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EDGE ARTICLE

# Binding, release, and functionalization of CO<sub>2</sub> at a nucleophilic oxo anion complex of titanium†

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The titanium oxo anion complex [(Et<sub>2</sub>O)<sub>2</sub>Li][OTi(N<sup>i</sup>Bu)<sub>3</sub>,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>] [(Et<sub>2</sub>O)<sub>2</sub>Li][1] reacts with CO<sub>2</sub> in diethyl ether to form the carbonate complex ([Li][O<sub>2</sub>COTi(N<sup>i</sup>Bu)<sub>3</sub>,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>]<sub>6</sub> ([Li][2]). The solid-state structure of complex [Li][2] is a hexamer with a hexagonal prismatic core comprised of six lithium cations bridged by the carbonate functionality. In the monomeric subunits of [Li][2], the carbonate ligand is bound κ<sup>1</sup>- to the titanium metal center and pseudo κ<sup>2</sup>- to the lithium counteranion. The hexameric structure persists in benzene solutions as determined by <sup>1</sup>H DOSY NMR techniques. The binding of CO<sub>2</sub> in complex [Li][2] is reversible and can be effected by the introduction of the lithium sequestration reagent 12-crown-4 to diethyl ether solutions of [Li][2]. Complex [Li][2] is readily functionalized with Me<sub>3</sub>SiOS(O)<sub>2</sub>CF<sub>3</sub> to yield the silyl carbonate complex Me<sub>3</sub>SiOC(O)OTi(N<sup>i</sup>Bu)<sub>3</sub>,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (3), the solid-state structure of which is presented. Functionalization with pivaloyl chloride results in the rapid loss of CO<sub>2</sub> and formation of the pivalate complex <sup>i</sup>BuC(O)OTi(N<sup>i</sup>Bu)<sub>3</sub>,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (4).

## Introduction

The reversible reaction of CO<sub>2</sub> with metal oxides has been an area of investigation by chemists for over a century.<sup>1</sup> Such research has received renewed interest in recent years for possible application in carbon capture and sequestration strategies.<sup>2</sup> Furthermore, metal oxides containing lithium have been shown to be very effective at absorbing CO<sub>2</sub>,<sup>3</sup> with lithium silicates and zirconates having received considerable attention for their ability to bind CO<sub>2</sub> reversibly at elevated temperatures.<sup>4</sup> In addition to sorption studies, the activation of CO<sub>2</sub> with photoactive metal oxides such as titania to give reduced carbon fragments has been a growing area of research.<sup>5</sup> In most cases, characterization of the CO<sub>2</sub> bound species is limited to IR spectroscopy,<sup>6</sup> thermogravimetric analysis, and powder X-ray diffraction studies,<sup>4</sup> thus limiting a detailed understanding of the bonding and structures in these systems. The development of a homogeneous system that may mimic the interaction of CO<sub>2</sub> with charged metal oxides and could be studied using a greater variety of spectroscopic and structural techniques would complement the existing body of work and provide a greater understanding of the processes at play.

Presented here are the results of studies focused on the reactivity of CO<sub>2</sub> with the terminal oxide anion complex [(Et<sub>2</sub>O)<sub>2</sub>Li][OTi(N<sup>i</sup>Bu)Ar<sub>3</sub>] [(Et<sub>2</sub>O)<sub>2</sub>Li][1], Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Generated

from the deprotonation of a titanium(IV) formate complex with concomitant generation of CO,<sup>7</sup> complex [(Et<sub>2</sub>O)<sub>2</sub>Li][1] is one of the few examples of an anionic terminal oxo complex of titanium.<sup>8,9</sup> In addition to the clear parallels with CO<sub>2</sub> absorption on metal oxides, inspiration for studying the reaction of CO<sub>2</sub> with [(Et<sub>2</sub>O)<sub>2</sub>Li][1] came from discoveries within our group. Previous studies involving the reactivity of CO<sub>2</sub> with the terminal nitride anion complexes [Na][NV(N<sup>i</sup>Bu)Ar<sub>3</sub>] and [Na][NNb(N<sup>i</sup>Bu)Ar<sub>3</sub>] had shown that CO<sub>2</sub> binding to the terminal nitride ligand was rapid and irreversible, and in the case of niobium, activated the CO<sub>2</sub> for eventual deoxygenation and conversion to CO.<sup>10,11</sup> Given the electronic similarities between [(Et<sub>2</sub>O)<sub>2</sub>Li][1] and the terminal nitride anions, it was of interest to compare the binding of CO<sub>2</sub> to [(Et<sub>2</sub>O)<sub>2</sub>Li][1] with these closely related systems, and perhaps discover a new system that would be capable of mediating the conversion of CO<sub>2</sub> to CO.

