

# Backbone reactivity of lithium $\beta$ -diketiminate (NacNac) complexes with $\text{CO}_2$ , $t\text{-BuNCO}$ and $i\text{-PrNCO}$

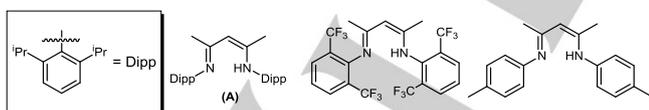
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Dedication ((optional))

**Abstract:** Though alkali metal NacNac ( $\beta$ -diketiminate) complexes have been utilised in synthesis as NacNac transfer agents, studies of them in their own right with small molecules are exceptionally rare. Here, the lithium compound of the common 2,6-diisopropylphenyl- $\beta$ -methylidenediketiminato [NacNac(Dipp, Me)] ligand is investigated with carbon dioxide and isocyanates. In all four cases reaction occurs at the backbone  $\gamma$ -C atom of the NacNac ligand, which redistributes electronically into a diimine. Insertion of  $\text{CO}_2$  gives an 8-atom carboxylate ( $\text{Li}_2\text{O}_4\text{C}_2$ ) ring at the  $\gamma$ -C site in a dimer. Insertion of  $t\text{-BuNCO}$  gives a secondary amide at the  $\gamma$ -C site in a monomer with TMEDA chelating lithium. Double insertion of  $t\text{-BuNCO}$  and (adventitious) oxygen gives a dimer with a  $(\text{LiO})_2$  central core involving the former source. Insertion of less bulky ( $i\text{-PrNCO}$ ) gives a dimer with dimerisation through the C=O bonds of the emergent secondary amide function.

## Introduction

Now well established in the premier league of ligands,<sup>[1]</sup>  $\beta$ -diketiminate (BDI or NacNac) molecules exhibit a wide ranging chemistry, with extensive applications spanning the main group, transition metal and lanthanide blocks of the periodic table.<sup>[2]</sup> The NacNac class of ligands are distinguished by a highly versatile structure capable of supporting metal ions in a number of oxidation states and chemical environments.<sup>[3]</sup> This versatility, reviewed by Lappert in 2002,<sup>[4]</sup> is a consequence of the huge variation that can be introduced into the system *via* changing the pendent groups attached to the NCCCN backbone, with varying degrees of steric bulk and electronic effects able to be implanted in this way.



**Figure 1.** Selection of common NacNac(H) type proligands previously utilised in synthesis.

A simple procedure for the high yielding synthesis of the parent NacNac(H) proligand was developed in 2001 by Power *et al.*, who also synthesised and characterised the deprotonated lithium salts, either unsolvated or solvated with THF or  $\text{Et}_2\text{O}$ .<sup>[5]</sup> Other examples of s-block complexes featuring the NacNac ligand include  $\text{NacNacMg}^n\text{Bu}$  utilised by Hill *et al.* in catalytic and insertion reactions<sup>[6]</sup> and  $\text{NacNacMgTMP}$  (TMP is 2,2,6,6-tetramethylpiperidide) synthesised by Hevia *et al.*<sup>[7, 8]</sup> Both complexes have been structurally characterised and their reactivity probed, with the latter complex being a stronger base, showing proficiency in C-H deprotonation reactions. The former meanwhile is proficient in C-F activation reactions, as well as exhibiting catalytic activity in hydroboration reactions of internal and terminal alkynes.<sup>[8, 9]</sup> In deprotonation reactions the NacNac ligand is not involved directly in the metalation (C-H to C-M transformation) step, but its role as a bulky ligand is to help magnesium trap and stabilise the emergent anions.<sup>[8]</sup>

Other examples of NacNac complexes have been synthesised and crystallographically characterised containing metals from across the periodic table, including aluminium,<sup>[10]</sup> scandium<sup>[11]</sup> and magnesium examples other than those above.<sup>[12, 13]</sup> The magnesium complexes exhibit remarkably diverse reactivity, spanning cycloaddition reactions, deprotonation reactions and addition reactions of alkynes to the backbone NacNac  $\gamma$ -carbon atom. They can also display interesting coordination modes, for example,  $\eta^3$  coordination to toluene and benzene.<sup>[13, 14]</sup> Aluminium NacNac species have also been shown to engage in the fixation of small molecules such as white phosphorus and sulfur,<sup>[10]</sup> and can react with elemental oxygen to form alkyl(alkoxy)aluminium complexes, or aluminium oxide species.<sup>[15]</sup>

In many of these examples, the NacNac ligand is utilised as a protective scaffold upon which the reactive centre of the complex rests. However, the NacNac ligand does not always act as an inert sterically bulky spectator, with some studies reporting decomposition products, redox non-innocence and cooperative activity between metal complexes and substrates.<sup>[16]</sup> Germane to the present study, in 2012 Piers *et al.*<sup>[17]</sup> exposed a scandium NacNac complex to an excess of  $\text{CO}_2$ , resulting in a dimeric scandium carboxylate wherein the  $\text{CO}_2$  addition occurred at the central carbon atom of the NacNac backbone, as evidenced by  $^{13}\text{C}$  NMR spectroscopic investigations using  $^{13}\text{CO}_2$ .

