[66] The first species formed are zwitterionic carbamates with a small charge-separation (only two bonds). However, because of their inherent instability, rapid proton transfer from the attacking nitrogen to another sufficiently basic site occurs. In the vast majority of examples, the base that abstracts the acidic proton is a second equivalent of the attacking amine. Such is the case for monoethanolamine (MEA), where a discrete cation/anion pair is generated (see Scheme 2A). If there is a moiety within the *same* molecule that is sufficiently basic, a zwitterionic species may form (Scheme 2B), such as is observed in the case of diethylenetriamine (DETA). Both types of carbamate have characteristically short C–N bond lengths, reflecting delocalization that leads to the bond having partial double-bond character. The O–C–O bond angles, while generally wider than 120°, are seldom more than 130°. Also worth mentioning are the very rare cases where addition of CO_2 to an amino group results in proton transfer to the newly-formed carboxylate group, generating a carbamic acid (Scheme 2C). Carbamic acids are notoriously unstable towards hydrolysis, as are carbamates; however, they have been isolated and characterized in a few cases.[67-70] Tertiary amines are not known to react with CO_2 on their own. There is no simple way to alleviate the small charge separation that results from addition of a tertiary amine to the CO_2 molecule (*i.e.* there is no proton to transfer).
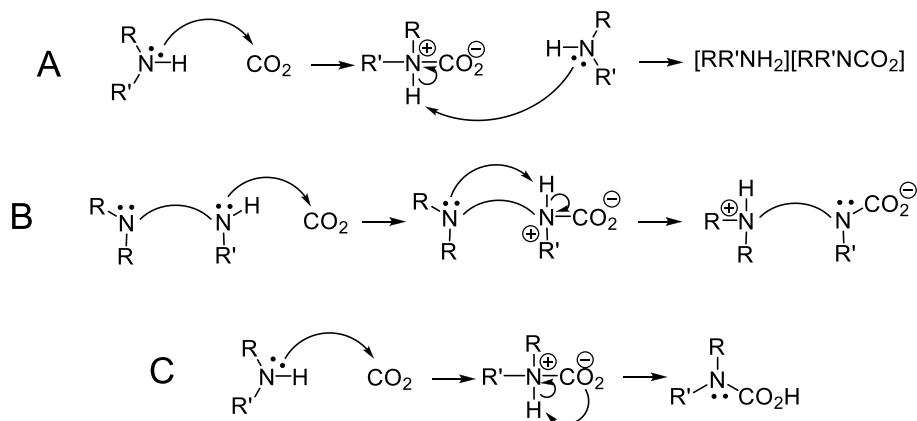

Scheme 2: Reaction of a primary (if R' = H) or secondary amine with carbon dioxide followed by a proton-transfer to (A) a second equivalent of amine to generate a carbamate salt or to (B) another amine group in the same molecule to generate a zwitterionic carbamate or to (C) the produced carboxylate group to form a carbamic acid. In (B) the curved bond represents any groups joining two separated amino moieties in the same molecule.

In an aqueous environment, or even simply in the presence of moisture, the ultimate product of many reactions between amines and CO_2 is a bicarbonate salt. For example, Kuhn *et al.*[71] found that commercial samples of what was supposed to be ammonium carbonate ($[NH_4]_2CO_3$) actually contained ammonium carbamate ($[NH_4][H_2NCO_2]$) which then readily hydrolyzed to ammonium bicarbonate ($[NH_4][HCO_3]$). It is also likely that in high pH aqueous systems (such as in an aqueous amine solution), the high concentration of hydroxide ions leads to a direct reaction with CO_2 to generate bicarbonate, bypassing the carbamate stage altogether.

The products of the reaction shown in Scheme 2A represent the majority of the carbamates found in the literature. The simplest such salt, ammonium carbamate, was crystallographically characterized in 1973,[72] and re-determined in 2006[73] and 2007,[71] revealing the existence of two different polymorphs (α and β). The original α-structure features an extensive hydrogen bond network and a short C–N bond length of 1.361(5) Å. This bond length is indicative of partial double-bond character and stems from the delocalization of the lone pair on the nitrogen into the carboxylate group. As mentioned earlier, the shortened bond length, relative to other C–N single bonds, is characteristic of all carbamates.

Sterically hindered 2-amino-2-methyl-1-propanol has been proposed as an alternative to MEA, the current industry standard for amine-based CO_2 capture. The crystal structure of its CO_2-derived carbamate salt was first reported by Jo *et al*. in 2010.[74] The authors suggested that it might be superior to MEA, if it could be shown to have a weaker bond to CO_2, as this would reduce the energy required to release the captured CO_2. They used theoretical calculations to determine that the bond was indeed weaker, since no crystal structure of MEA-CO_2 was available for comparison. They also observed the hydrolysis of the carbamate to a bicarbonate salt. Interestingly, in another spectroscopic and computational study, it was shown that increased steric bulk around the amino group in amines, such as is observed in *t*-butylaminoethanol or *t*-butylaminopropanol, resulted in CO_2 addition to the hydroxyl end of the molecule rather than to the amino end. Oxygen-bound CO_2 adducts (carbonates) resulted,[75] demonstrating that sterics must be considered when trying to obtain a specific product.