We report herein that CO<sub>2</sub> reacts readily with [(Et<sub>2</sub>O)<sub>2</sub>Li][1] in diethyl ether to yield the carbonate complex ([Li][O<sub>2</sub>COTi(N<sup>i</sup>Bu)Ar<sub>3</sub>])<sub>6</sub> ([Li][2]). The solid-state structure of [Li][2] was determined using single-crystal X-ray diffraction methods. Although stable under vacuum when dissolved in diethyl ether or in the solid state, complex [Li][2] readily liberates CO<sub>2</sub> when dissolved in the presence of the lithium sequestration reagent 12-crown-4. Furthermore, complex [Li][2] readily reacts with electrophiles resulting in simple functionalization or CO<sub>2</sub> extrusion.

## Results and discussion

### Synthesis of the titanium carbonate complex [Li][2]

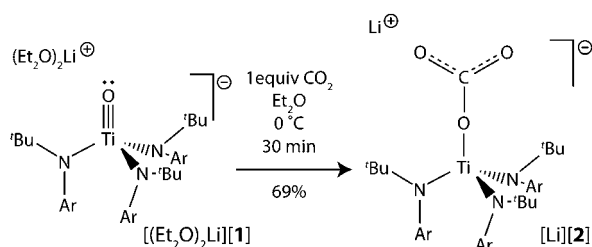
Treatment of complex [(Et<sub>2</sub>O)<sub>2</sub>Li][1] in diethyl ether with one equivalent of CO<sub>2</sub> produced a gradual colour change from pale

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† Electronic supplementary information (ESI) available: Full experimental, crystallographic, and computational details and spectroscopic data. CCDC [Li][2], 819846; 3, 819847. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1sc00215e

yellow to bright orange over the course of minutes.<sup>‡</sup> Following removal of solvent, the product was isolated as a bright yellow powder in 69% yield upon washing the residual solids with *n*-hexane (Scheme 1). The solids have minimal solubility in *n*-hexane and *n*-pentane, but are sufficiently soluble in benzene to allow for NMR spectroscopic characterization. The <sup>1</sup>H NMR spectrum indicates that the product is isolated free of ethereal solvents in contrast with complex [(Et<sub>2</sub>O)<sub>2</sub>Li][1]. The IR spectrum of the material contains a very broad absorbance at 1590 cm<sup>-1</sup>, overlapping with the stretching modes of the aryl groups on the anilide ligands and precluding definitive assignment of a carbonate moiety. Further confirmation for the uptake of CO<sub>2</sub> by complex [(Et<sub>2</sub>O)<sub>2</sub>Li][1] was achieved through a <sup>13</sup>C labelling study. After treatment of complex [(Et<sub>2</sub>O)<sub>2</sub>Li][1] with <sup>13</sup>CO<sub>2</sub>, the <sup>13</sup>C NMR spectrum of the reaction mixture contains an intense resonance at 160 ppm, characteristic of carbonates.<sup>12–14</sup>

Definitive structural assignment of [Li][2] was achieved by single-crystal X-ray diffraction methods (Fig. 1). Suitable crystals of [Li][2] were grown by slowly concentrating benzene solutions at room temperature. In the solid state, [Li][2] exists as a hexamer with a hexagonal prismatic core comprised of the six lithium counteranions bridged by oxygen atoms derived from the carbonate ligand (Fig. 2). Such laddering of carboxylates and heterocarboxylates is a common structural motif.<sup>15</sup> The carbonate ligand adopts a κ<sup>1</sup>-coordination mode to the titanium center and a pseudo κ<sup>2</sup>-coordination mode to the lithium ion. The titanium–oxygen interatomic distance (1.849(2) Å) is significantly longer than the titanium–oxygen distance found in [(Et<sub>2</sub>O)<sub>2</sub>Li][1] (1.712(2) Å). This lengthening is likely the result of a significant decrease in the π bonding between the titanium and oxygen atom as supported by DFT calculations (*vide infra*). The titanium–oxygen π bond is anti-bonding with respect to the titanium–anilide σ bonds, and as expected, the titanium–anilide distance is shorter in [Li][2] (1.930(3) Å) than in [(Et<sub>2</sub>O)<sub>2</sub>Li][1] (1.990(4) Å). The titanium–oxygen–carbon angle is also notable in its near linearity (174.7(2)°). A search of the Cambridge Structural Database revealed only one other carbonate complex with a comparable titanium–oxygen–carbon angle, the bimetallic carbonate complex [Cp<sup>\*</sup><sub>2</sub>Ti]<sub>2</sub>(μ-κ<sup>1</sup>:κ<sup>2</sup>-CO<sub>3</sub>) (175.43°).<sup>16</sup> In this case the steric bulk of the Cp<sup>\*</sup> ligand forces the titanium metal centers apart, preventing κ<sup>2</sup>:κ<sup>2</sup> coordination. In the case of [Li][2], the linearity of the carbonate linkage is likely imposed by the steric bulk of the ligands and the propensity to chelate to the lithium counteranion. Other examples of CO<sub>2</sub> binding to a titanyle moiety include equilibrium formation of κ<sup>2</sup>-carbonato ligands through cycloaddition reactions.<sup>17,18</sup>



Scheme 1 Synthesis of [Li][2].