Recently our group joined the growing number of scientists interested in the field of  $\text{CO}_2$  activation/fixation chemistry. Despite the many studies probing  $\text{CO}_2$  fixation, we noted how few considered the insertion of  $\text{CO}_2$  into reactive Li-N bonds,<sup>[18]</sup> even

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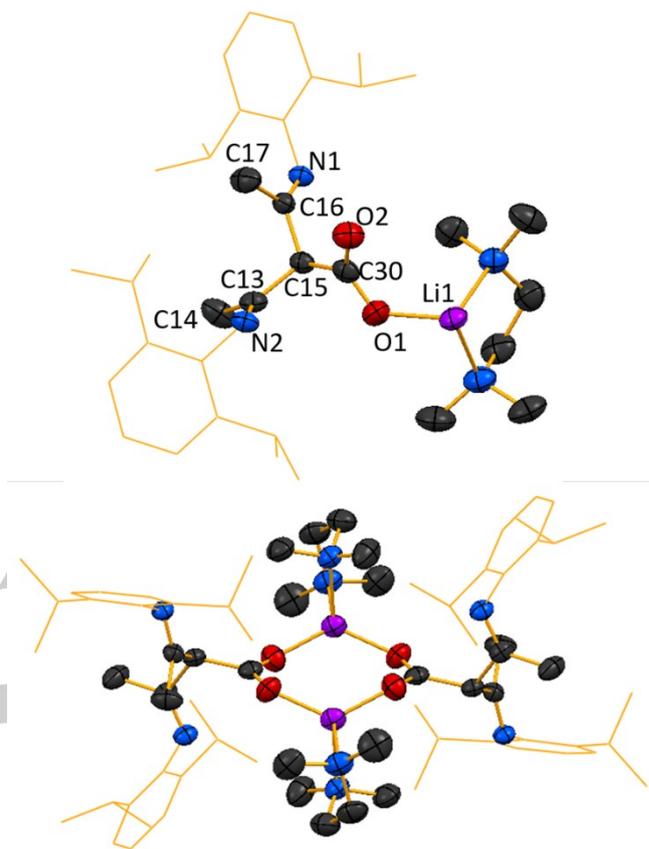
though such bonds are found in synthetically important lithium (and sodium) amide reagents. Our study showed that reaction between a series of common utility metal amides and CO<sub>2</sub> resulted in insertion into the M-N bonds affording a range of new metal carbamate complexes with interesting structural motifs (polymeric ladders, carbamate anhydride mixed sodium lithium polymers).<sup>[19]</sup> Inspired by this study, we decided to expand our efforts into researching the popular NaCNac ligand, to examine the effects of CO<sub>2</sub> fixation on their lithium derivatives, anticipating CO<sub>2</sub> insertion into the reactive N-Li bonds present in these species. The fact that alkali metal complexes are agents supreme for transferring the NaCNac anion,<sup>[20]</sup> and numerous other ligands, adds an extra incentive for elaborating fully the chemistry of alkali metal NaCNac complexes. Reported herein are our results focusing on the fixation of small molecules with lithium NaCNac complexes of the commonly studied 2,6-diisopropylphenyl-β-methyldiketiminato [NaCNac(Dipp, Me) or (DIPPBDI) **A** Figure 1]. A novel lithium β-diimine based dimer, where CO<sub>2</sub> is inserted into the backbone of the NaCNac ligand is reported. Surprisingly to the best of our knowledge this is first such crystallographically characterised backbone insertion of CO<sub>2</sub> with an alkali metal NaCNac salt. Extension of small molecules used to isocyanates, results in a series of backbone fixated products featuring dual imine and amide functionality, providing straightforward access to potentially useful ditopic ligands.

## Results and Discussion

The parent NaCNac(H) proligand **A** was synthesised as per the literature procedure.<sup>[5]</sup> Following isolation, the proligand was reacted with *n*-butyllithium in hexane at 0 °C, generating *in situ* the lithium NaCNac complex. The common chelating donor *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was then added to the suspension resulting in a dark solution. CO<sub>2</sub> was then bubbled through the mixture for 30 minutes and the resulting solution concentrated and cooled to -20 °C, resulting in the formation of colourless crystals of the dimeric product [(MeCN-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>CH(CO<sub>2</sub>)Li.TMEDA]<sub>2</sub> in 46% yield (**1**). Determined by X-ray crystallography, the centrosymmetric structure of **1** is composed of deprotonated NaCNac units, linked by the backbone of the NaCNac framework, *via* an eight-membered carboxylate (Li<sub>2</sub>O<sub>4</sub>C<sub>2</sub>) ring (Figure 2). The single lithium environment present in the solid state structure is further confirmed in solution state NMR studies (see ESI for details).

