Lithium and Aluminium Carbamato Derivatives of the Utility Amide 2, 2, 6, 6-Tetramethylpiperidide †

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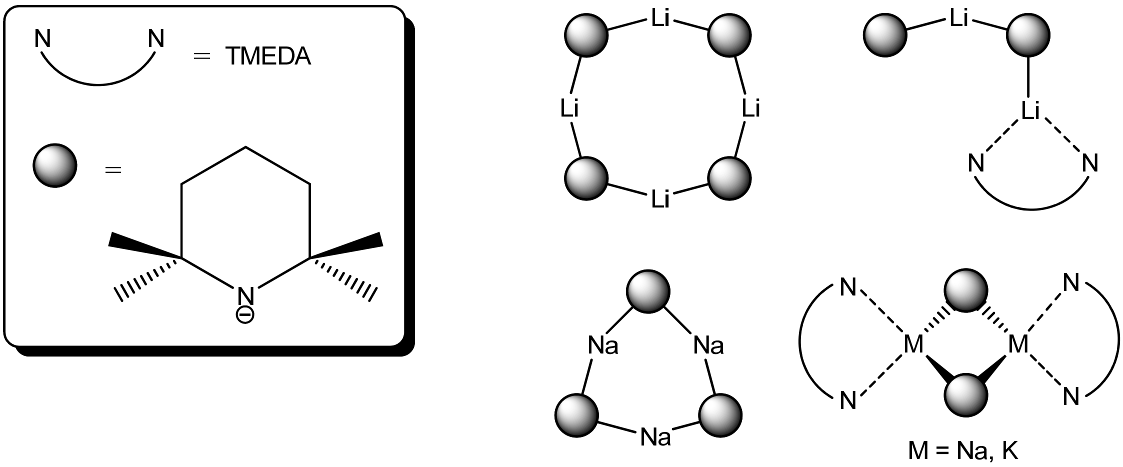
† Dedicated to Professor David W.H. Rankin on the occasion of his retirement for his many outstanding contributions to molecular structural chemistry.

Insertion of CO_2 into the metal-N bond of a series of synthetically-important alkali-metal TMP (2,2,6,6-tetramethylpiperidide) complexes has been studied. Determined by X-ray crystallography, the molecular structure of the TMEDA-solvated Li derivative shows a central 8-membered $(LiOCO)_2$ ring lying in a chair conformation with distorted tetrahedral lithium centres. While trying to obtain crystals of a THF solvated derivative, a mixed carbonato/carbamato dodecanuclear lithium cluster was formed containing two central $(CO_3)^{2-}$ fragments and eight O_2CTMP ligands with four distinct bonding modes. A bisalkylaluminium carbamato complex has also been prepared via two different methods (CO_2 insertion into a pre-formed Al-N bond and ligand transfer from the corresponding lithium reagent) which adopts a dimeric structure in the solid state.

Introduction

One of the most important reactions in chemistry is deprotonative metallation, where a relatively inert C-H bond is replaced with a more reactive C-M bond (where M is typically an alkali-metal). Of the reagents capable of effecting such a transformation, alkali-metal secondary amides (MNR_2) are among the most widely utilized. Sterically demanding lithium 2,2,6,6-tetramethylpiperidide (LiTMP) is one of the most popular such utility amides. First reported as a base in 1972,[1] LiTMP is favoured by synthetic chemists due to its blend of relatively strong Brønsted basicity, slightly inferior to that of alkyllithium reagents, coupled with its low nucleophilicity, which is superior to that of the common alkyllithium reagents ^{n}BuLi or ^{t}BuLi. These properties of LiTMP are further enhanced by high solubility in ethereal and hydrocarbon solvents, its ready preparation from commercially available reagents [^{n}BuLi and the parent amine TMP(H)] and relative ease of handling with respect to alkyllithium reagents.

With reactivity closely correlated to structure, there has also been widespread interest in the solid-state structures of alkali-metal utility amides including LiTMP. When pure in the crystalline state, LiTMP adopts a cyclotetrameric molecular structure (scheme 1), which was elucidated by Lappert and Atwood in 1983.[2] In the presence of the popular bidentate donor *N*, *N*, *N*', *N*'-tetramethylethylenediamine (TMEDA) this crystalline form changes to a hemisolvated ‘open dimer’.[3] These alkali-metal amide structures are highly dependent on the identity of the alkali-metal, since the unsolvated sodium derivative is a smaller cyclotrimer[4] and the TMEDA-solvated sodium and potassium derivatives[5] are more conventional cyclic $(MN)_2$ dimers with a donor molecule capping each metal. The donor-deficient open dimer structure is presumably preferred so as to alleviate the strain which a four-membered Li_2N_2 ring would experience; the closed dimer would also bring the bulky diamine and amide moieties into too close proximity as a consequence of shorter Li-N bonds.



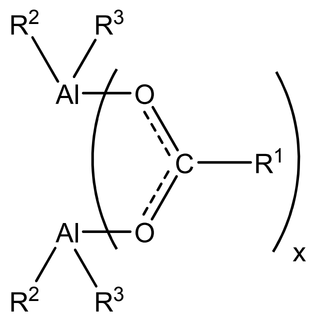
Scheme 1

Despite the picture being clear with regards to the structures of these compounds in the solid-state, the solution-state structures are less clear cut. Collum has, however, shown through ^{6}Li and ^{15}N NMR spectroscopy in hydrocarbon solvent that the unsolvated lithium derivative consists of a complicated mixture of four distinct cyclic tetramers along with a cyclic trimer,[6] while the TMEDA solvated congener exists as both the open dimer and a monomer.[7]