Zwitterionic carbamates, while far less common than discrete carbamate salts, have been prepared and crystallographically characterized. The first such example, the carbamate of ethylenediamine, *N*-(2-ammonioethyl)carbamate (Figure 4), was reported in 1983. The original paper describes two different polymorphs, both of which feature O⋯H–N hydrogen bonds between neighbouring molecules.[76] Later, the structure of the monohydrate was published and, as one might expect with additional hydrogen bond donors and acceptors available, it shows a more extensive hydrogen-bonding network. [77] Crystal structures of similar zwitterionic carbamates are known[78–80] and all of these feature some form of H-bonding to the carboxylate group.
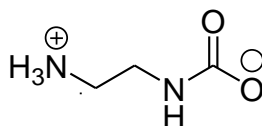
Figure 4: Structural diagram of *N*-(2-ammonioethyl)carbamate, the first crystallographically characterized zwitterionic carbamate.[76]

There is a general trend that emerges upon examination of the crystal metrics of carbamate species, zwitterionic or otherwise. As the C–N bond length of the carbamate fragment increases, there is typically a concomitant increase in the O–C–O bond angle and a decrease in the C–O bond lengths. This observation does not come as a surprise as an increase in the C–N bond length likely reflects it weakening as well. This means that the carboxylate fragment begins to adopt a structure much closer to that of free CO_2. The O–C–O bond angle widens (to approach linearity) and the C–O bonds become shorter with more double-bond character. One could

imagine this effect becoming more and more pronounced until a 'tipping point' is reached where linear CO_2 is released from the base.

Teague *et al.*[81] calculated interaction energies for species of differing Lewis basicity (RO⁻, cyclohexanolate and phenolate ions) with carbon dioxide. Varying the degree of fluorination of the cyclohexanolate and phenolate anions was found to have a direct influence on the calculated CO_2-anion interaction energies as well as on the geometries around the CO_2 fragment. Increased fluorination pulls electron density away from the anionic oxygen atom, decreasing its basicity and lowering the calculated interaction energies. This effect leads to longer C–O(R) bond lengths and wider O–C–O bond angles in the CO_2 fragment. The calculated bond lengths ranged from inarguably covalent (O–CO_2 = 1.506 Å) to much weaker interactions (O–CO_2 = 2.429 Å), such as those observed in the inclusion complexes of CO_2 described in the previous section.

3. Carbamato and Carboxylato Complexes

Hydrogen bonding is not the only interaction that adds to the stability of carbamates. Coordination of carboxylate oxygen atoms to metals or main group elements has been observed in a variety of complexes. Carbamato complexes are normally produced through formal insertion of CO_2 into a bond between nitrogen and, most commonly, a metal atom. Insertions of CO_2 into Mg–N bonds have been the most frequently reported. These result in the formation of polynuclear Mg-carbamato complexes, investigations of which are often geared towards CO_2 activation.[82,83] Others have drawn comparisons between these complexes and those that may be generated in the magnesium-containing active site of the enzyme Rubisco (Ribulose-1,5-biphosphate carboxylase/oxygenase) during the biochemical fixation of CO_2.[84] Various binding modes have been identified in Mg-carbamato complexes,[85,86] some of which are shown in Figure 5. The C–N bond lengths and O–C–O bond angles generally remain comparable to those in H-bonded carbamate salts and zwitterions, suggesting that these species are no less stable.
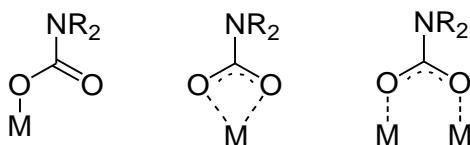
**Figure 5:** Some examples of binding modes of carbamato ligands to metal centers.

Insertions of carbon dioxide into Li–N,[87-89] B–N,[90] Al–N[91,92] and Ga–N[93] bonds have also been reported, all resulting in the generation of polynuclear carbamate complexes with multiple O–A bonds (where A = Li, B, Al or Ga). CO_2 insertions into Cu–N,[94] Zn–N,[94] Sb–N[95] and Sn–N[95] bonds have been shown to give more than one carbamato ligand bonded to the central atom and, in the case of tin, bridging carbamato ligands are sometimes present as well.[95,96] The only other carbamato complexes that need to be mentioned here are two phosphorus-carbamato examples, prepared from P(V) compounds. Fluorinated ligands (or fluoride itself) bound to the phosphorus increase its electrophilicity, which certainly aids in the stabilization of these species.[97,98]

CO_2 insertion reactions are, of course, not limited to the production of carbamato complexes. Utilizing phosphorus as a base (rather than as an acid as in the last examples), a number of CO_2 insertion complexes have been prepared, all containing new P–C bonds. This

normally occurs in conjunction with coordination of CO_2 *via* its oxygen atoms to a Lewis acidic center, again typically a metal or a group 13 element. Similar complexes of activated CO_2 that do not stem from true insertion reactions are also well known, most of these coming from the rapidly expanding field of frustrated Lewis pair (FLP) chemistry (*vide infra*). These latter complexes are typically derived from attack of a bulky Lewis base, most commonly a phosphine, on the electrophilic carbon atom of CO_2, while simultaneously an interaction forms between oxygen of the CO_2 and a Lewis acid, often a borane or an alane.