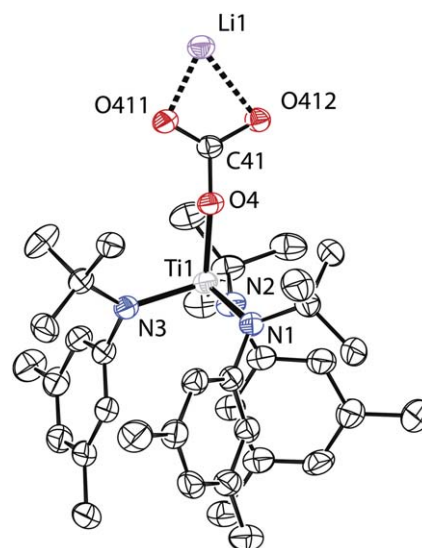


Fig. 1 Solid-state structure of the asymmetric unit of [Li][2] · (C<sub>6</sub>H<sub>6</sub>)<sub>1.33</sub> with thermal ellipsoids at 50% probability and hydrogen atoms and interstitial benzene omitted for clarity. Selected distances (Å) and angles (°): Ti1–O4 1.849(2), O4–C41 1.319(3), C41–O411 1.232(3), C41–O412 1.292(3), O411–Li1 1.911(5), O412–Li1 2.257(5), O411–C41–O412 122.1(2), Ti1–O41–C41 174.7(2).<sup>20</sup>

To determine whether the hexameric structure observed in the solid state persists in solution, we investigated the diffusion properties of the complex using <sup>1</sup>H DOSY NMR techniques. As was shown by Waldeck *et al.*, the diffusion coefficients of two molecules in the same solvent are proportional to the cube root of the inverse ratio of the molecular weights (eqn (1)).<sup>19</sup>

$$\frac{D_1}{D_2} = \sqrt[3]{\frac{MW_2}{MW_1}} \quad (1)$$

Two assumptions are made in deriving this relationship: 1) the Stokes–Einstein theory of diffusion holds for the molecules of

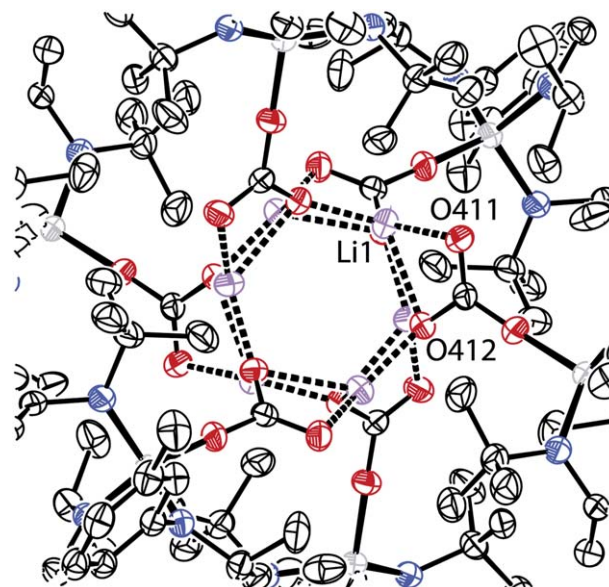


Fig. 2 Hexagonal prismatic Li<sub>6</sub>O<sub>6</sub> core of [Li][2] with thermal ellipsoids drawn at 50% probability and hydrogen atoms and interstitial benzene molecules omitted for clarity.<sup>20</sup>

interest, and 2) the molecules can be approximated as uniform spheres. For our purposes, we selected the complex [(12-crown-4)Li][OTi(N<sup>t</sup>Bu)Ar]<sub>3</sub> [(12-crown-4)Li][1] as an external reference.<sup>‡</sup> The 12-crown-4 ensures that the complex remains monomeric in solution by satisfying the coordination sphere of lithium. A salt was selected to stay as consistent as possible to the nature of [Li][2]. The diffusion coefficient of [(12-crown-4)Li][1] was determined to be  $6.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  and the diffusion coefficient of [Li][2] was determined to be  $3.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . Using the relationship from eqn (1) and the molecular weight of [(12-crown-4)Li][1] of  $775.68 \text{ g mol}^{-1}$ , the calculated value of the molecular weight of [Li][2] is  $4064 \text{ g mol}^{-1}$ . This value is very close to the expected value of  $3862 \text{ g mol}^{-1}$  for the hexamer [Li][2]. We take this measured value to provide strong evidence that the hexameric structure of [Li][2] observed in the solid state persists in solution in the absence of strongly coordinating agents.