TMP is also an important amide in aluminium chemistry, particularly in the guise of bisalkylaluminium amido reagents. Amongst others, Yamamoto has found utility for these reagents in a variety of organic transformations such as the regio/stereospecific isomerisation of epoxides to allylic alcohols,[8] conversion of epoxy silyl ethers to 1,2-diols,[9] addition of an ester/ketone enolate to an aldehyde,[10] diastereoselective acetal cleavage[11] and Fischer indole synthesis.[12] These organo-aluminium compounds have recently enjoyed a renaissance in the flourishing field of mixed-metalate chemistry,[13] where the juxtaposition of $^iBu_2Al(TMP)$ with an alkali-metal TMP reagent can effect the usually difficult α-C deprotonation of TMEDA or PMDETA (N, N, N', N'', N'' – pentamethyldiethylenetriamine) resulting in a new N-CH_2-Al bond.[14] Indeed, this reagent has even been applied in the deprotonation of a methyl group of KTMP to give the erstwhile unknown TMP^{2-} dianion (N-H, CH_3 deprotonated).[15]

Closely related to metal amides are the metal carbamate family of compounds. Alkali-metal carbamates (MO_2CNR_2) are of interest in industrial chemistry as a convenient precursor to isocyanates[16] and are useful intermediates in areas as diverse as agricultural[17] and medicinal chemistry.[18] They can be synthesised in various ways such as by reaction of an alkali-metal tetraphenylborate salt,[19] or the alkali-metal itself,[20] with a solution of the desired amine in the presence of CO_2. This facile approach of inserting a CO_2 molecule into a metal-nitrogen bond has been well documented for transition metal carbamates but has seen much less attention for the alkali-metal analogues.[21] Carbon dioxide is a useful reagent due to its ease of handling and widespread availability. Indeed, CO_2 insertion to produce carbamates is the current synthetic route of choice given that the original method involved both the use of highly toxic phosgene and the production of HCl as a by-product. Katritzky has published a series of papers using CO_2 as a reagent for simultaneous protection of nucleophilic centres and the activation of alternative locations to nucleophilic attack,[22] while Otero *et al*. have inserted CO_2 into organolithium species to yield lithium carboxylate species.[23] Aluminium carbamates have seen marginally more interest than their alkali-metal counterparts, due in part to the ease with which CO_2 can be inserted into the Al-N bond. The first example involved CO_2 insertion into Et_2AlNEt_2, a reaction whose rate was enhanced by the presence of a donor such as TMEDA.[24]

Aluminium carbamates with a 1:1, 1:2, 1:3 or 2:3 aluminium:carbamate ratio have recently been crystallographically characterised, with the recurring structural motif in these complexes being the $(AlOCO)_2$ ring with the carbamate functionality acting as a bridge between metal atoms. The carbamate rich species $Al_2(O_2CN^iPr_2)_6$ (**A** – scheme 2), which contains both bridging and terminal carbamate groups, was prepared from reaction of $AlCl_3$ with HN^iPr_2 in the presence of CO_2 [25] and was subsequently converted to the tetranuclear μ_3-oxo derivative $[Al_4(\mu_3\text{-}O)_2(O_2CN^iPr_2)_8]$ by stoichiometric hydrolysis with H_2O.[26] Nöth fortuitously obtained the 1:2 species $[MeAl(O_2CTMP)_2]_2$ (**B**) [27] and the 2:3 ionic species $[(^tBuAl)_2(O_2CTMP)_3]^+[(^tBu_3Al)_2Br]^-$ (**C**) [28] when trying to recrystallise the parent bisalkylaluminium amide using dry ice as a cooling source, while Chang obtained $[Me_2Al(O_2CNR_2)]_2$ (R = Et, ^{i}Pr, **D**) as one of the products upon bubbling CO_2 through the mixed metal cluster $[Me_2Al(\mu\text{-}NR_2)_2Mg(\mu\text{-}Me)]_x$ (R = Et, x = 2; R = ^{i}Pr, x = 4).[29] Interestingly, reaction of $(TMP)_2AlCl$ with excess CO_2 resulted in selective insertion into only one Al-N bond to give the alkylamido aluminium carbamate $[(TMP)(O_2CTMP)AlCl]_2$ (**E**).[30]



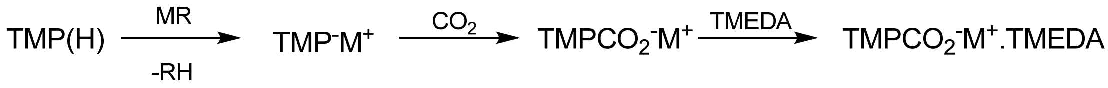
A x = 2; R^1 = N^iPr_2; R^2 = R^3 = $O_2CN^iPr_2$
B x = 4; R^1 = TMP; R^2 = Me; R^3 = nothing
C x = 3; R^1 = TMP; R^2 = ^{t}Bu; R^3 = nothing *
D x = 2; R^1 = N^iPr_2; R^2 = R^3 = Me
E x = 2; R^1 = TMP; R^2 = TMP; R^3 = Cl

Scheme 2 Crystallographically characterised aluminium carbamates. * Fragment is cationic moiety of an ion-pair with a $[(^tBu_3Al)_2Br]^-$ counter-anion.

Considering the widespread interest in alkali-metal amides it is surprising to learn that only two solid-state structures are known for alkali-metal carbamates, neither being derived from an important utility alkali-metal amide. Snaith reported the TMEDA solvated-structure of the diphenylamido carbamate LiO_2CNPh_2 [31] and the THF-solvated structure of an indole-based lithium carbamate [32] as a dimer and tetramer respectively, both products being obtained by inserting CO_2 into a pre-formed Li-N bond. $LiO_2C(TMP)$ has been prepared previously and found application as a carbamate source in a metathesis reaction to yield a bisamido gallium carbamate species, however, beyond elemental analysis and an IR spectrum, no characterisation of this lithium TMP-carbamate was carried out.[33] Given the structural diversity of alkali-metal amides (vide supra) we set our sights on addressing the paucity of alkali-metal carbamates based on utility amides. Due to our burgeoning interest in the chemistry of diisobutyl aluminium TMP we also studied its carbamato derivative, both via insertion of CO_2 into the Al-N bond of $^iBu_2AlTMP$ and also by using the lithium TMP carbamate as a ligand transfer agent and report our findings herein.