The insertion reactions of CO_2 are often touted as being reversible, and sometimes easily so. This implies some degree of instability relative to their carbamato cousins which are usually quite stable. In carbamato complexes, the orbital overlap between CO_2 and the lone pair-bearing nitrogen results in a relatively strong C–N bond with partial double-bond character. Due to the mismatch of orbitals that is introduced on moving down the periodic table to phosphorus, it can be assumed that the C–P bond-shortening will not be as pronounced, giving an overall weaker interaction compared to that resulting in C–N bond formation. For instance, Dickie *et al.*[99] generated a bridging CO_2 complex through insertion into a tin-phosphorus bond. The new P–C bond lengths were significantly longer than the other P–C single bonds present in the structure, and the complex was found to release its CO_2 upon heating or standing. A zinc-phosphorus insertion product was also prepared and, although its stability was not specifically investigated, the corresponding CS_2 adduct was found to dissociate readily in solution.[100] Binding of carbon dioxide between aluminum and phosphorus centers in the complex, $Al(C_6H_4(o\text{-}PPh_2))_3$, could be reversed by simple exposure to a nitrogen atmosphere.[101]

Activation of carbon dioxide is one of the 'tests' performed to investigate potential FLP activity. With the vast number of Lewis acids and Lewis bases available for these applications, there are many FLP systems that should be capable of activating carbon dioxide. In terms of Lewis bases, phosphines, amines and carbenes have all been used, while boranes and alanes remain the acids of choice. The increased reactivity of alanes (compared to boranes) toward oxygen-containing compounds is a useful feature. It diminishes the need for highly-fluorinated groups around the group 13 center, the preparation of which can be rather costly, while still maintaining reactivity. However, while alane-based FLPs are quite capable of activating CO_2, the resultant adducts are often quite stable,[102,103] and in some cases the reaction becomes irreversible.[104] Because of this stability, reactions at the CO_2 center can be accomplished without its release, facilitating its reduction to, for example, carbon monoxide[105,106] or methanol.[107]
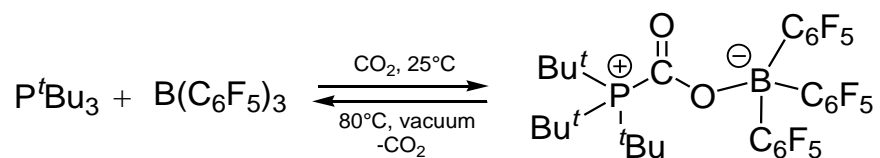
Scheme 3: One example of an FLP activating CO_2 to generate a complex. This particular reaction is reversed through heating under vacuum.[108]

Many borane-based FLPs also bind CO_2 to form stable adducts, requiring the use of forcing conditions (typically high temperature and vacuum) to release the CO_2.[109,110] Again, the fact that these complexes are so stable is not necessarily a disadvantage, depending on their ultimate use. Easily-reversible binding of carbon dioxide requires the formation of weak

interactions between the Lewis acid and the base, and there are already examples of FLPs that bind CO_2 and release it at remarkably low temperatures (~ −20°C).[108, 111] Drawing useful comparisons between FLP systems is quite difficult as there simply are not enough complexes of a single 'type' to reliably identify trends. For instance, a bridged-FLP, $(Me_3C_6H_2)_2P-CH_2CH_2-B(C_6F_5)_2$, was found to bind CO_2 but released it above −20°C in dichloromethane.[108] Meanwhile, another bridged-FLP not dissimilar in structure, $tBu_2P-CH_2-BPh_2$, was stable to CO_2 loss even at 100°C under vacuum.[109] The increased stability of the latter was attributed to its smaller bite angle (one less carbon in the $P-(CH_2)_x-B$ chain), but the borane fragment was also not fluorinated. Using a non-fluorinated borane in an FLP system to activate CO_2 was unprecedented and gave no basis for comparison of its effect on the stability of the product.

The vast majority of the Lewis bases used in FLP chemistry (with the exception of carbenes) do not react with carbon dioxide on their own. It is the presence of the Lewis acid that stabilizes the adduct formed, just as it is with the CO_2 adducts described in previous sections. For instance, neither tertiary amines nor phosphines react with carbon dioxide on their own, but both have been used in FLP systems to activate CO_2.[112] One FLP combination that was found to activate CO_2 clearly stands above the others in terms of the fragility of the complex produced. The combination of N,N-dimethylaniline (a tertiary amine) and tris(pentafluorophenyl)borane reacts with carbon dioxide at low temperatures (−32°C) to give the adduct shown in Figure 6A.[113] As with some other FLP combinations, CO_2 is released at low temperatures (> −20°C), but it is not this fact alone that makes this particular example so remarkable. The crystal structure of the adduct reveals an O=C bond length in the CO_2 fragment of only 1.193(3) Å, much closer to that of gaseous CO_2 (1.1602(8) Å)6 than many of the other structures discussed thus far. Furthermore, the O–C–O angle of the fragment was found to be 133.1(2)°, which is wider than that of any carbamate yet reported. The angle is also wider than that in any known NHC-CO_2 adduct, with the sole exception of the super-bulky imidazol-2-carboxylate shown in Figure 6B (O–C–O = 133.8(5)°).[114]
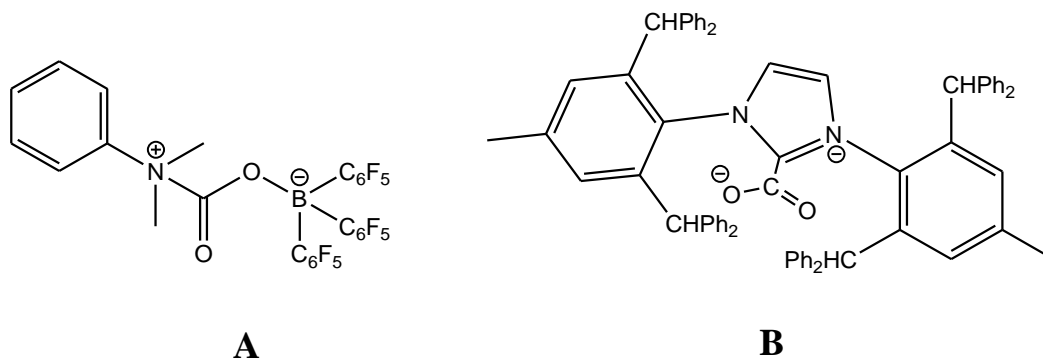
Figure 6: Structural diagrams of (A) the CO_2 complex of the FLP combination of tris(pentafluorophenyl)borane and N,N-dimethylaniline,[113] and (B) the carboxylate adduct of the super-bulky carbene, 1,3-bis(2,6-dibenzhydryl-4-methylphenyl)imidazol-2-ylidene.[114] Both of these complexes have O–C–O bond angles greater than 133°.