The lithium centre is four coordinate, bonded to two oxygens from the carboxylate unit and two TMEDA nitrogen atoms in a distorted tetrahedral environment, with bond angles ranging from 84.6(2)° to 127.0(3)°. The level of distortion can be quantified by the parameter τ<sub>4</sub> introduced by Houser *et al.*<sup>[21]</sup> In **1** τ<sub>4</sub> = 0.84 (a value of 1 relates to a perfect tetrahedral geometry and 0 to a square-planar geometry). The lithium centre is bonded to an oxygen from each symmetry equivalent carboxylate unit [Li-O<sub>1</sub> 1.867(7) Å; Li-O<sub>2</sub> 1.923(5) Å]. C-O bond distances in the carboxylate unit are elongated compared to those in the parent CO<sub>2</sub> molecule (1.1615 Å),<sup>[22]</sup> indicating significant π-delocalisation within the CO<sub>2</sub> moiety [C<sub>30</sub>-O<sub>1</sub> and C<sub>30</sub>-O<sub>2</sub> distances are 1.245(4)

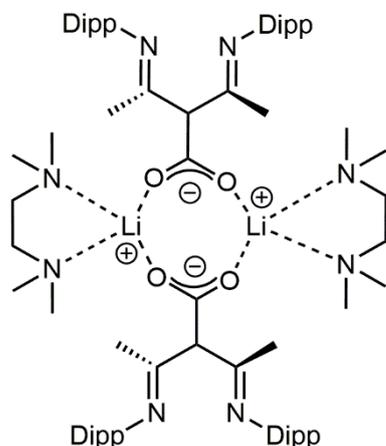
and 1.250(4) Å respectively]. Such elongation of C-O bonds has been observed in several studies of carboxylates, all of which contained bonds of similar length to those in **1**.<sup>[23]</sup>



**Figure 2.** Top: Molecular structure of the asymmetric unit of [(MeCN-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>CH(CO<sub>2</sub>)Li.TMEDA]<sub>2</sub> (**1**) with key atoms labelled; and bottom: Dimeric structure of (**1**). Hydrogen atoms are omitted and the NaCNac Dipp groups are shown as wire frame for clarity. Thermal ellipsoids are displayed at 40% probability level. Symmetry transformations used to generate equivalent atoms: -x, -y, -z.

Of special interest in **1** is the fact that the CO<sub>2</sub> does not insert into the seemingly more reactive Li-N bond present in the alkali metal complex, instead redistributing to the NaCNac backbone and forming a new carbon-carbon bond, providing on one hand carboxylate functionality in the backbone at the γ-carbon position, and on the other hand diimine (C=N) functionality in the main body of the NaCNac ligand (Figure 3). The presence of the imine components were confirmed in the solid state *via* the C-N bond lengths [C<sub>13</sub>-N<sub>2</sub>, 1.268(3) Å and C<sub>16</sub>-N<sub>1</sub>, 1.269(3) Å] which compare favourably with the average C-N bond lengths in imines of 1.279 Å (Table 1).<sup>[24]</sup> The carboxylate functionality is detectable in <sup>13</sup>C NMR experiments, with the central carboxylate carbon resonance at 170 ppm. IR spectroscopy confirms the symmetrical carboxylate stretching and imine C=N stretching at 1636 and 1591 cm<sup>-1</sup> respectively. The NaCNac ligand itself is also heavily distorted in this structure relative to the parent amine or lithium salt, presumably a consequence of the loss of resonance across the NCCCN unit compared with the parent ligand. For example, in **A** the methyl groups lie 2.50 Å from the γ-carbon, whereas in **1** the methyl groups are elongated ([C<sub>15</sub>-C<sub>17</sub> 2.577(5) Å and C<sub>15</sub>-C<sub>14</sub>

2.560(5) Å]. The N<sub>1</sub>...N<sub>2</sub> separation distance also shows a marked distinction, being 2.685(3) Å in the parent amine, compared to 4.513(3) Å in **1**, a consequence both of the loss of conjugation and a lack of lithium with which to bond. Further, the bond angles in the NacNac backbone, of C<sub>13</sub>-C<sub>15</sub>-C<sub>16</sub> narrow in **1** [112.6(3)<sup>o</sup> compared to 125.9(3)<sup>o</sup> in the parent NacNac(H)].



