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Redox active aluminium(III) complexes convert CO₂ into MgCO₃ or CaCO₃ in a synthetic cycle using Mg or Ca metal†‡

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Redox-active Group 13 molecules possess the unusual combination of concomitant redox and acid–base reactivity. These combined properties enable regeneration of a metal hydroxide complex in a cycle for conversion of CO_2 into carbonate salts. Reaction of $(IP^-)_2Al(OH)$ (M = Al, Ga) with 1 atm of CO_2 affords $[(IP^-)_2Al]_2(\mu^2\kappa^1{:}\kappa^2\text{-}OCO_2)$. Subsequent reduction affords $MgCO_3$ or $CaCO_3$ and two equivalents of $[(IP^{2-})_2Al]^-$, which can be reoxidized to $(IP^-)_2Al(OH)$ to close a cycle.
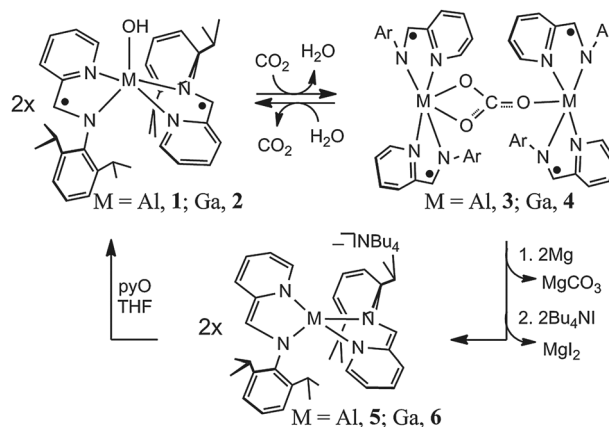
The activation and functionalization of CO_2 is under investigation for formation of fuels and commodity chemicals such as CO,[1] methanol,[2] and formate or formic acid,[3] amongst others. The formation of carbonate salts from CO_2 is another example of a potential means to sequester and store CO_2 as a useful product.[4] For example, the aragonite form of $CaCO_3$ is used industrially on extremely large scales as the major ingredient for concrete and $MgCO_3$ is important, also on large scales, in a variety of applications such as fillers, drying agents, or whiteners. The removal of CO_2 from smoke stacks is desirable for the reduction of greenhouse gases in the atmosphere, and the use of CO_2 as a feedstock for fuels and chemical could contribute to its consumption and recycling. It is well-known that strong bases react with CO_2 to form carbonate salts as in the Solvay process,[5] however methods are needed to recycle the large quantities of base currently used for such processes. Thus, the use of a regenerable hydroxide to afford carbonates from CO_2 would be a desirable process.

We have been interested in redox active iminopyridine (IP) ligand complexes of the Group 13 metals, and these complexes possess an unusual combination of properties.[6] The complexes have highly Lewis acidic metal centres combined with a capability for performing redox reactions. In addition, the high Lewis acidity of aluminium(III) and gallium(III) should render their hydroxide

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complexes, $(IP^-)_2M(OH)$ (where M = Al, **1**; or Ga, **2**), highly nucleophilic and reactive toward CO_2.[7,8] In combination with the relative scarcity of monomeric Al(III)–OH and Ga(III)–OH complexes, and hence their relatively unexplored reactivity,[9] this unusual combination of properties prompted us to explore the reactivity of $(IP^-)_2M(OH)$ with small molecules.

Reactions of the zinc-containing carbonic anhydrase enzyme,[10] its model complexes,[11] and hydroxo complexes of acidic ions such as Cd(II),[12] and Sn(IV),[13] with CO_2 have demonstrated that formation of a carbonate complexes results from reaction of the basic M–OH unit with CO_2. Dinuclear μ-OH-bridged binuclear transition metal complexes have also been shown to afford carbonate from CO_2.[14] In most of these examples, the metal carbonate complex is the final product of the reaction.