4. Simple Base→CO_2 Adducts

All the structures described in the previous sections have stabilizing interactions which help to keep the carbon dioxide bound to whatever has managed to complex it. At one end of the spectrum are the inclusion complexes of carbon dioxide described in Section 1. These materials are capable of adsorbing carbon dioxide without significantly altering its structure (*i.e.* the CO_2 is not bent). Certain ionic liquids are also able to dissolve surprisingly large amounts of carbon dioxide, even when there is no moiety within the ionic liquid designed to chemically react with the gas. In these cases, especially for imidazolium-based ILs, weak cation-anion interactions and hydrogen bonds are often invoked to explain the observed solubility.[115,116]

Beyond the realm of simple capture-and-release applications of carbon dioxide, bending/activating carbon dioxide for its use as a chemical feedstock is required. This leads to the other end of the spectrum, *i.e.* strong nucleophiles which take advantage of the fact that the carbon atom of CO_2 is weakly electrophilic to form N_{nucl}–C bonds. The issue with such activating reactions lies with the difficulty in reversing them. Breaking the bond to the carbon atom of CO_2 is clearly the dominant interaction that must be overcome to reverse the reaction, however, other weaker interactions, if present, must be overcome as well. For instance, H-bonding and/or coordination through oxygen to Lewis acidic sites are prevalent in all the structures described in Sections 2 and 3, although admittedly the contributions of these interactions in solution are not known. Eliminating these interactions may render the CO_2 adducts less stable or even completely unstable. A balance must be struck between the stabilizing effect of the interactions on the complex and minimizing them in order to potentially access novel chemistry about the carbon atom of CO_2.

4A. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)

In the literature, examples of CO_2 adducts with minimal stabilizing interactions are very rare. The properties of a complex, including its experimentally observed stability and, particularly, the geometry around the carboxylate fragment, are helpful in deducing the strength of the CO_2 interaction. One example of such a weak complex is the adduct formed between carbon dioxide and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) which was crystallized, after repeated failures, by Villiers *et al.*[117] in 2010.
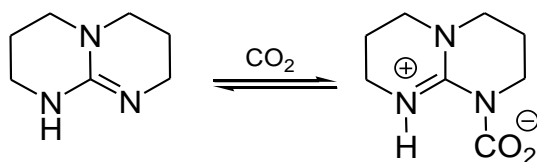
Scheme 4: Reaction of carbon dioxide with TBD to generate a zwitterionic adduct.[117]

The only apparent stabilizing factor in the TBD-CO_2 adduct, other than charge delocalization in the ring, is a sole internal hydrogen bond (1.73Å, derived from N···O = 2.535(2) Å, N–H = 0.95 Å, and N–H···O = 139.8°) between a carboxylate oxygen and the protonated nitrogen in the same zwitterion. Although there are other, intermolecular, hydrogen bonds present in the solid state structure, they are quite long (H···X ranging from 2.50-2.55 Å). The adduct is, unsurprisingly, sensitive to hydrolysis, which leads to formation of the corresponding [TBDH]$^+$ bicarbonate salt. The same salt was repeatedly isolated during attempted

preparations of the zwitterion. This adduct not only has the widest O–C–O angle of any characterized carbamate (128.6(2)°) it also has the longest N–C bond (1.480(3) Å). Short N–C lengths are typical of carbamates due to the delocalization effect of the carboxylate group described earlier.

The isolation of the TBD-CO_2 adduct substantiated the previously proposed mechanism for the TBD-catalyzed production of organic carbonates, which had been speculated to proceed *via* the generation of the zwitterionic species shown in Scheme 4. [118] 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 3,3,6,9,9-pentamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene (PMDBD), both of which have reactivities similar to that of TBD, also form zwitterionic complexes with CO_2, as confirmed by NMR spectroscopy. To date, no crystal structures of these particular adducts have been obtained; rather, all attempts at crystallization have led to bicarbonate salts.[119,120] 1,4,5,6-tetrahydropyrimidine (THP) and its derivatives have also been speculated to form similar zwitterionic CO_2 adducts.[121,122]