Results and Discussion

Following established protocols, the congeneric alkali-metal TMP salts (**1**) were prepared by deprotonation of the parent secondary amine with ^nBuLi, ^nBuNa and KCH_2SiMe_3 respectively. These amides were converted to the corresponding carbamates (**2**) by bubbling gaseous CO_2 (from a Schlenk flask containing dry ice) through a hexane solution of **1** via a cannula (scheme 3). In each case a white solid precipitated, which was conveniently collected by Schlenk filtration and washed with hexane.



(**1**) (**2**) (**3**)

Scheme 3

These unsolvated products proved to be largely insoluble in non (lone-pair) donating solvents such as benzene and toluene suggesting that they are polymeric in nature. However, **2-Li** did produce weak ^{1}H and ^{13}C NMR spectra in C_7D_8 solution. In addition to anticipated resonances, these spectra showed others attributable to TMP(H), however, given the relative insolubility of the carbamate we believe that the TMP(H) is merely a minor impurity rather than a hydrolysis product. Significantly, the ^{1}H NMR spectrum shows a reversal in the expected or normal order of the TMP resonances with the methyl groups now at highest frequency (1.74 ppm) and the γ hydrogen atoms at the lowest frequency (1.54 ppm). This reversal was witnessed previously in Linti's gallium carbamate.[33] All the carbon centres are accounted for in the ^{13}C NMR spectrum, with the most significant being that in the CO_2 group which resonates at 168.2 ppm, a typical value for a carbamate. For example this functionality in a series of functionalized pyrrolidine lithium carbamates resonates at approximately 158 ppm [34] while that of a Mg carbamate tetramer resonates at 164 ppm.[35]

2-Na did not give suitable NMR spectra in non-donating solvents, therefore a d_8-THF solution was consequently studied. While there was still a noticeable amount of undissolved solid visible in the NMR tube, **2-Na** was sufficiently soluble for useful spectra to be obtained. This suggests that THF has almost certainly caused deaggregation of at least some of the original polymer. The ^{1}H NMR spectrum again shows a minor amount of TMP(H). Resonances representing the carbamate are slightly broader than those of the parent amine, with the β and γ protons appearing at a coincidental chemical shift of 1.53 ppm. What is noticeable here is that in the presence of the Lewis donating THF, the reversal of resonance chemical shifts as seen in **2-Li** is not witnessed with the methyl group now upfield at 1.45 ppm. Again, the CO_2 fragment is witnessed in the ^{13}C NMR spectrum with a chemical shift of 166.6 ppm. Unfortunately, NMR spectra of **2-K** could not be obtained due to its exceptionally poor solubility.

Having determined that carbon dioxide had inserted into the metal-nitrogen bonds to produce some type of polymeric carbamate, we attempted to prepare lower aggregates by introducing the bidentate Lewis donor TMEDA to a hexane suspension of **2**. This only caused dissolution in the case of **2-Li** and even then the solution was partially cloudy. Cooling of this solution to -30°C yielded a crop of colourless crystals in a 66% isolated yield. A single crystal was subsequently subjected to an X-ray diffraction study. Crystallographic data are listed in table 1.

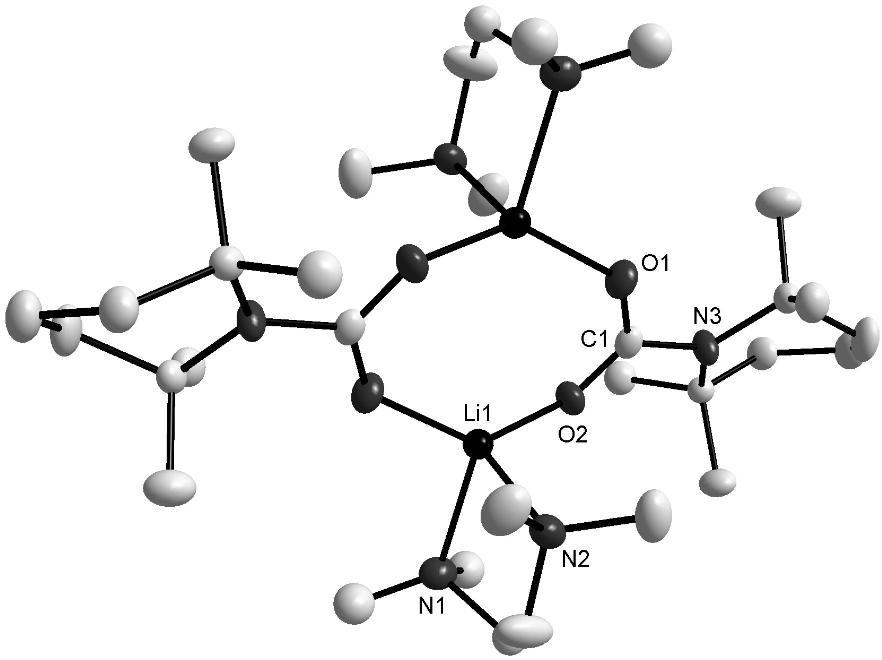


Figure 1. Molecular structure of the lithium TMP-carbamate [($TMPCO_2$) Li·TMEDA]$_2$ (**3-Li**) with selective atom labelling. Hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability level. TMP and TMEDA fragments were modelled as disordered over two positions in a 77:23 and 61:39 ratio respectively; only the major component is shown. Symmetry transformations used to generate equivalent atoms: 1-x, 1-y, 1-z. Selected bond lengths (Å) and angles (^{o}): Li(1)-O(1A) 1.881(2), Li(1)-O(2) 1.880(2), C(1)-O(1) 1.261(2), C(1)-O(2) 1.255(2), C(1)-N(3) 1.401(2); O(1)-C(1)-O(2) 124.3(1), O(1)-C(1)-N(3) 118.0(1), O(2)-C(1)-N(3) 117.7(1), C(1)-O(1)-Li(1A) 132.1(1) C(1)-O(2)-Li(1) 127.2(1) O(2)-Li(1)-O(1A) 134.1(1).