### Computational studies of [Li][2]

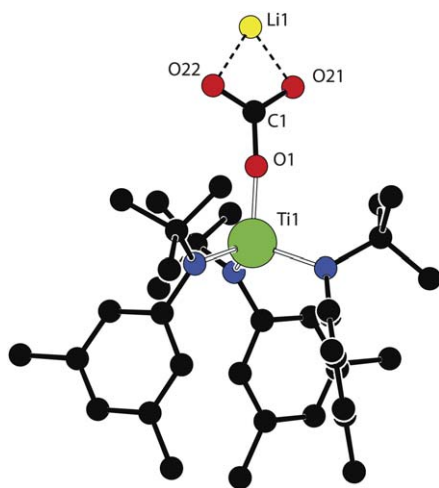
To gain insight into the electronic structure of [Li][2], DFT calculations were carried out. The large number of atoms associated with the hexameric structure led us to model [Li][2] as a monomer in the gas phase. The optimized geometry of the monomer [Li][2] contains a carbonate ligand in a  $\kappa^1$ -titanium,  $\kappa^2$ -lithium binding motif (Fig. 3). The titanium–oxygen distance (1.857 Å), titanium-bound oxygen–carbon distance (1.326 Å), and titanium–oxygen–carbon angle (174.34°) all agree well with crystallographically determined values. A vibrational mode analysis of the optimized geometry predicts the  $\nu_{\text{OCO}}$  stretching mode to be observed at  $1585 \text{ cm}^{-1}$ , in good agreement with the experimentally observed value of  $1590 \text{ cm}^{-1}$ . Similarly, the chemical shift of the carbonate carbon was predicted to be 162 ppm, in good agreement with experimentally observed 160 ppm. The agreement with observed structural and spectroscopic values supports the notion that the simplified monomeric model is sufficiently similar to the hexamer for the purpose of our

analysis. The HOMO of [Li][2] is dominated by the nitrogen lone pair orbitals of the anilide ligands. An analysis of the frontier molecular orbitals from the DFT calculations reveals no clear  $\pi$ -bonding interactions between the titanium and the bound oxygen atom. Earlier DFT computational studies of [(Et<sub>2</sub>O)<sub>2</sub>Li][1] had revealed a substantial degree of  $\pi$ -bonding between the titanium and oxo ligand.<sup>7</sup> This change in the bonding agrees well with our earlier hypothesis based on the structural data. Bonding to CO<sub>2</sub> likely results in a contraction and lowering in the energy of the *p*-orbitals at the bound oxygen, making the bonding interaction with the titanium much less favourable. Such effects on bonding have been observed previously when terminal oxos were functionalized with Lewis acids.<sup>21</sup> This apparent weakening of the titanium–oxygen bond contrasts sharply with the analogous niobium nitride system. In that system, the short niobium–nitrogen interatomic distance persists in going from the terminal nitride to the *N*-bound carbamate complex and was taken as support for assigning the presence of a niobium nitrogen triple-bond both with and without CO<sub>2</sub>.<sup>11</sup>

### Releasing CO<sub>2</sub> from [Li][2]

As previously mentioned, [Li][2] is isolated free of ethereal solvents and shows marked stability in the solid state under vacuum at room temperature. Furthermore, in the synthesis of [Li][2], the diethyl ether reaction mixture is dried under dynamic vacuum, and the NMR spectra of crude reaction mixtures reveal near quantitative formation of [Li][2] with no observable amounts of [(Et<sub>2</sub>O)<sub>2</sub>Li][1]. However, when attempts were made to recrystallize [Li][2] for X-ray diffraction studies, complex [(Et<sub>2</sub>O)<sub>2</sub>Li][1] would often be found as a contaminant or as the sole anilide containing species in the isolated material. Clearly, CO<sub>2</sub> was being released slowly as solutions of [Li][2] were allowed to stand. Preliminary observations indicated that the choice of solvent played an important role in the resulting amount of [(Et<sub>2</sub>O)<sub>2</sub>Li][1] that was isolated from these crystallization experiments, with strongly coordinating ethereal solvents giving rise to significantly more oxo. Specifically, this effect was most pronounced when 12-crown-4 was added to solutions of [Li][2].