The TBD-CO_2 complex was subsequently used as a base, promoting reductive and reversible insertion of CO_2 into O–H and N–H bonds.[123] These latter reactions are important in the field of switchable solvents. The first ambient pressure switchable solvent discovered involved insertion of CO_2 into the O–H bond of an alcohol. The system was the combination of a nitrogen base, DBU, and 1-hexanol, both neutral molecules, which gave an ionic liquid with markedly altered physical properties upon the addition of CO_2. This was achieved through the formation of an alkoxide salt of the protonated base through CO_2 insertion into the O–H bond, followed by proton transfer to the base. The reaction could be reversed under incredibly mild conditions (*e.g.*, bubbling nitrogen through the solution to remove the CO_2).[124] Other switchable solvent systems have been discovered since then.[125]

### 4B. Imidazol-2-Carboxylates and Related Complexes

Another interesting class of CO_2 adducts with small bond dissociation energies are those formed with N-heterocyclic carbenes (NHCs). It was not until nearly a decade after the first stable crystalline carbene had been isolated and characterized by Arduengo *et al.*[126] that the first NHC-carboxylate was prepared by Kuhn *et al.*[127] Reaction of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene with carbon dioxide generated the corresponding imidazol-2-carboxylate (Scheme 5). The carboxylate was found to be reactive toward thionyl chloride giving the cationic acid chloride, which was then converted to its corresponding methyl ester with methanol.
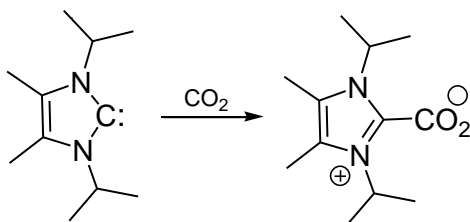
Scheme 5: The preparation of the first imidazol-2-carboxylate, 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, as reported by Kuhn *et al.*[127]

The imidazol-2-carboxylates, also known as NHC-carboxylates (NHC-CO_2), are an important class of CO_2 coordination complexes. In the most common preparation, the carbene

precursor donates its lone pair to the electrophilic carbon atom of CO_2 generating a zwitterionic carboxylate, as shown in the example in Scheme 5. There are, however, other methods that can be used to prepare these complexes. For example, Holbrey *et al.*[128] synthesized an NHC-CO_2 complex through the reaction of the imidazole precursor with dimethylcarbonate (DMC), which they proposed to occur *via* generation of a carbene intermediate as shown in Scheme 6.
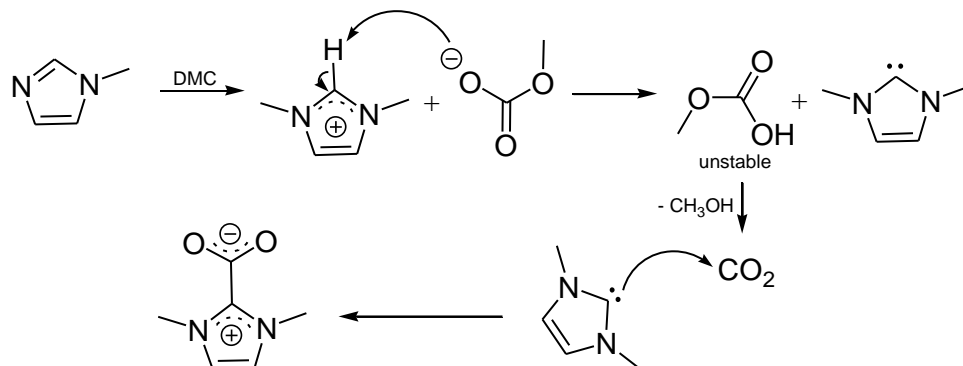
Scheme 6: Proposed mechanism of NHC-CO_2 synthesis from the imidazole precursor and dimethylcarbonate (DMC), proceeding through a carbene intermediate.[128]

The earliest reported work with NHC-carboxylates focused on the ability of Me_2I^iPr-CO_2 to ligate to transition metal centers, also the most common application of its carbene precursors at the time. Kuhn *et al.* found that the rather weak interaction of NHC-carboxylates to titanium centers was more akin to those of dithiocarboxylates rather than those of the more structurally similar classic carboxylates, probably since the charge-neutral (zwitterionic) adduct forms a weaker interaction with a metal center than an anionic species would.[129] It should be noted that a carbene-like carbodiphosphorane adduct of CO_2 has also been prepared.[130] It has a C–C bond length of 1.494(3) Å[131] and displayed better metal-coordinating abilities than Kuhn's carbene-CO_2 adduct (1.536(5) Å),[127] although it was also found to be more sensitive to hydrolysis.[132]

The utility of NHC-CO_2 adducts as ligands was limited, so focus instead turned to the nature of the generated C–C bond between the carbene and CO_2. Duong *et al.* addressed the issue of bond stability experimentally.[133] Complexes of CO_2 with 1,3-dimesitylimidazol-2-ylidene (IMes) or 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) could be prepared as air-stable solids, but decomposed in aerated solution. Furthermore, exchange of the carboxylate group with $^{13}CO_2$ was observed by NMR spectroscopy, and thermal decarboxylation could be seen in the TGA. Finally, crossover experiments were conducted with IMes-CO_2, IPr-CO_2 and Me_2I^iPr-CO_2. Addition of Me_2I^iPr to either IMes-CO_2 or IPr-CO_2 generated iPr_2Im-CO_2 and IMes or IPr, respectively, after CO_2 transfer. Addition of IMes to IPr-CO_2 gave IMes-CO_2 and IPr. The relative stabilities of the NHC-carboxylates could be ordered based on these observations: Me_2I^iPr-CO_2 > IMes-CO_2 > IPr-CO_2. NHC-carboxylates were also found to be sensitive to decarboxylation by protic acids such as HPF_6, HCl, H_2SO_4 and picric acid, generating the corresponding imidazolium salts of the conjugate base of the acid. A novel route for the synthesis of imidazolium-based ionic liquids was thus discovered.[134] It is also interesting to note that imidazolium-based ionic liquids have been converted electrochemically to the corresponding carbene, with simultaneous addition of CO_2 being used to generate NHC-carboxylates. Decarboxylation was achieved by heating, returning the generated carbene.[135]