The solid state structure (Figure 1) shows **3-Li** exists as a cyclodimer lying about an inversion centre, with a central eight-membered (LiOCO)$_2$ ring, sharing similar parameters with that seen previously by Snaith for [LiO_2CNPh_2·TMEDA][31] and also with that of an ether solvated lithium carboxylate complex.[36] As emphasised in figure

2, the carbon and oxygen atoms lie in the same plane, with the two lithium centres positioned above and below this plane at either end [deviation of 0.585(2)Å], such that the ring lies in a chair conformation. This deviation from planarity is presumably largely a consequence of the lone pairs on oxygen. Lying in a distorted tetrahedral environment, the lithium atoms have their coordination sphere completed by the nitrogen atoms of a chelating TMEDA molecule. The carbamate carbon atoms are three coordinate, trigonal planar (Σ<C = 360.0^{o}). As is often the case, the TMP and TMEDA skeletons are disordered and a detailed description of their parameters is unwarranted.

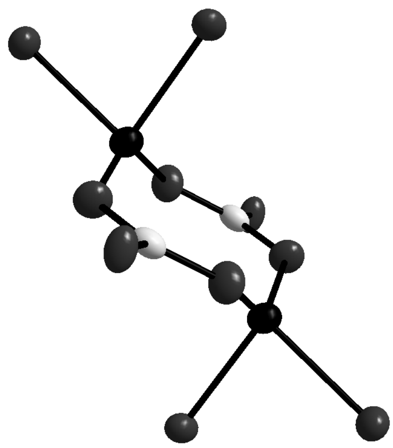


Figure 2. Central core of **3-Li**.

Despite TMEDA causing the unsolvated lithium carbamate to deaggregate to a dimeric species, **3-Li** still proved to be insoluble in non-donating solvents. Consequently its NMR spectra had to be collected in d_8-THF. The ^{1}H NMR spectrum was similar to that of **2-Na** in THF, with the β and γ protons appearing at a coincidental chemical shift of 1.52 ppm. This resonance, along with that representing the methyl groups of the TMP appendage, were deshielded with respect to those of TMP(H). Two resonances were witnessed for TMEDA, with the ethylene backbone at a higher frequency (2.30 ppm) than the methyl hydrogens (2.15 ppm), consistent with uncoordinated TMEDA[37] and suggesting that THF has displaced TMEDA in the solution structure (indeed **2-Li** in d_8-THF displays an identical ^{1}H spectrum). Integration values showed that TMEDA was present in a 1:1 ratio with respect to the TMP-carbamate, consistent with the solid-state structure. Of most significance in the ^{13}C NMR spectrum was the CO_2 peak at 167.2 ppm. All the other carbon atoms displayed resonances at similar chemical shifts to those in **2-Li** and **2-Na**.

We also attempted to grow crystals of the THF solvated derivative so as to carry out a true comparison on the effect of the donor on aggregation state of the lithium carbamate. A suspension of **2-Li** in hexane had THF added until it turned clear and was then chilled to -30^{o}C. After several weeks, a few crystals were evident. X-ray analysis (figure 3) showed that rather than a THF solvate, this structure was actually $[Li_{12}(\mu_8\eta^8\text{-}CO_3)_2(O_2CTMP)_8{\cdot}4THF]$ (**4**); a dodecanuclear lithium carbamate cluster containing a pair of central carbonato CO_3 groups. The organic periphery of this structure was heavily disordered and therefore a detailed analysis of the structure is unwarranted, however a number of salient features regarding the central core were evident.