**Figure 3.** ChemDraw representation of the structure of  $[(\text{MeCN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{CH}(\text{CO}_2)]\text{Li.TMEDA}]_2$  (**1**) showing the diimine conformation.

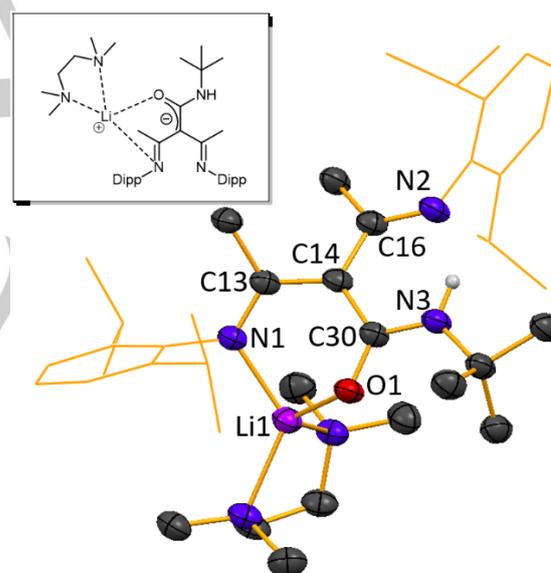
To the best of our knowledge this is the first example of backbone attack on CO<sub>2</sub> using an alkali metal NacNac complex, despite the widespread synthetic utilisation of such complexes. The most relevant related study is that carried out by Hayton *et al.* probing the fixation of CS<sub>2</sub> via a bimetallic nickel-potassium complex, resulting in redistribution of the CS<sub>2</sub> unit to the backbone of the NacNac ligand.<sup>[25]</sup> In **1** the redistribution of CO<sub>2</sub> to the  $\gamma$  position can be considered as a nucleophilic attack on the electrophilic CO<sub>2</sub> carbon by the anionic NacNac ligand. Supporting this reactivity, theoretical calculations on the NacNac anion have demonstrated that there is significant electron density located at the  $\gamma$ -carbon.<sup>[26]</sup> Arnold reported that while the negative charge is effectively delocalised over the NCCCN part of the anion, the HOMO and HOMO-1 are located at the  $\alpha$ -nitrogen and  $\gamma$ -carbon respectively, which bestows them with nucleophilic properties.<sup>[16]</sup> This reactivity facet has been utilised by a number of groups in the synthesis of related functionalised NacNac species. Examples include the CO<sub>2</sub> fixation by a scandium complex reported by Piers,<sup>[17]</sup> and Erker's attachment of a nitrile to  $\gamma$ -carbon position following an initial deprotonation reaction.<sup>[27]</sup> Harder has recently unveiled a new variation of the DIPPBDI ligand which has been termed DIPPDPM, based upon a related dipyrromethene scaffold.<sup>[28]</sup> In contrast to the negatively charged central backbone carbon found in DIPPBDI offering nucleophilic reactivity, that in DIPPDPM is effectively neutral. This makes it a less nucleophilic and less Brønsted basic molecule, as appropriate for a true spectator ligand.<sup>[28]</sup>

Next we extended our studies to another class of small molecule, namely isocyanates. This seemed a pertinent choice given recent work by Ma *et al.* that explored the activation of small molecules, including isothiocyanates, by a magnesium alkyl NacNac complex.<sup>[29]</sup> We decided to focus our efforts on the isoelectronic isocyanates since these compounds have a similar

bonding situation to that in carbon dioxide, with the synthetic advantage that exact stoichiometric amounts of the liquid isocyanates can be easily added to reactions. Insertion of isocyanates into s-block metal complexes is known,<sup>[30]</sup> albeit a systematic investigation of isocyanate fixation using lithium NacNac complexes is required to investigate chemoselectivity of such a process.

With this in mind, the parent NacNac(H) ligand was deprotonated using *n*-butyllithium in hexane at 0 °C. To this mixture was added TMEDA, followed by tert-butylisocyanate (*t*-BuNCO), giving a green suspension. This mixture was heated at reflux for one hour, forming a dark brown solution. Concentrating this solution and cooling at -30 °C, gave colourless crystals of the isocyanate insertion product  $[(\text{MeCN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{C}(\text{CONH}(t\text{-Bu}))\text{Li.TMEDA}]$  (**2**) in 48% isolated yield. Interestingly, in this reaction we did not observe any isocyanate trimerization, which is somewhat surprising given that lithium amides are known to facilitate this process.<sup>[31]</sup>

X-ray crystallography determined the monomeric arrangement of **2** (Figure 4) comprising a deprotonated NacNac scaffold with *t*-BuNCO inserted into the backbone  $\gamma$ -C-H bond to form a new carbon-carbon bond.