When 1 atm of CO_2 was introduced into a hexanes solution of $(IP^-)_2Al(OH)$ a green precipitate was formed within 3 h (**3**, Scheme 1). Single crystals of **3** were grown by the diffusion of pentane into a concentrated THF solution of **3** at $-25\ ^\circ C$ over 1 week (Fig. 1, Tables S1, S2, ESI‡). The solid state structure revealed that an acid–base reaction occurred and no change to the IP^- ligand oxidation state was apparent. Each of the four IP ligands has bond lengths and angles consistent with the
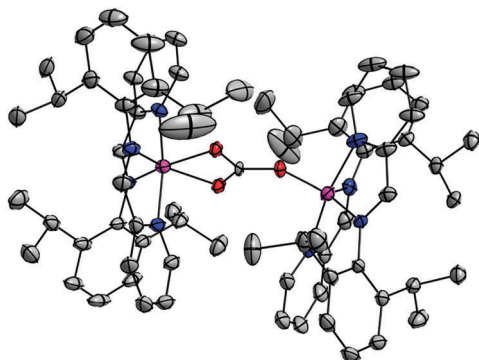

Scheme 1

Fig. 1 Solid state structure of $[(IP^-)_2Al]_2(\mu^2\kappa^1:\kappa^2\text{-}OCO_2)$ in **3**. Pink, grey, blue, and red, ellipsoids represent Al, C, N, and O atoms, respectively. Ellipsoids at 50% and H atoms are omitted.
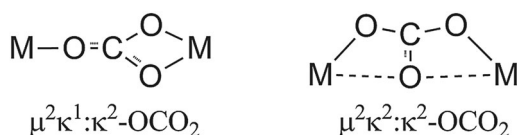

Chart 1

one-electron reduced oxidation state,[6a] and there are two inequivalent aluminium centres in **3**: one is five-coordinate and the other is six coordinate. Overall, the molecular formula for **3** is $\{(IP^-)_2Al\}_2(\mu^2\kappa^1:\kappa^2\text{-}OCO_2)$. One unusual feature associated with the five-coordinate aluminium centre is the very low τ value of 0.552, as compared with our previously reported work on five-coordinate complexes of the form $(IP^-)_2AlX$.[15] We think this is likely an effect of strain imposed by the bridging carbonate arrangement. The bridging carbonate ligand itself has C–O bond lengths of 1.279(6), 1.257(9), and 1.301(9) Å. These bond lengths agree well with those observed in the handful of other structurally characterized complexes containing the unsymmetrical $\mu^2\kappa^1:\kappa^2\text{-}OCO_2$ moiety observed herein (Chart 1, left). These other examples involve the metal ions Zn(II),[14] Ti(IV), Rh(I), Co(II), Fe(II), and U(IV).[16] The other common coordination mode for a $\mu^2\text{-}OCO_2$ ligand is the symmetrical bridging mode described as $\mu^2\kappa^2:\kappa^2\text{-}OCO_2$ (Chart 1, right).[14,17]
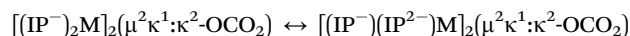
The analogous gallium complex, $(IP^-)_2Ga(OH)$,[8] displayed similar reactivity with CO_2 and that reaction afforded green

crystals of **4**. Crystals of **4** were of sufficient quality to identify the unit cell parameters as isostructural with **3** although a full crystal structure determination was not possible.
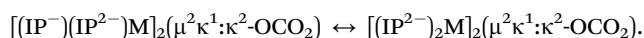
Further characterization of **3** and **4** was achieved using IR spectroscopy and magnetic susceptibility measurements. The OCO_2 moiety in **3** was labeled with ^{13}C which enabled assignment of C–O stretches in the IR spectrum at 1540 and 1519 cm^{-1} for **3** (Fig. 2 left, Table S3, ESI‡). The corresponding ^{13}C–O absorption bands were observed at 1507 and 1489 cm^{-1}. By analogy, the C–O absorptions for **4** were identified at 1540 and 1516 cm^{-1}. The electronic structures of **3** and **4** were probed using temperature dependent susceptibility measurements and EPR spectroscopy and were found to be consistent with a ligand-based antiferro-magnetically coupled biradical electronic structure at each of the metal centres (Fig. S1, ESI‡). The room temperature magnetic moments for **3** and **4** are 3.47 and 3.52 μ_B, respectively, and are consistent with this model.[18]