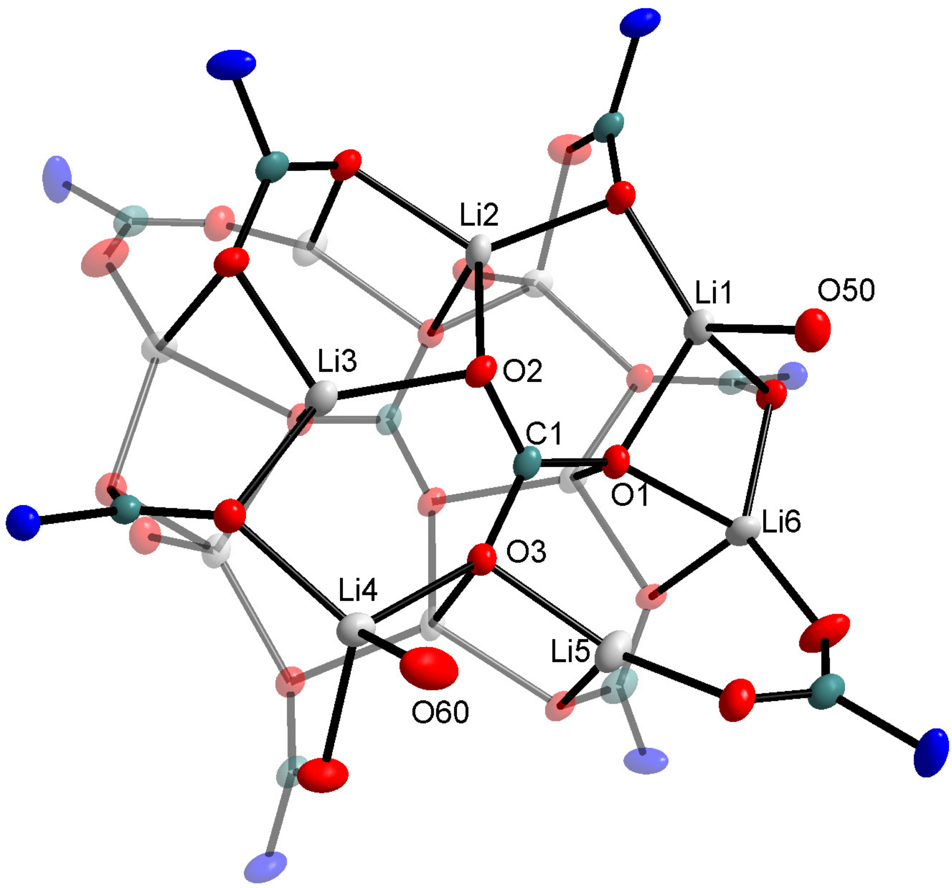


Figure 3 Molecular structure of [$Li_{12}(\mu_8\eta^8-CO_3)_2(O_2CTMP)_8\cdot 4THF$] (**4**) with selective atom labelling. Hydrogen atoms and carbon atoms of THF and TMP fragments are omitted for clarity and thermal ellipsoids are displayed at 50% probability level. Symmetry transformations used to generate equivalent atoms: 1-x, 1-y, -z. Selected bond lengths (Å) and angles (^{o}): C(1)-O(1) 1.292(3), C(1)-O(2) 1.269(3), C(1)-O(3) 1.2903(3), Li(1)-O(1) 1.970(5), Li(2)-O(2) 1.923(5), Li(3)-O(2) 1.908(5), Li(4)-O(3) 1.938(5), Li(5)-O(3) 1.947(5), Li(6)-O(1) 2.080(5), Li(2A)-O(3) 2.085(5), Li(3A)-O(1) 2.196(5); O(1)-C(1)-O(2) 121.1(2), O(1)-C(1)-O(3) 118.6(2), O(2)-C(1)-O(3) 120.3(2).

Presumably this unexpected product was formed as a consequence of adventitious oxidation. The structure is best described as a pair of antiparallel trigonal planar carbonate units (as a consequence of an inversion centre) each surrounded by six lithium atoms (Σ<C = 360.0^{o}). Each carbonate oxygen atom coordinates to two of these six lithium atoms [range of Li-O bond lengths = 1.908(5) – 2.080(5)Å] while O(1) and O(3) also show interactions to a lithium atom of the adjacent plane [Li(3A)-O(1) = 2.196(5)Å; Li(2A)-O(3) = 2.085(5)Å]. The bonding in the CO_3Li_6 unit is consistent with that witnessed by Hyvärinen *et al* in their carbonate-centred lithium cluster {[Li_4(μ_3-Cl)(μ_6-$OSiMe_2OMe_2SiO$)(μ-HMPA)$(HMPA)_3]_3$(μ_3-Cl)(μ_9-CO_3)}·2THF [Li-O = 1.92(2) – 2.08(2)Å].[38] The lithium atoms in **4** are consequently held together by a framework of eight bridging O_2CTMP units while Li(1), Li(1A), Li(4) and Li(4A) also have THF completing their coordination sphere. This results in all the lithium atoms being in a distorted tetrahedral LiO_4 arrangement, with the exception of Li(5) which is LiO_3 distorted trigonal planar. An unusual and highly interesting feature is that the O_2CTMP units display three of the seven different bridging modes proposed by Chang (figure 4).[39] Specifically, these are $\mu_2\eta^2$ between Li(5) and Li(6), $\mu_3\eta^3$ between Li(1), Li(2) and Li(4A) and $\mu_4\eta^4$ between Li(3), Li(4), Li(1A) and Li(6A) and between Li(3), Li(6A), Li(2) and Li(5A).

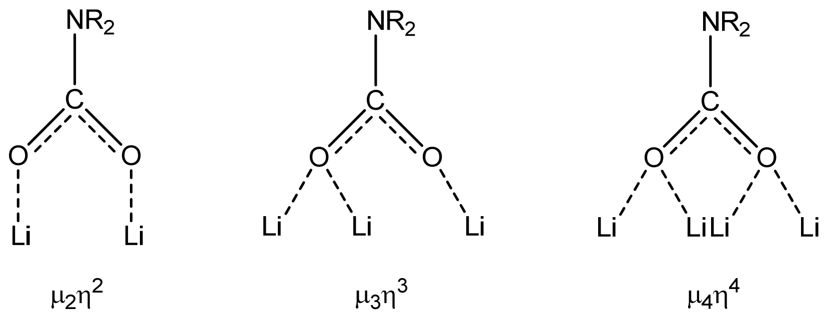
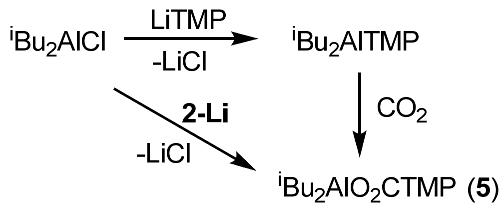


Figure 4 Unique bridging modes found in the carbamate anions found in **4**

The $\mu_4\eta^4$ mode of bridging can be further sub-divided in complex **4** since one of the bonding modes involves each oxygen atom bonding to two lithium atoms from the same plane while the other involves each oxygen atom bonding to one lithium atom from each plane such that the carbamato groups are essentially perpendicular to one another. This essentially results in four distinct bonding modes, two more than in the pentanuclear Mg carbamato cluster of Chang. The Li-O(carbamato) distances vary considerably, however a definite trend is evident. The shortest interactions occur between those oxygen atoms which bind only to one lithium atom, that is both from the $\mu_2\eta^2$ carbamate [1.857(6) and 1.820(6)Å] and one from the $\mu_3\eta^3$ carbamate [1.891(5)Å]. Those bonds between a bridging oxygen and lithium fall in the range 1.911(6) – 1.974(6)Å.

The fact that we only obtained a small amount of this fortuitous product, coupled with its poor solubility, meant that we were unable to obtain any further analysis other than a weak ^{1}H NMR spectrum. Coordinated THF was evident from two appropriate resonances at chemical shifts of 3.57 and 1.42 ppm. The carbamate resonances were broad, which is to be expected since four chemically inequivalent but closely related O_2CTMP groups are present in the crystal structure. The methyl groups resonated at 1.37 ppm with broad signals at 1.32 and 0.92 ppm tentatively assigned to the β and γ hydrogen atoms respectively.