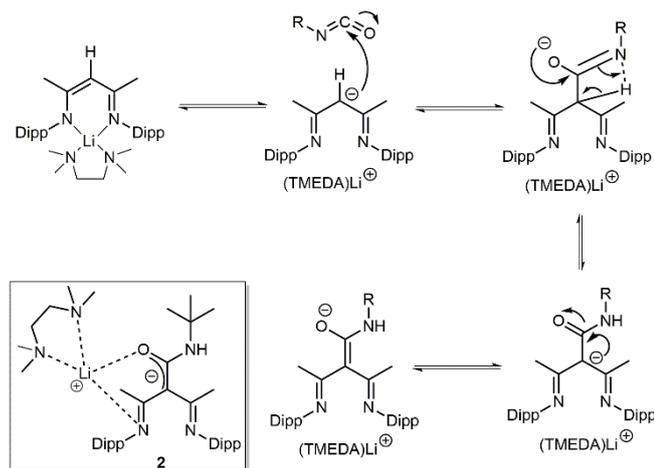
**Figure 4.** Molecular structure of  $[(\text{MeCN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{C}(\text{CONH}(t\text{-Bu}))\text{Li.TMEDA}]$  (**2**) with key atoms labelled. Hydrogen atoms except the amide NH are omitted and the NacNac Dipp groups are shown as wire frame for clarity. Thermal ellipsoids are displayed at 40% probability level. Symmetry transformations used to generate equivalent atoms: -x, -y, -z. Inset shows ChemDraw representation showing resonance structure of (**2**) as implied by the X-ray crystallographic metrics.

The highly distorted tetrahedral lithium [with bond angles ranging from 91.5(2)<sup>o</sup> to 129.6(3)<sup>o</sup> ( $\tau_4 = 0.76$ )],<sup>[21]</sup> coordinates to the oxygen of the *t*-BuNCO unit and one nitrogen of the NacNac ligand, and completes its coordination sphere via TMEDA chelation. There is also uncoordinated TMEDA cocrystallised with **2**. The lithium sits  $\kappa^2$  relative to the ligand, lying closer to the smaller oxygen atom of the *t*-BuNCO unit than the NacNac nitrogen atom [Li-N distance

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of 1.990(5) Å vs. Li-O distance of 1.839(6) Å]. The *t*-BuNCO fragment of the complex features secondary amide functionality with a C<sub>30</sub>-O<sub>1</sub> bond length of 1.258(3) Å and C<sub>30</sub>-N<sub>3</sub> bond length of 1.336(5) Å. The presence of the amine NH was also established through spectroscopic studies, with a resonance at 11.46 ppm in the <sup>1</sup>H NMR spectrum and a broad stretch at 3413 cm<sup>-1</sup> in the IR spectrum.

The presence of a hydrogen atom residing in the secondary amide nitrogen can be attributed to a sigmatropic rearrangement from the backbone hydrogen atom of the  $\gamma$ -carbon within the NacNac ligand (Scheme 1).

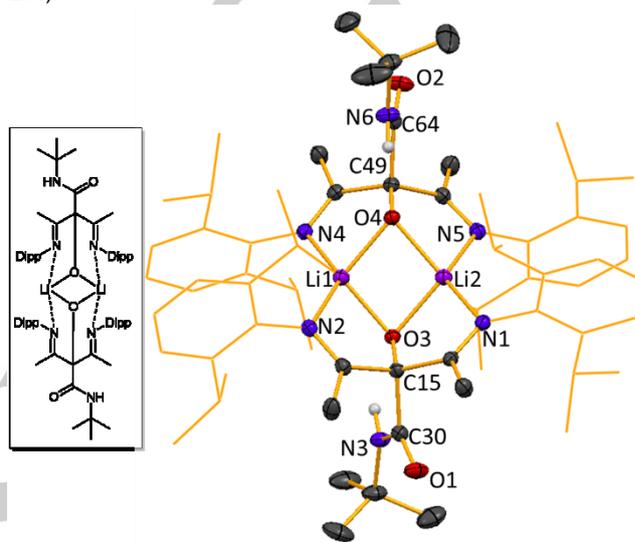


**Scheme 1.** Potential pathway to form products **2** (and **4**) via a sigmatropic hydride rearrangement of the backbone  $\gamma$ -carbon proton.