A balanced reaction scheme for the formation of **3** suggested that the byproduct of the reactions of $(IP^-)_2Al(OH)$ with CO_2 should be an equivalent of H_2O (Scheme 1). We were unable to detect any water in the reaction solution and so to probe the reaction mechanism further, reaction of **3** with one equivalent of H_2O in THF was investigated. The starting complex **1** was regenerated, as identified by IR spectroscopy, and CO_2 was released in 80% yield as measured by GC-TCD analysis of the reaction headspace. As further confirmation that H_2O is liberated as a side product, 3 Å molecular sieves were added to the reaction mixture to absorb any water released. Under these conditions, the yield of **3** increased from 68% to 82%. Compound **4** behaved similarly to **3**.

Electrochemical measurements were performed on **3** and **4** in 0.3 M Bu_4NPF_6 THF solutions using cyclic voltammetry (CV). The CV measurements revealed quasi-reversible oxidation events associated with the IP ligands (Fig. 2 right, Table S4, ESI‡). Complexes **3** and **4** were oxidized in two, successive quasi-reversible events at −0.56 V and −0.16 V for **3**, and at very similar potentials for **4**. The two events presumably each represent a two-electron process, i.e. one IP$^-$ ligand at each metal centre of the dinuclear molecule is oxidized in each event. The complexes also each display two two-electron reduction events associated with the IP ligands at −1.61 V and −1.95 V for **3** and at −1.52 V and −1.82 V for **4**. In **3** both of the two-electron reduction events are quasi-reversible, but neither of these events is reversible in **4**.[19] These redox events correspond to the processes:

$$[(IP^-)_2M]_2(\mu^2\kappa^1:\kappa^2\text{-}OCO_2) \leftrightarrow [(IP^-)(IP^{2-})M]_2(\mu^2\kappa^1:\kappa^2\text{-}OCO_2)$$

and

$$[(IP^-)(IP^{2-})M]_2(\mu^2\kappa^1:\kappa^2\text{-}OCO_2) \leftrightarrow [(IP^{2-})_2M]_2(\mu^2\kappa^1:\kappa^2\text{-}OCO_2).$$

The accessible reduction events observed electrochemically in **3** and **4** implied that chemical reduction of the complexes should be possible. As discussed earlier, the formation of both magnesium and calcium carbonates from CO_2 is desirable, and so the reduction of **3** was attempted with both Mg and Ca metal. In THF solution, a mixture of **3** and Mg turnings held at 60 °C for 12 h produced $MgCO_3$ and the magnesium salt of $[(IP^{2-})_2Al]^-$
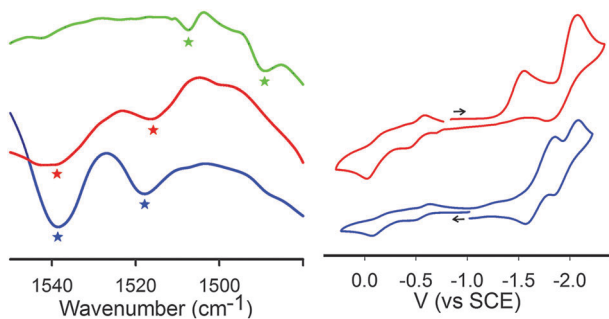

Fig. 2 (left) IR spectra for **3** (blue), **3C^{13}** (green), and **4** (red). Absorptions for CO_3^{2-} labeled with ★. (right) CV's for **3** (blue) and **4** (red), recorded in 0.3 M Bu_4NPF_6 THF solution. Glassy carbon electrode 100 mV s^{-1}.