Dissolving [Li][2] in diethyl ether containing one equivalent of 12-crown-4 followed by introduction of dynamic vacuum to concentrate the solution resulted in a colour change from deep orange to pale yellow in a matter of seconds. The IR spectrum of the material contained no absorbance that could be attributed to a carbonate linkage. The NMR spectrum of the resulting off-white powder revealed a single anilide containing species in solution, along with resonances attributable to 12-crown-4; the chemical shift of the signals agreed perfectly with the spectroscopic signature of [(12-crown-4)Li][1]. This result indicates that the binding affinity of CO<sub>2</sub> to the oxo ligand is strongly dependent on the coordination environment of the counteranion and perhaps on the ability of the complex to form the hexagonal prismatic core. The formation of multiple lithium–oxygen interactions in [Li][2] might be required to overcome the entropically disfavoured reaction of trapping CO<sub>2</sub>. Hence, it appears that the combination of the nucleophilicity of the oxo ligand and the electrophilicity of the lithium is critical for effective binding of CO<sub>2</sub>.



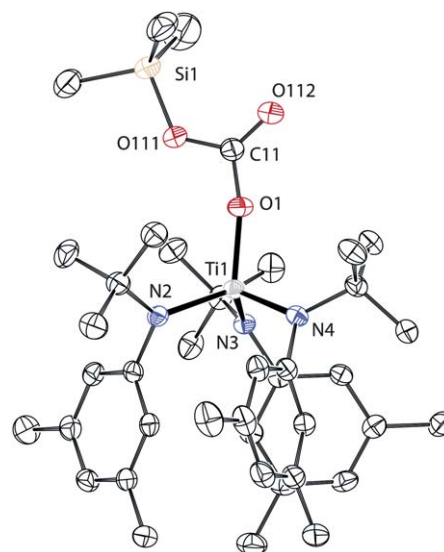
**Fig. 3** Optimized geometry of [Li][2] as a monomer. Selected distances (Å) and angles (°): Ti1–O1 1.857, O1–C1 1.326, C1–O21 1.275, C1–O22 1.277, Ti1–O1–C1 174.3, O22–C1–O21 121.9.



## Functionalization of [Li][2]

Although the binding of CO<sub>2</sub> in [Li][2] was chemically reversible, the persistence of the carbonate functionality in the absence of the strongly coordinating 12-crown-4 ether led us to investigate methods to functionalize [Li][2]. If suitable functionalization reagents could be discovered, developing a method for deoxygenating [Li][2] and eventually releasing CO might be possible. In this vein, functionalization of [Li][2] can be achieved using select electrophiles. Treatment of [Li][2] with one equivalent of trimethylsilyl triflate in diethyl ether produced a gradual colour change of bright orange to red with concomitant formation of a colourless precipitate. Analysis of the crude reaction mixture by NMR spectroscopy confirmed the formation of a single product assigned as the trimethylsilyl carbonate complex Me<sub>3</sub>SiOC(O)OTi(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (**3**, Scheme 2). Complex **3** was isolated in crystalline form by storing saturated solutions of **3** in diethyl ether at –35 °C. The IR spectrum of the isolated material contains a strong absorbance at 1691 cm<sup>–1</sup> that can be attributed to ν<sub>CO</sub> of the carbonate ligand. The solid-state structure of **3** was determined by X-ray crystallographic methods (Fig. 4). The carbon–oxygen distances in the carbonate ligand are reasonable for the expected carbon–oxygen single and double bonds. The titanium–oxygen interatomic distance (1.857(2) Å) is not significantly longer than the titanium–oxygen distance found in [Li][2] (1.849(2) Å) indicating little change in the bonding interaction between the titanium and the oxygen. Complex **3** is stable under ambient conditions, but loses CO<sub>2</sub> at elevated temperatures to give the siloxide complex Me<sub>3</sub>SiOTi(N[<sup>t</sup>Bu]Ar)<sub>3</sub>.<sup>‡</sup> Thus, it is proposed that complex **3** is isolable for kinetic reasons (*vide infra*).