Such rearrangements have been observed before in small molecule fixation. Notably Fulton *et al.*, used lead and tin NacNac complexes to activate phenyl isocyanate, and Ren and Ma utilised magnesium NacNac complexes to activate phenyl isothiocyanate.<sup>[29, 32]</sup> The diimine functionality present within **2** was also confirmed from the C<sub>13</sub>-N<sub>1</sub> and C<sub>16</sub>-N<sub>2</sub> bond lengths of 1.299(4) Å and 1.295(5) Å respectively, again comparable with the standard imine C-N bond length of 1.279 Å.<sup>[24]</sup> The imine was further confirmed via IR spectroscopic studies, which revealed a vibration at 1602 cm<sup>-1</sup>, attributable to the C=N stretch (see ESI).

Given our group's long standing interest in the polydentate donor molecule Me<sub>6</sub>TREN,<sup>[33]</sup> we decided to extend the activation of isocyanates to include Me<sub>6</sub>TREN, to establish whether its large steric profile would impact upon the resulting structure, and whether all four of its donor arms would be involved in metal ion coordination. For example, one arm is free in the structure of [Me<sub>6</sub>TREN-Mg-N(SiMe<sub>3</sub>)<sub>2</sub>][B{C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub>] reported recently by Venugopal.<sup>[34]</sup> In this regard, NacNac(H) was deprotonated by the action of *n*-butyllithium in hexane at 0 °C and Me<sub>6</sub>TREN was added, causing the formation of a white precipitate. A change to a yellow solution occurred upon adding one equivalent of *t*-BuNCO and heating the mixture at reflux. Concentrating this solution and cooling it to -30 °C led to colourless crystals, identified as [(MeCN-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C(O)Li{NH(*t*-Bu)CO}]<sub>2</sub> (**3**) in an isolated yield of 68%. This complex is dimeric in the crystal,

composed of a deprotonated NacNac ligand, with a *t*-BuNCO moiety inserted into the  $\gamma$ -C-H backbone position and consequently forming a new C-C bond (Figure 5). Despite its presence in the reaction mixture, Me<sub>6</sub>TREN is absent from the structure. Surprisingly, oxygen has also been inserted into the same  $\gamma$ -C position, leading to the formation of a new C-O bond with the two lithium cations present forming a planar four-membered (LiO)<sub>2</sub> ring. The equivalence of the lithium centres was also established in the solution state via <sup>7</sup>Li NMR studies (See ESI).



**Figure 5.** Molecular structure of [(MeCN-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C(O)Li{NH(*t*-Bu)CO}]<sub>2</sub> (**3**). Hydrogen atoms except the amide NH are omitted and the NacNac Dipp groups are shown as wire frame for clarity. Thermal ellipsoids are displayed at 40% probability level. Symmetry transformations used to generate equivalent atoms: 1/2-x, 1/2+y, 1/2-z; -x, -y, -z; 1/2+x, 1/2-y, 1/2+z. Inset shows ChemDraw representation showing resonance structure of (**3**) implied by X-ray crystallographic metrics.

Though crystallographically distinct, the two lithium centres within non-centrosymmetric **3** are essentially equivalent. The Li-O bond lengths in the central core, for example, are identical within experimental error [Li<sub>1</sub>-O<sub>3</sub>, 1.892(3) Å; Li<sub>1</sub>-O<sub>4</sub>, 1.894(3) Å; Li<sub>2</sub>-O<sub>3</sub>, 1.895(3) Å and Li<sub>2</sub>-O<sub>4</sub>, 1.905(3) Å] and are broadly similar to those seen in **2**. The bond angles subtended at lithium are also broadly similar to each other (N<sub>2</sub>-Li<sub>1</sub>-N<sub>4</sub>, 134.2(1)°; N<sub>1</sub>-Li<sub>2</sub>-N<sub>5</sub>, 129.1(2)°; O<sub>4</sub>-Li<sub>1</sub>-O<sub>3</sub>, 99.4(1)°; O<sub>4</sub>-Li<sub>2</sub>-O<sub>3</sub>, 99.0(1)°). Each lithium is four coordinate, bound to two central oxygen atoms and two nitrogen atoms from the backbone of two separate NacNac ligands, exhibiting distorted tetrahedral geometries ( $\tau_4 = 0.65$  and  $0.66$  respectively).<sup>[21]</sup>

Mimicking the arrangements in **2**, each *t*-BuNCO fragment has a secondary amide function, characterised by the C-N single bond lengths of 1.329(2) Å (C<sub>64</sub>-N<sub>6</sub>) and 1.328(2) Å (C<sub>30</sub>-N<sub>3</sub>). The C=N bond lengths within the NacNac moiety are generally close to 1.28 Å [N<sub>1</sub>-C<sub>13</sub>, 1.278(2) Å; N<sub>2</sub>-C<sub>16</sub>, 1.277(2) Å; N<sub>4</sub>-C<sub>47</sub>, 1.275(2) Å; N<sub>5</sub>-C<sub>50</sub>, 1.276(2) Å], consistent with the presence of imine C=N double bonds.<sup>[24]</sup> Two distinct types of C-O bonds reside within the structure; namely those of the secondary amide functionality (C<sub>30</sub>-O<sub>1</sub> length of 1.226(2) Å and C<sub>64</sub>-O<sub>2</sub> length of 1.228(2) Å) and those at the centre of the (LiO)<sub>2</sub> core (C<sub>49</sub>-O<sub>4</sub> and C<sub>15</sub>-O<sub>3</sub> bond lengths of 1.357(2) and 1.358(2) Å respectively). The presence of