Next, we extended our attention to bisalkylaluminium carbamates. Of most interest to us was the diisobutyl TMP derivative due to its recent utilisation in mixed metallate chemistry (vide supra). We determined that two different paths could be taken to the desired species (scheme 4).



Scheme 4

The first path involved insertion of CO_2 into the Al-N bond; a circumstance which has been previously reported.[24-25, 27-29] The bisalkylaluminium amide was prepared by a metathesis reaction using $^{i}Bu_2AlCl$ and LiTMP, filtered to remove LiCl and then CO_2 was passed through in an identical manner to that described for **2**. The solution turned cloudy and was chilled to -30°C to afford a crop of colourless crystals of the new aluminium carbamate **5**. An X-ray diffraction study on a single crystal of **5** established its molecular structure (figure 5).

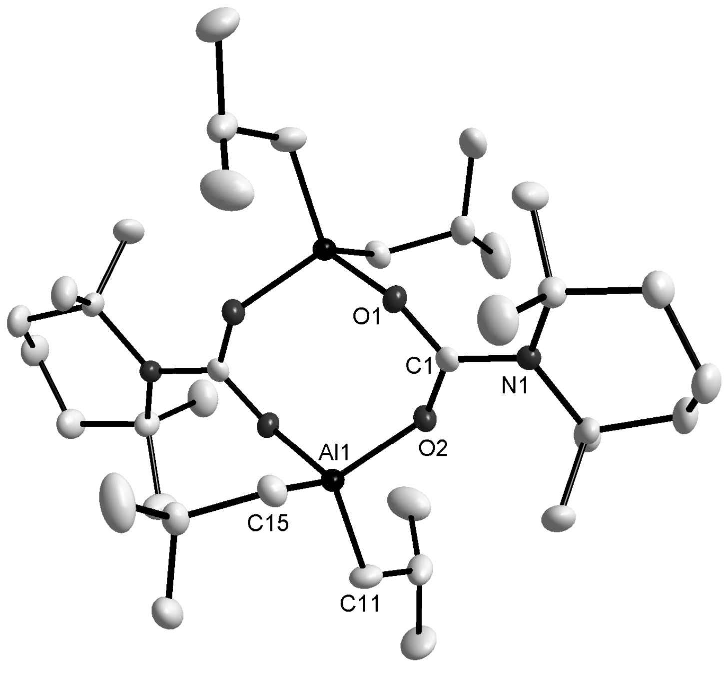


Figure 5. Molecular structure of the diisobutyl aluminium TMP-carbamate $[^{i}Bu_2Al(O_2CTMP)]_2$ (**5**) with selective atom labelling. Hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability level. C(12) was modelled as disordered over two positions in a 66:34 ratio; only the major component

is shown. Symmetry transformations used to generate equivalent atoms: 1-x, -y, 1-z. Selected bond lengths (Å) and angles (^{o}): Al(1)-O(1A) 1.827(1), Al(1)-O(2) 1.826(1), C(1)-O(1) 1.284(2), C(1)-O(2) 1.282(2), C(1)-N(1) 1.347(2), Al(1)-C(11) 1.974(2), Al(1)-C(15) 1.975(2); O(1)-C(1)-O(2) 120.0(1), O(1)-C(1)-N(1) 119.9(1), O(2)-C(1)-N(1) 120.1(1), C(1)-O(1)-Al(1A) 129.0(1) C(1)-O(2)-Al(1) 132.4(1) O(2)-Al(1)-O(1A) 107.03(5), C(11)-Al(1)-C(15) 120.22(7).

This dimeric structure, which lies about an inversion centre, is similar to that witnessed by Chang in the closely related dimethyl aluminium diisopropylcarbamate,[29] with a central $(AlOCO)_2$ ring. In **5**, this ring has two co-planar OCO fragments with the metal atoms lying above and below this plane by 0.949Å. This deviation is considerably greater than that witnessed in **3-Li** despite the M-O bonds being shorter in **5** and may be due to the lesser steric bulk around Al (2 x ^{i}Bu group) versus that around Li (1 x TMEDA). Like Chang's structure, the aluminium centres lie in a pseudo-tetrahedral environment, with the greatest distortion occurring between the pendant ^{i}Bu arms [C-Al-C = 120.22(7)^o], probably to keep these branched alkyl groups apart. The near-identical C-O bond distances [1.282(2) and 1.284(2)Å] indicate delocalised bonding while the C-N bond of the carbamate [1.347(2)Å] is considerably shorter than a typical C-N single bond [CN single bonds of TMP in **5** are 1.526(2) and 1.528(2)Å]. The carbamate carbon atom lies in an almost perfect trigonal planar environment with each angle no greater than 0.1^o from 120^o.

The ^{1}H and ^{13}C NMR spectra of **5**, recorded in C_6D_6, were as expected. As witnessed earlier for **2-Li**, the order of the resonances for the TMP fragment are reversed with respect to TMP(H), with the methyl group at 1.47 ppm and the β and γ CH_2 groups upfield of this at 1.28 and 1.20 ppm respectively. In the ^{13}C spectrum the carbamate carbon resonates at 160.8 ppm, which again is a typical value for such functionality.

As shown in scheme 4, a second route to **5** also exists; that is by using **2-Li** as a ligand transfer reagent with the parent bisalkylaluminium chloride. Such a route has previously been employed by Linti to give a gallium carbamate[33] but to the best of our knowledge has never been used in the synthesis of an aluminium derivative. The two reagents were allowed to stir overnight in hexane before precipitated LiCl was removed via filtration. Concentration and cooling of the sample gave a crop of crystals which were shown by ^{1}H NMR spectroscopy to also be the desired product **5**. The crystalline yield (25%) is comparable to that obtained from the CO_2 insertion route (28%). While this at first seems low, it is actually at the high end of the yields obtained for other aluminium carbamates mentioned earlier.