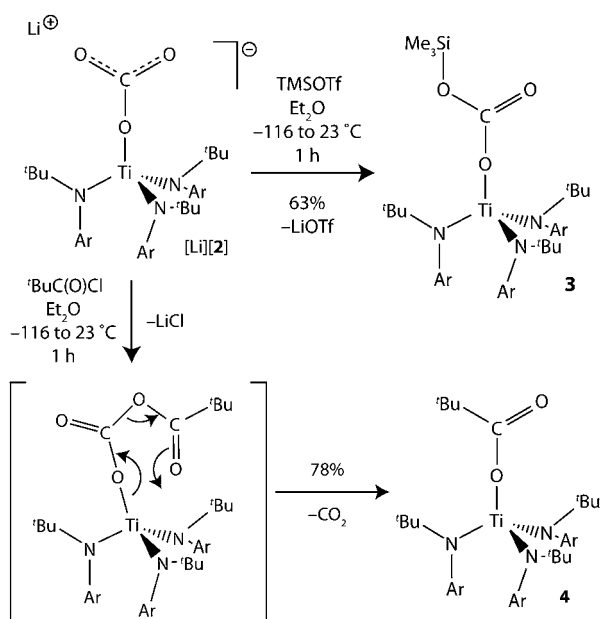
Knowing that functionalization of [Li][2] was possible, attempts to deoxygenate the complex were pursued. Building on precedent observed in deoxygenating the related niobium carbamate complex [Na][O<sub>2</sub>CNNb(N[<sup>t</sup>Bu]Ar)<sub>3</sub>],<sup>11</sup> treatment of [Li][2] with acylating reagents was investigated. Treatment of [Li]



**Fig. 4** Solid-state structure of **3** with thermal ellipsoids at 50% probability and hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Ti1–O1 1.857(2), O1–C11 1.317(3), C11–O111 1.336(3), C11–O112 1.197(3), Ti1–O1–C11 166.9(2), O1–C11–O111 111.2(2), O1–C11–O112 124.4(2).<sup>20</sup>

[2] with <sup>t</sup>BuC(O)Cl in diethyl ether resulted in formation of a white precipitate and an observed colour change of yellow to orange. Analysis of the reaction mixture by proton NMR spectroscopy confirmed clean formation of a single product. The IR spectrum of the crude reaction mixture contained a strong absorbance at 1680 cm<sup>–1</sup>, characteristic of a ν<sub>CO</sub> stretching mode for a carbonyl moiety. If the salt-elimination reaction had taken place with no further reaction, the expected anhydride moiety would have two IR active modes, symmetric and antisymmetric stretching.<sup>22</sup> The single IR absorbance in the carbonyl region led us to interpret the reaction in terms of titanium pivalate complex <sup>t</sup>BuC(O)OTi(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (**4**) formation with loss of CO<sub>2</sub> (Scheme 2). This was confirmed through independent synthesis of **4** from the reaction of <sup>t</sup>BuC(O)Cl with [(Et<sub>2</sub>O)<sub>2</sub>Li][1], with identical spectroscopic signatures being observed in both reactions. It is not clear when the CO<sub>2</sub> loss occurs in the reaction of [Li][2] with <sup>t</sup>BuC(O)Cl, but it is tempting to suggest that the expected salt elimination occurs to give an intermediate anhydride complex that then undergoes a rapid intramolecular rearrangement to lose CO<sub>2</sub> (Scheme 2). This is consistent with the previously observed reaction of organic acid chlorides and acid anhydrides with the niobium complex [Na][O<sub>2</sub>CNNb(N[<sup>t</sup>Bu]Ar)<sub>3</sub>] to give the five-coordinate complexes of the type (RC(O)O)(OCN)Nb(N[<sup>t</sup>Bu]Ar)<sub>3</sub>.<sup>11</sup> Although other possible mechanisms (*e.g.* bimolecular, insertion of carbonyl into the titanium–oxygen bond) cannot be ruled out, the proposed pathway is consistent with the data presented.

The rapid loss of CO<sub>2</sub> upon acylation is rationalized by recognizing the ease of forming the proposed six-membered metallacyclic intermediate. Such a transition state is not possible in the case of silylation. Loss of CO<sub>2</sub> from complex **3** likely proceeds through a four-membered metallacyclic intermediate, if an intramolecular rearrangement is operative. Such a transition state would result in a greater kinetic barrier. Hence, the



**Scheme 2** Functionalization reactions of [Li][2]: synthesis of **3** and **4**.

silylcarbonate complex **3** is isolable at ambient conditions, whereas the intermediate carbonic anhydride species is not.

Attempts to intercept the intermediate anhydride complex with an *in situ* reductant such as cobaltocene did not change the outcome of the reaction. In addition, oxygen abstraction reagents such as three-coordinate vanadium(III) complexes (e.g.  $V[N^iBuAr]_3$ )<sup>23</sup> show no reactivity with  $[Li][2]$ . Perhaps the hexameric structure and steric bulk of  $[Li][2]$  prevents such reagents from accessing the carbonate oxygens.