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the central oxygen anions could be through adventitious hydrolysis, though the reaction is reproducible with yields of around 68 %, or by fixation of molecular oxygen, as has been observed in many other complexes.<sup>[14][35]</sup> Subsequent experiments have shown that reaction of compound **1** with molecular oxygen *via* a drying tube did not produce **3**, suggesting that adventitious moisture is the source of the oxygen atom. The definite point is that such systems are able to undergo double small molecule fixation within the same system. In any event, the product is unusual for containing not only a newly formed C-C bond between the  $\gamma$ -carbon of the NacNac and the carbon of the *t*-BuNCO but also for containing a new C-O bond at the same  $\gamma$ -carbon position.

Next we tried to expand the isocyanate scope to less bulky examples, to explore whether the backbone insertion reactivity could be maintained. With this in mind, the parent NacNac(H) ligand was deprotonated using *n*-butyllithium in hexane at 0 °C. To this mixture was added PMDETA, followed by the less bulky isopropyl isocyanate (*i*-PrNCO), forming a green suspension. Addition of THF and gentle heating formed a brown solution, which was concentrated and cooled at -20 °C to obtain colourless crystals of the dimeric isocyanate insertion product  $[(\text{MeCN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{C}(\text{CONH}(i\text{-Pr}))]\text{Li}\cdot\text{THF}_2$  (**4**) in 41% yield. X-ray crystallographic studies established the centrosymmetric dimeric structure adopted by **4** (Figure 6).

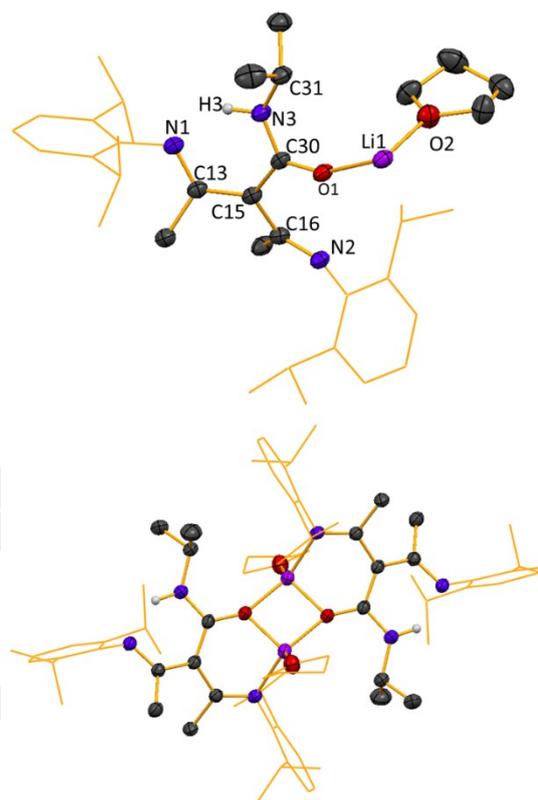
**Table 1.** Selected bond distances (Å) showing delocalization within NacNac backbone.

Bond	1	2	3	4
N1-C2	1.269(3)	1.299(3)	1.278(2)	1.311(3)
C2-C3	1.507(4)	1.451(4)	1.564(2)	1.435(4)
C3-C4	1.514(4)	1.443(3)	1.561(2)	1.467(3)
C4-N5	1.286(3)	1.295(4)	1.277(2)	1.298(3)

For a fuller analysis of further bond lengths and angles for compounds 1-4 see Table 2 in ESI