Conclusion

In summary, we have successfully inserted CO_2 into the metal-nitrogen bond of the lithium and sodium derivatives of the utility amide 2, 2, 6, 6 – tetramethylpiperidide. The TMEDA solvated lithium carbamate is a dimer in the solid state with a central $(LiOCO)_2$ ring. Attempts to isolate a THF solvated derivative resulted instead in the formation of a $(CO_3)^{2-}$ centred lithium carbamato cluster which displays four distinct bonding modes of the carbamato functionality towards the metal centres. Finally, the carbamato derivative of the important bisalkylaluminium amide $^{i}Bu_2AlTMP$ has been prepared via two different routes, namely salt metathesis via the lithium carbamate with the parent bisalkylaluminium chloride or by insertion of CO_2 into the N-Al bond of a bisalkylaluminium TMP complex.

Experimental Section

Reagents and general procedures

All reactions and manipulations were performed under a protective argon atmosphere using either standard Schlenk techniques or a glove box. Hexane was dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. TMEDA was distilled over CaH_2 and stored over 4Å molecular sieves prior to use. ^{n}Butyllithium (1.6M in hexane) and $^{i}Bu_2AlCl$ were purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer operating at 400.13 MHz for ^{1}H, 155.47 MHz for ^{7}Li and 100.62 MHz for ^{13}C. All ^{13}C spectra were proton decoupled.

Synthesis of 2-Li

^{n}BuLi (1 mL, 1.6 M, 1.6 mmol) was added slowly to a stirred solution of TMP(H) (0.27 mL, 1.6 mmol) in hexane (10mL). After 1 h, CO_2 was bubbled through this solution via a cannula from an adjacent Schlenk flask filled with dry ice. A white precipitate started to form immediately. After 30 mins, the CO_2 cannula was removed and the solid was filtered and washed with more hexane to give the final product as a white powder (0.238 g, 78 %). Small resonances representing traces of unreacted TMP(H) were witnessed, only resonances representing the product are reported here. ^{1}H NMR (300 K, C_7D_8): δ 1.74, (12H, s, TMP Me), 1.62 (4H, t, TMP β CH_2), 1.54 (2H, m, TMP γ CH_2). ^{13}C NMR (300 K, C_7D_8): δ 168.2 (CO_2), 55.9 (TMP α), 43.1 (TMP β), 31.3 (TMP Me), 17.1 (TMP γ).

Synthesis of 2-Na

This was prepared using the same procedure as described above for **2-Li** except ^{n}BuNa was used instead of ^{n}BuLi to afford the final product as a white powder (0.229 g, 69 %). As in the previous case, trace amounts of unreacted TMP(H) were detected. ^{1}H NMR (300 K, d_8-THF): δ 1.53 (6H, br s, TMP β and γ CH_2), 1.45, (12H, s, TMP Me). ^{13}C NMR (300 K, d_8-THF): δ 166.6 (CO_2), 54.7 (TMP α), 43.6 (TMP β), 31.3 (TMP Me), 17.6 (TMP γ).

Synthesis of 3-Li

2-Li was prepared as described above. This time, instead of collecting the solid by filtration, an excess of TMEDA (0.90 mL, 6.0 mmol) was added to the hexane suspension to give a cloudy solution. This was cooled to -30^{o}C. After 24 h, a crop of X-ray quality colourless crystals had deposited (0.311 g, 66 %). ^{1}H NMR (300 K, d_8-THF): δ 2.30 (4H, s, TMEDA CH_2), 2.15 (12H, s, TMEDA Me), 1.52 (6H, br s, TMP β and γ CH_2), 1.47 (12H, s, TMP Me). ^{13}C NMR (300 K, d_8-THF): δ 167.2 (CO_2), 58.9 (TMEDA CH_2), 55.2 (TMP α), 46.2 (TMEDA Me), 44.1 (TMP β), 31.1 (TMP Me), 17.7 (TMP γ). ^{7}Li NMR (300 K, d_8-THF): δ -1.3.

Synthesis of 4

This was prepared in the same manner as **3-Li** but instead of TMEDA, THF was added to give a homogenous solution. After several weeks at -30^{o}C, a few crystals had deposited. ^{1}H NMR (300 K, C_6D_6): δ 3.57 (m, THF OCH_2), 1.42 (m, THF CH_2), 1.37 (s, TMP Me), 1.32 (br s, TMP β), 0.92 (br s, TMP γ).

Synthesis of 5

Method A. A solution of LiTMP (3.2 mmol, prepared *in situ* from TMP(H) and ^{n}BuLi) in hexane (5mL) was prepared and $^{i}Bu_2AlCl$ (0.61 mL, 3.2 mmol) was added via syringe. After stirring at room temperature for 1 h, this was filtered to remove

LiCl and CO_2 was bubbled through as described above for **2-Li**. This was reduced in volume and cooled to -30°C. After 24 h, a crop of X-ray quality colourless crystals had deposited (0.295 g, 28 %).

Method B. $^{i}Bu_2AlCl$ (0.38 mL, 2.0 mmol) was added via syringe to a stirred suspension of **2-Li** (0.382g, 2.0 mmol) in hexane (10 mL). This was allowed to stir overnight and was then filtered, reduced in volume and cooled to -30°C. After 24 h, a crop of X-ray quality colourless crystals had deposited (0.162 g, 25 %). ^{1}H NMR (300 K, C_6D_6): δ 2.22 (2H, sept, $^{3}J_{H,H}$ = 7Hz, ^{i}Bu CH), 1.47, (12H, s, TMP Me), 1.34 (t, 4H, $^{3}J_{H,H}$ = 7Hz, TMP β), 1.28 (d, 12H, $^{3}J_{H,H}$ = 7Hz, $^{i}Bu\ CH_3$), 1.22 (m, 2H, $^{3}J_{H,H}$ = 7Hz, TMP γ), 0.39 (d, 4H, $^{3}J_{H,H}$ = 7Hz, $^{i}Bu\ CH_2$). ^{13}C NMR (300 K, d_8-THF): δ 160.8 (CO_2), 58.1 (TMP α), 39.3 (TMP β), 29.7 (TMP Me), 28.8 (^{i}Bu Me), 26.5 (^{i}Bu CH), 22.4 (TMP γ), 15.1 ($^{i}Bu\ CH_2$).