## Conclusions

In summary, we have observed chemically reversible binding of  $CO_2$  to an anionic terminal oxo complex of titanium. The resulting  $\kappa^1$ -carbonate complex  $[Li][2]$  can be isolated in good yield as a bright yellow powder. The solid-state structure of  $[Li][2]$  consists of a hexameric unit with the lithium counterions bridged by the carbonate functionality. DFT calculations on the system corroborate the conclusion that the titanium-oxygen bond undergoes a substantial decrease in  $\pi$ -bonding character concomitant with  $CO_2$  binding. Further, spectroscopic signatures of  $[Li][2]$  agree well with DFT calculated values. The release of  $CO_2$  can be effected by introducing strong coordination reagents such as 12-crown-4 to solutions of  $[Li][2]$ . This reactivity contrasts sharply with the previously investigated vanadium and niobium nitride systems. In those systems, the binding of  $CO_2$  was found to be very robust and irreversible, even when the counterion was fully sequestered.<sup>10,11</sup> The nitride complexes are expected to be more nucleophilic than the oxo complex, and this characteristic likely explains the observed difference in reactivity. Complex  $[Li][2]$  can be functionalized readily with  $Me_3SiOTf$  to give the silyl carbonate complex **3**, but acylation with pivaloyl chloride results in rapid loss of  $CO_2$  at ambient conditions to give the carboxylate complex **4**.

This work complements several previous studies focused on the nucleophilic activation of  $CO_2$ . The binding of  $CO_2$  to  $[(Et_2O)_2Li][1]$  relies both on the nucleophilicity of the oxo ligand and on the acidity of the lithium counterion. This contrasts with the binding of  $CO_2$  by strong nucleophiles such as *N*-heterocyclic carbenes,<sup>24</sup> guanidines,<sup>25</sup> and terminal nitrides,<sup>11</sup> which is effective in the absence of an external Lewis acid. Instead, a better comparison for the reaction between  $[(Et_2O)_2Li][1]$  and  $CO_2$  might be the binding of  $CO_2$  by frustrated Lewis pairs,<sup>26</sup> where cooperative interactions lead to a greater binding affinity. Our system also shows marked similarities to model complexes of carbonic anhydrase, whose operative mechanism involves nucleophilic attack of a hydroxide ligand on  $CO_2$ .<sup>27</sup> Of course, the major difference in our system is the need for strictly aprotic conditions due to the hydrolytic sensitivity of titanium-anilide linkages. Also in this vein, the binding of  $CO_2$  in transition metal alkoxide, hydroxide, and oxide complexes is known and is occasionally reversible,<sup>13,28–32</sup> and the concept of cation dependent binding has been illustrated for systems involving the direct interaction of  $CO_2$  with electron-rich, low-coordinate metal centers.<sup>33,34</sup> To contrast, our discovery provides a system for study where the binding affinity for  $CO_2$  can be externally modified (e.g., by altering coordination sphere of  $Li^+$ ). This work also builds upon the extensive literature precedent for the binding of  $CO_2$  by heterogeneous metal oxide systems, as

mentioned in the introduction. We are currently expanding our investigations to understand the thermodynamic parameters of  $CO_2$  uptake by  $[(Et_2O)_2Li][1]$ , to probe cation effects on binding affinity, and to explore alternative oxide platforms to determine if this  $CO_2$  binding modality can be generalized.

## Acknowledgements

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## Notes and references

‡ If treated with an excess of  $CO_2$ ,  $[Li][2]$  reacts further to give other products. We suspect that the products are the result of  $CO_2$  insertion into the titanium-anilide bonds to give carbamate moieties. Such reactivity has been observed in titanium-anilide chemistry.<sup>35</sup> Complex [(12-crown-4)Li][1] is synthesized by adding one equivalent of 12-crown-4 to solutions of  $[(Et_2O)_2Li][1]$  in diethyl ether. Thermal stability study of complex **3** was performed by heating a solution of **3** in  $C_6D_6$  at 80 °C for 12 h in a flame-sealed NMR tube. See ESI for details.†