Van Ausdall *et al.* have investigated the underlying factors responsible for the decarboxylation of NHC-carboxylates and proposed a number of relationships between decarboxylation temperature (as determined by TGA) and structural features of the complexes.[136] Additional electron density in the imidazolium ring, provided by alkylation of the backbone, was found to have a stabilizing effect, likely due to the enhanced basicity of the carbene. This effect was also reflected in a shortening of the $C-CO_2$ bond lengths. Furthermore, the dihedral angle between the plane of the imidazolium ring and the plane of the carboxylate group directly correlated with the temperature required for decarboxylation. As the bulkiness of the *N*-substituents increased, the carboxylate group was typically oriented more perpendicularly to the ring, which led to a lengthening of the C–C bond and a lowering of the decarboxylation temperature. These observations were explained by a decreased orbital interaction between the carboxylate and the imidazolium ring. A subsequent computational study by Ajitha and Suresh supported these findings and also found that the inclusion of *N*-substituents containing H-bond donors markedly increased the binding affinity of CO_2 to the carbene.[137] This should come as no surprise considering the effect H-bonding has on the other CO_2 adducts described.

The dynamic nature of NHC-carboxylates, coupled with their surprising air-stability in the solid state, was soon recognized as advantageous in terms of their use as protected versions of NHCs. NHCs are versatile ligands and catalysts in a variety of applications, even though they are very moisture sensitive. As a result, the *in situ* generation of carbenes, after decarboxylation of an NHC-carboxylate precursor, was found to be effective. The method has been utilized in the coupling of CO_2 with epoxides or aziridines,[138 - 140] polyurethane synthesis,[141] transcarboxylation,[142] transesterification and benzoin condensation reactions,[143,144] and ring-opening polymerization.[145] In fact, in one polymerization study[114] a remarkable solvent effect was observed. Reaction times decreased for the IMes-CO_2 catalysed polymerization of *rac-β*-butyrolactone while yields increased dramatically as the solvent polarity was increased (*e.g.*, 71% yield over 300 minutes for toluene, compared to 95% yield over 150 minutes for DMSO) even though the authors claim that dissociation of IMes-CO_2 is not promoted in polar solvents. On the contrary, an earlier work describes the decarboxylation of a nitronyl carboxylate (Figure 7), structurally similar to imidazol-2-carboxylates, as occurring readily in polar solvents. These authors suggest that this to be due to the weak $C-CO_2$ bond in the complex.[146]
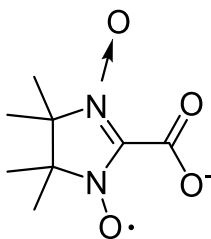
Figure 7: Structural diagram of a nitronyl carboxylate as reported by Tretyakov *et al.*[146]

As with the inclusion complexes of gaseous CO_2, H-bonding interactions are observed in some NHC-CO_2 complexes. These typically involve backbone hydrogen atoms and undoubtedly they help in the stabilization of the resulting complex.[147] Benzimidazole-2-carboxylates also feature extensive hydrogen bonding in the solid state. The added stability provided by their fused ring structures allows the *N*-substituents to be hydrogen atoms, as opposed to the bulky side groups utilized in most NHCs.[148-151]

Gurau *et al.* [152] found that bubbling CO_2 into the ionic liquid 1-ethyl-3-methylimidazolium acetate, [EMIM]OAc, promoted the deprotonation of the cation by the acetate anion, generating acetic acid. Subsequent addition of CO_2 to the generated carbene gave a complex which was crystallized as the [EMIM][H(OAc)$_2$][EMIM-CO$_2$]. The solid state structure features stabilizing H-bonds between the [EMIM]$^+$ cation and the carboxylate group, as well as an acetate-acetic acid anion dimer, as shown in Scheme 7.
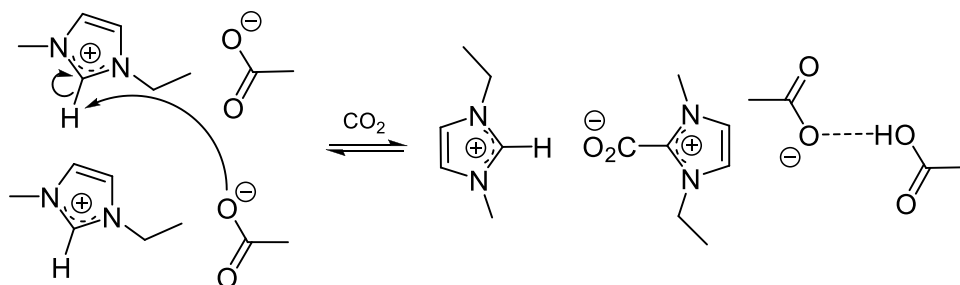
Scheme 7: Scheme for the reaction between two molecules of [EMIM]OAc and CO_2. An acetate ion deprotonates an [EMIM]$^+$ ion, generating the corresponding carbene that goes on to form an NHC-CO$_2$ complex. The generated acetic acid forms a complex with a second acetate ion, balanced by a second [EMIM]$^+$ cation.[152]