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(5) in good yield. We have previously reported $[(IP^{2-})_2Al]^-$ as a sodium salt. Similarly, reaction of **3** with Ca metal at 60 °C for 1 h afforded $CaCO_3$ and the calcium salt of **5**. The carbonate salts were identified by IR spectroscopy and could be filtered off from the reaction mixture. We have previously demonstrated that $(IP^-)_2Al(OH)$ are formed by the two-electron oxidation of four-electron reduced $[(IP^{2-})_2Al]^-$. Therefore, the reactions described above close a synthetic cycle that generates $MgCO_3$ or $CaCO_3$ from CO_2 with regeneration of the metal hydroxide necessary for CO_2 activation. The cycle incorporates compounds **1**, **3**, and **5** (Scheme 1). A similar cycle was demonstrated for the analogous gallium complexes **2**, **4**, and $[(IP^{2-})_2Ga]^-$ (**6**).

To further illustrate the utility of the aluminium-based synthetic cycle for interconversion of **1**, **3**, and **5** and the formation of $MgCO_3$ or $CaCO_3$ from CO_2 we performed the reaction in a one-pot procedure. By successive addition of CO_2 to **1**, removal of CO_2 *in vacuo*, addition of Mg (or Ca), followed by Bu_4NI and then pyridine-*N*-oxide (pyO), $MgCO_3$ (or $CaCO_3$) could be generated from CO_2 in one system (Scheme 1).[20] These cycles could be repeated in the same vessel at least three times to generate 1.4 turnovers of $MgCO_3$, or 2.3 turnovers of $CaCO_3$ as an isolated white solid. We have already found that addition of 3 Å molecular sieves to the reaction increases the isolated yield of $MgCO_3$ from 1.1 to 1.4 turnovers, and the isolated yield of $CaCO_3$ from 1.7 to 2.3 turnovers. We anticipate that further optimization of the reaction conditions will provide even greater improvements to the isolated yields of $MgCO_3$ and $CaCO_3$. A related synthetic cycle for conversion of CO_2 has recently been reported by Meyer and coworkers using a uranium-mediated process. In that case the CO_2 activating complex consists of a U–O–U core which affords a uranium carbonate complex along with CO gas upon reaction with CO_2.[17c]

Alternative synthetic pathways for the functionalization of the trapped CO_2 in complexes **3** are of interest and so we also investigated the reactivity of **3** with Me_3SiCl. Upon addition of Me_3SiCl to a solution of **3**, formation of $(IP^-)_2AlCl$ along with $Me_3SiOC(O)OSiMe_3$ was observed as confirmed by IR spectroscopy and GC-MS.

Taken together, the chemistry described herein demonstrates that redox-active Group 13 complexes can possess both Lewis acidic properties and redox activity, and these properties can be utilized in a synthetic cycle for CO_2 conversion into either $MgCO_3$ or $CaCO_3$. In future work we will take further advantage of the combined redox and Lewis acid reactivity afforded us by these complexes to effect transformations on small molecules. We will also extend this demonstrated formation of C–O bonds to investigate the formation of C–N and C–S bonds with CO_2 through substitution of the OH ligand in $(IP^-)_2M(OH)$ with *S*- and *N*-donor ligands.

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18 No attempts were made to fit the data. These results are consistent with our previous work on biradical complexes of the form $(IP^-)_2MX$.[6,7]

19 Reduction peak heights are higher than oxidation peak heights as observed for other complexes in this class. We ascribe this to partial loss of the IP ligand upon oxidation. Moreover, free IP in solution is reduced concomitant with the reduction events for **3** and **4**.

20 Control experiments demonstrated that pyO reacts only very slowly with Mg metal, presumably because the reaction is heterogeneous.