- 1 J. Johnston, *J. Am. Chem. Soc.*, 1910, **32**, 938–946.
- 2 J. Blamey, E. J. Anthony, J. Wang and P. S. Fennell, *Prog. Energy Combust. Sci.*, 2010, **36**, 260–279.
- 3 H. A. Mosqueda, C. Vazquez, P. Bosch and H. Pfeiffer, *Chem. Mater.*, 2006, **18**, 2307–2310.
- 4 B. N. Nair, R. P. Burwood, V. J. Goh, K. Nakagawa and T. Yamaguchi, *Prog. Mater. Sci.*, 2009, **54**, 511–541.
- 5 V. P. Indrakanti, J. D. Kubicki and H. H. Schobert, *Energy Environ. Sci.*, 2009, **2**, 745–758.
- 6 G. Busca and V. Lorenzelli, *Mater. Chem.*, 1982, **7**, 89–126.
- 7 A. Mendiratta, J. S. Figueroa and C. C. Cummins, *Chem. Commun.*, 2005, 3403–3405.
- 8 W. W. Lukens, P. T. Matsunaga and R. A. Andersen, *Organometallics*, 1998, **17**, 5240–5247.
- 9 S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1995, **14**, 4505–4512.
- 10 J. K. Brask, V. Durá-Vilá, P. L. Diaconescu and C. C. Cummins, *Chem. Commun.*, 2002, 902–903.
- 11 J. S. Silvia and C. C. Cummins, *J. Am. Chem. Soc.*, 2010, **132**, 2169–2171.
- 12 D. J. Darensbourg, K. M. Sanchez and A. L. Rheingold, *J. Am. Chem. Soc.*, 1987, **109**, 290–292.
- 13 D. J. Darensbourg, M. L. M. Jones and J. H. Reibenspies, *Inorg. Chem.*, 1996, **35**, 4406–4413.
- 14 D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgoda, P. Rainey, J. B. Robertson, J. D. Draper and J. H. Reibenspies, *J. Am. Chem. Soc.*, 1999, **121**, 107–116.
- 15 A. Downard and T. Chivers, *Eur. J. Inorg. Chem.*, 2001, **2001**, 2193–2201.
- 16 V. V. Burlakov, F. M. Dolgushin, A. I. Yanovsky, Y. T. Struchkov, V. B. Shur, U. Rosenthal and U. Thewalt, *J. Organomet. Chem.*, 1996, **522**, 241–247.
- 17 V. L. Goedken and J. A. Ladd, *J. Chem. Soc., Chem. Commun.*, 1982, 142–144.
- 18 C. E. Housmekerides, D. L. Ramage, C. M. Kretz, J. T. Shontz, R. S. Pilato, G. L. Geoffroy, A. L. Rheingold and B. S. Haggerty, *Inorg. Chem.*, 1992, **31**, 4453–4468.
- 19 A. R. Waldeck, P. W. Kuchel, A. J. Lennon and B. E. Chapman, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1997, **30**, 39–68.
- 20 A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
- 21 F. Wolff, R. Choukroun, C. Lorber and B. Donnadieu, *Eur. J. Inorg. Chem.*, 2003, **2003**, 628–632.
- 22 J. B. Lambert, H. F. Shurvell, D. A. Lightner and R. G. Cooks, *Organic Structural Spectroscopy*, Prentice-Hall, Inc., Upper Saddle River, NJ, 1998.
- 23 M. G. Fickes, Ph.D. thesis, Massachusetts Institute of Technology, Cambridge, MA, 1998.

- 
- 24 H. A. Duong, T. N. Tekavec, A. M. Arif and J. Louie, *Chem. Commun.*, 2004, 112–113.
- 25 C. Villiers, J. P. Dognon, R. Pollet, P. Thuery and M. Ephritikhine, *Angew. Chem., Int. Ed.*, 2010, **49**, 3465–3468.
- 26 C. M. Momming, E. Otten, G. Kehr, R. Frohlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2009, **48**, 6643–6646.
- 27 G. Parkin, *Chem. Rev.*, 2004, **104**, 699–767.
- 28 O. P. Lam, S. C. Bart, H. Kameo, F. W. Heinemann and K. Meyer, *Chem. Commun.*, 2010, **46**, 3137–3139.
- 29 Y. Dussart, C. Harding, P. Dalgaard, C. McKenzie, R. Kadirvelraj, V. McKee and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 2002, 1704–1713.
- 30 T. Tsuda, Y. Chujo and T. Saegusa, *J. Am. Chem. Soc.*, 1980, **102**, 431–433.
- 31 S. K. Mandal, D. M. Ho and M. Orchin, *Organometallics*, 1993, **12**, 1714–1719.
- 32 A. M. Appel, R. Newell, D. L. DuBois and M. Rakowski DuBois, *Inorg. Chem.*, 2005, **44**, 3046–3056.
- 33 G. Fachinetti, C. Floriani and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1978, **100**, 7405–7407.
- 34 M. H. Schmidt, G. M. Miskelly and N. S. Lewis, *J. Am. Chem. Soc.*, 1990, **112**, 3420–3426.
- 35 A. Mendiratta, C. C. Cummins, F. A. Cotton, S. A. Ibragimov, C. A. Murillo and D. Villagran, *Inorg. Chem.*, 2006, **45**, 4328–4330.