Finally, on a related note, *N*-heterocylic olefins (NHOs) have also been found to display remarkable reactivity towards CO_2. NHOs can be thought of as derivatives of NHCs. Their main structural difference is the presence of an exocyclic double bond at the, formerly, carbeneic carbon atom. Because the imidazolium ring can delocalize a positive charge, this exocyclic double bond is highly polarized. There are significant contributions from several different resonance structures rendering the exocyclic carbon nucleophilic. A general scheme for the reaction of an NHO with CO_2 is shown in Scheme 8.
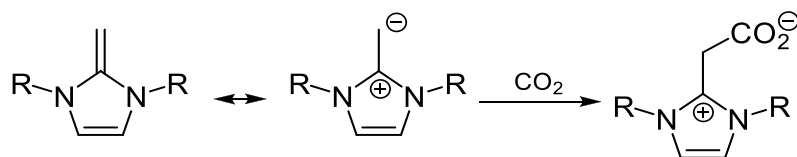
Scheme 8: Reaction of a general *N*-heterocyclic olefin with carbon dioxide. Two possible resonance structures are shown for the *N*-heterocyclic olefin.

NHO-CO$_2$ adducts have been prepared by Wang *et al.*[153] and they feature C–CO$_2$ bond lengths that are significantly longer than those in corresponding NHC-CO$_2$ adducts. They also have wide O–C–O angles, approaching 130°. These features, the authors suggest, should lead to easier decarboxylation. Indeed, they did observe decarboxylation of some samples in dichloromethane at moderate temperatures (40-80°C). These same NHO-CO$_2$ adducts were also found to be 10-200 times more effective at catalyzing the formation of cyclic carbonates than the corresponding NHC-CO$_2$ adducts, again supporting the idea that facile decarboxylation generates an active NHO catalyst.

4C. Halide and Pseudo-halide Adducts of CO_2

The simplest possible adducts of CO_2 with a Lewis base would be those wherein the base is composed of only one or two atoms, *i.e.* the halides and pseudo-halides. The two most commonly encountered examples that could be argued to fall into this category are the complexes of CO_2 with hydroxide ion (bicarbonate) and hydride ion (formate). It is important to remember that, by definition, a weak adduct of a base and CO_2 must have individual constituents that are nearly as stable as the complex. Adhering to this definition eliminates formate, as the hydride ion is not stable. While the hydroxide ion is certainly more stable than hydride, bicarbonate salts tend to pack in complicated hydrogen bonded networks that serve to shift the equilibrium toward their formation, accounting for the abundance of HCO_3^- salts in the literature.

The only halide-CO_2 complex that has been isolated and structurally characterized is a salt containing the fluorocarbonate anion.[154] Unlike the other halides, fluoride has long been predicted to bond with CO_2, giving (at least theoretically) complexes held together by more than simple electrostatic interactions.[155,156] More recently, the chemistry of CO_2 with the heavier halides has been studied both computationally and in gas phase experiments. Hiraoka *et al.*[157] investigated clusters of CO_2 around a chloride ion and observed very small enthalpy changes indicative of the formation of electrostatic interactions. Calculations also revealed small deviations from linearity in the CO_2 molecules, which they tentatively attributed to the contribution of weak charge-transfer interactions. Soon afterward, they expanded their study to bromide and iodide ions whose interactions with CO_2 they deemed likely to be primarily electrostatic as well.[158]

Photoelectron spectroscopic studies of halogen-CO_2 clusters have shed more light on the interactions present in these types of systems. Arnold *et al.*[159] generated photoelectron spectra of $I^-(CO_2)_n$ clusters and deduced from their observations that perturbations in the O–C–O bond angle of CO_2 were being caused by the iodide ion. Subsequent studies found similar distortions in the CO_2 clusters of bromide and chloride ions. In such a charge-quadrupole interaction, the negative charge (the halide ion) attracts the center of the quadrupole (the carbon atom of CO_2) and repels the ends of the quadrupole (the oxygen atoms), distorting the molecule. The cause of these distortions was thought by the authors to be predominately electrostatic, though small contributions from charge-transfer interactions were postulated to be a factor as well.[160,161]