**4** comprises two deprotonated NacNac scaffolds, linked *via* a four-membered (LiO)<sub>2</sub> ring, with *i*-PrNCO inserted into the  $\gamma$ -carbon position to form a new C-C bond. The distorted tetrahedral lithium centre is four coordinate, with bond angles ranging from 91.5(2)° to 136.7(3)° ( $\tau_4 = 0.72$ ),<sup>[21]</sup> bonded to one nitrogen of the NacNac ligand, the oxygen atoms of two *i*-PrNCO units, and a THF ligand. Respective bond distances are 2.021(6) Å (Li<sub>1</sub>-N<sub>2</sub>), 1.915(5) Å (Li<sub>1</sub>-O<sub>1</sub>), 1.896(6) Å (Li<sub>1</sub>-O<sub>1</sub>) and 1.991(5) Å (Li<sub>1</sub>-O<sub>2</sub>). A sigmatropic hydride rearrangement is implicated again with the amide functionality discernable from the <sup>1</sup>H NMR spectrum (resonance at 11.0 ppm, see ESI). As in both **2** and **3**, it is the isocyanate (*i*-PrNCO) fragment of the complex which features such secondary amide functionality, as ascertained from the C<sub>30</sub>-O<sub>1</sub> and C<sub>30</sub>-N<sub>3</sub> bond lengths of 1.270(4) Å and 1.348(4) Å respectively. Once more, **4** exhibits diimine character based on bond length evidence of 1.298(4) Å for C<sub>16</sub>-N<sub>2</sub> and 1.310(4) Å for C<sub>13</sub>-N<sub>1</sub> (see Table 1 for a comparison of important NacNac bond lengths highlighting the diimine character in each case). Of note is the fact that complex **4** being dimeric departs from the monomeric structure seen in **2**. This dimerisation is sterically

driven due to the use of a less bulky isocyanate. Moreover, as was the case in **3** with Me<sub>6</sub>TREN, in **4** the reaction PMDETA is not incorporated into the solid state structure. This may indicate that within these sterically congested architectures, the incorporation of larger (than THF or bidentate TMEDA) solvating ligands near the metal ion is prohibited.



**Figure 6.** Top: Molecular structure of the asymmetric unit of  $[(\text{MeCN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{C}(\text{CONH}(i\text{-Pr}))]\text{Li}\cdot\text{THF}_2$  (**4**) with key atoms labelled; and Bottom: Full dimeric structure of (**4**). Hydrogen atoms except the amide NH are omitted and the NacNac Dipp groups and solvating THF are shown as wire frame for clarity. Thermal ellipsoids are displayed at 40% probability level. Symmetry transformations used to generate equivalent atoms: -x, -y, -z.

## Conclusions

This study has uncovered unusual reactivity of a common lithium NacNac complex. Exposing lithium NacNac (Dipp, Me) to carbon dioxide forms a dimeric lithium carboxylate based NacNac product, where the CO<sub>2</sub> has reacted preferentially at the  $\gamma$ -carbon position, which is to the best of our knowledge, the first structurally authenticated example of such reactivity with alkali metal NacNac species. Extending this reactivity to isocyanates results in either monomeric or dimeric structures, depending on the identity/bulk of the isocyanate used.

On reacting *t*-BuNCO with LiNacNac and TMEDA, a monomeric structure is obtained, with isocyanate insertion into

the  $\gamma$ -carbon position resulting in both amide and imine functionality being present within the complex. When using the higher dentate donor Me<sub>6</sub>TREN, a serendipitous double insertion is accomplished comprising an isocyanate molecule and an oxygen atom, both at the same carbon position, establishing such systems as able to undergo dual small molecule activation.

Moving to the less bulky isocyanate, *i*-PrNCO, the reaction with LiNaCNac produces a dimeric complex, where the NaCNac units are linked via Li-O bonds arising from the amido functionality inserted within the  $\gamma$ -carbon position. Future work will explore the reactivity of other alkali metal NaCNac type ligands towards a range of small molecules, as well as attempting to apply the newly formed backbone-functionalised NaCNac metal complexes as a source of special ditopic ligands in synthesis and homogeneous catalysis. The functionalised ligands are ripe for investigations into their complexation behaviour and further reactivity, which are currently ongoing within our laboratory.

## Experimental Section

Full experimental characterisation and synthetic procedures are described in the supporting information.

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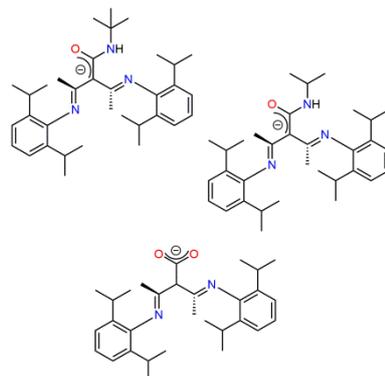
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**The Knack of NacNac Backbone**

**Functionalisation:** Reaction of the lithium NacNac(Dipp, Me) complex with carbon dioxide and isocyanates affords a series of structurally diverse products, with insertion of the small molecules at the  $\gamma$ -C site of the NacNac ligand, which rearranges into a diimine formulation.



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XX. – XX.

**Backbone reactivity of lithium  $\beta$ -diketiminato (NacNac) complexes towards CO<sub>2</sub>, *t*-BuNCO and *i*-PrNCO**

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