Surprisingly, only two complexes of CO_2 with small anionic donors have been isolated and conclusively characterized. The first is the adduct of carbon dioxide and fluoride mentioned above, isolated and characterized for the first time in 1995 by Zhang *et al.*[154] as the hexamethylpiperidinium salt [ZAQBIE].[45] The second is the complex of cyanide and carbon dioxide, a cyanoformate salt, which Murphy *et al.*[162] recently isolated and fully characterized [HOBBAD].[45] Both of these complexes were prepared through direct exposure of the fluoride or cyanide precursor salts to CO_2.
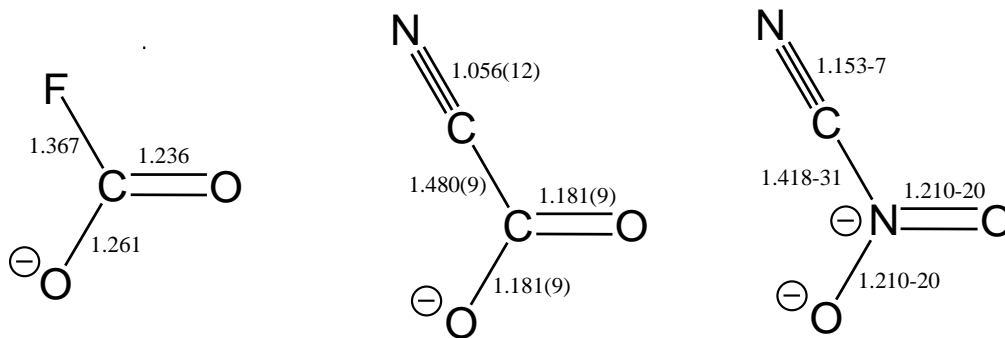
Figure 8: Structural diagrams of fluorocarbonate (left),[154] cyanoformate (middle)[162] and nitryl cyanide (right)[163] ions. Crystallographically determined bond lengths (Å) for fluorocarbonate and cyanoformate are included. The bond lengths reported for nitryl cyanide are calculated values. Estimated standard deviations for the bond lengths in the fluorocarbonate anion are not available.

Both fluorocarbonate and cyanoformate ions are sensitive to hydrolysis. This is not surprising considering the stable products formed upon addition of water (bicarbonate and either HF or HCN). Zhang *et al*. note the spontaneous formation of bicarbonate from fluorocarbonate in the presence of moisture and they also report the crystal structure of hexamethylpiperidinium bicarbonate (acetonitrile solvate).[154] Murphy *et al*. observed the same tendency toward hydrolysis, isolating crystals of tetraphenylphosphonium bicarbonate hydrate.[162]

The cyanoformate ion has been shown, by both experiment and computation, to be on the verge of dissociation. *In situ* infrared analysis revealed that cyanoformate fragments into its constituents in polar media (*e.g*., acetonitrile), while in non-polar media (*e.g*., toluene) it was stable for a longer time. This has been attributed to the delicate nature of the C–C bond, and the lower solubility of CO_2 in polar solvents, which minimizes the time it remains in solution after dissociation.

There is nothing in their geometries that would lead one to assume a weak C–F or C–C bond in [FCO$_2$]⁻ or [NCCO$_2$]⁻, respectively. Zhang *et al*. describe the C–F bond as strikingly long, however, the bond length they are referring to is one obtained computationally and it is indeed much longer than the bond found in their crystal structure (1.446-1.505 Å calculated, and 1.367 Å in the solid state).[154] In cyanoformate, the C–C bond length of 1.480(9) Å is only very slightly longer than that of a typical sp^2–sp C–C single bond.[164] However, looking at the other bonds in the cyanoformate ion does offer some insight into how close to fragmentation it is. The C–N and C–O bond lengths are actually shorter than what would typically be expected for nitrile and carboxylate groups, respectively. In fact, these lengths are much closer to what might be expected for the isolated constituents, *i.e*. cyanide ion and carbon dioxide. This is most pronounced in the length of the two equivalent C–O bonds, 1.181(9) Å. Carbon dioxide itself has C–O bond lengths of 1.1602(8) Å.6 The experimental O–C–O bond angle in cyanoformate is 125(1)° and was calculated to be 133° at various levels of theory. π-bonds of *sp*-hybridized carbon atoms (free CO_2) are stronger than π-bonds at sp^2-hybridized carbon atoms (bound CO_2),[165] and there is also a decrease in entropy upon complexation. Both of these facts favour dissociation of the cyanoformate ion. The relatively large angle of the O–C–O fragment suggests that CO_2 is poised to escape its bond and return to its linear form.[166,167]

The isolation of tetraphenylphosphonium cyanoformate by Murphy *et al*. was preceded by the gas phase identification of cyanoformate by several groups. Larson *et al*.[168] investigated the binding of cyanide ions with various Lewis acids using ion cyclotron resonance and high-pressure mass spectrometry. Their particular technique led to the generation of cyanoformate ions *via* dissociative electron attachment to ethyl cyanoformate. Later, Martin *et al*.[169] studied the photodissociation of $ICN^-(CO_2)_n$ clusters, which also led to the generation of gaseous cyanoformate ions through photofragmentation of ICN^- to CN^- and its subsequent addition to CO_2. They also calculated geometrical parameters for cyanoformate at various levels of theory, including O–C–O angles which ranged from 133-7°. Furthermore, cyanide was rotated into different positions relative to the central CO_2 as energy minima were searched for. Those obtained, other than the cyanoformate ion itself, corresponded to solvated complexes, with the CO_2 fragment adopting a slightly bent geometry. The O–C–O angles were observed to fall in the range of 169-175°, which the authors suggested was due to a weak charge-transfer effect.

Conclusions

The ability to reversibly form adducts of carbon dioxide with almost no energy barrier in either direction is an incredibly valuable tool. The complexes and subsequent reactions outlined in this review illustrate the remarkable advantages that come with the generation of weakly bound CO_2 species. While many of these species are highly sensitive to external conditions, particularly hydrolysis, others have proven to be more robust and are already finding uses in real world applications (*e.g*., switchable solvents). Further investigation of weak complexes of carbon dioxide will surely uncover new methods to more reliably prepare and handle these fragile species. The catalytic conversion of CO_2 to useful products, as well as carbon capture and release technologies, will benefit from continued research in this field.

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