Crystal structure determinations. Crystallographic data were collected at 123 K on an Oxford Diffraction Gemini S Diffractometer with Mo Kα radiation (λ = 0.71073 Å). Structures were solved using *SHELXS-97*,[40] and refined to convergence on F^2 and against all independent reflections by the full-matrix least-squares method using the *SHELXL-97* program.[40] The quality of structure **4** is limited by disorder and partial occupancy of the solvent THF molecules and disorder in the ligands. The model adopted is suitable for purpose here, that is, identifying chemical identity. CCDC-xxxxxx to CCDC-xxxxxx contain the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystallographic data and refinement details for compounds **3-Li**, **4** and **5**.

	3-Li	**4**	**5**
Empirical formula	$C_{32}H_{68}Li_2N_6O_4$	$C_{110}H_{200}Li_{12}N_8O_{29}$	$C_{36}H_{72}Al_2N_2O_4$
Mol. Mass	614.80	2182.06	650.92
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$
a [Å]	9.9473(7)	12.7355(7)	9.2755(3)
b [Å]	8.4476(6)	16.5468(7)	15.4153(5)
c [Å]	22.304(2)	17.0019(9)	13.9819(4)
α [°]	90	73.910(4)	90
β [°]	94.700(6)	68.784(5)	99.805(3)
γ [°]	90	89.123(4)	90
V [Å^3]	1867.9(2)	3194.7(3)	1970.0(1)
Z	2	1	2
ρ_{calcd} [Mg m^{-3}]	1.093	1.134	1.097
Measured reflections	12862	30301	34265
Unique reflections [$I>2\sigma(I)$]	4360 [R_{int} = 0.0405]	12497 [R_{int} = 0.0454]	4924 [R_{int} = 0.0349]
GooF on F^2	0.887	1.079	1.067
R_1, wR_2 [$I>2\sigma(I)$]	0.0445, 0.0912	0.0849, 0.2313	0.0435, 0.1238
R_1, wR_2 [all data]	0.0904, 0.0992	0.1184, 0.2490	0.0624, 0.1300
Largest diff. peak/hole [eÅ^{-3}]	0.208/-0.177	0.881/-0.422	0.419/-0.407

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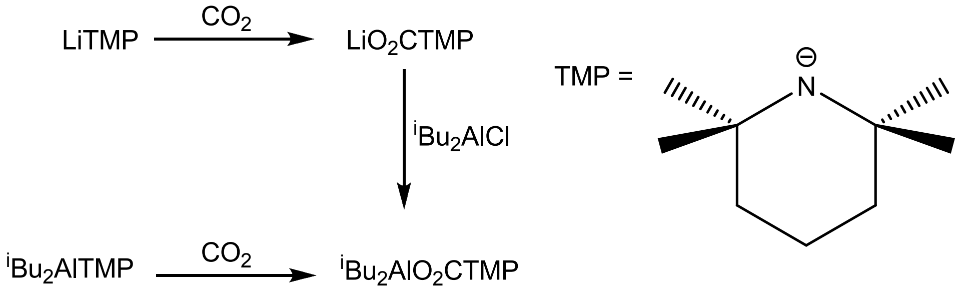
References

1. M. W. Rathke and R. Kow, *J. Am. Chem. Soc.*, 1972, **94**, 6854-6856.
2. M. F. Lappert, A. Singh, J. L. Atwood, R. D. Roger and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302-304.
3. P. G. Williard and Q.-Y. Liu, *J. Am. Chem. Soc.*, 1993, **115**, 3380-3381.
4. B. Gehrhus, P. B. Hitchcock, A. R. Kennedy, M. F. Lappert, R. E. Mulvey and P. J. A. Rodger, *J. Organomet. Chem.*, 1999, **587**, 88-92.
5. D. R. Armstrong, D. V. Graham, A. R. Kennedy, R. E. Mulvey and C. T. O'Hara, *Chem. Eur. J.*, 2008, **14**, 8025-8034.
6. B. L. Lucht and D. B. Collum, *J. Am. Chem. Soc.*, 1994, **116**, 7949-7950.
7. J. F. Remenar, B. L. Lucht, D. Kruglyak, F. E. Romesberg, J. H. Gilchrist and D. B. Collum, *J. Org. Chem.*, 1997, **62**, 5748-5754.
8. (a) A. Yasuda, S. Tanaka, K. Oshima, H. Yamamoto and H. Nozaki, *J. Am. Chem. Soc.*, 1974, **96**, 6513-6514; (b) A. Yasuda, H. Yamamoto and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1705-1708.
9. S. Tanaka, A. Yasuda, H. Yamamoto and H. Nozaki, *J. Am. Chem. Soc.*, 1975, **97**, 3252-3254.
10. H. Nozaki, K. Oshima, K. Takai and S. Ozawa, *Chem. Lett.*, 1979, 379-380.
11. Y. Naruse and H. Yamamoto, *Tetrahedron*, 1988, **44**, 6021-6029.
12. K. Maruoka, M. Oishi and H. Yamamoto, *J. Org. Chem.*, 1993, **58**, 7638-7639.
13. (a) R. E. Mulvey, *Organometallics*, 2006, **25**, 1060-1075; (b) R. E. Mulvey, F. Mongin, M. Uchiyama and Y. Kondo, *Angew. Chem. Int. Ed.*, 2007, **46**, 3802-3824; (c) R. E. Mulvey, *Acc. Chem. Res.*, 2009, **42**, 743-755.
14. (a) J. Garcia-Álvarez, D. V. Graham, A. R. Kennedy, R. E. Mulvey and S. Weatherstone, *Chem. Commun.*, 2006, 3208-3210; (b) B. Conway, J. Garcia-Álvarez, E. Hevia, A. R. Kennedy, R. E. Mulvey and S. D. Robertson, *Organometallics*, 2009, **28**, 6462-6468.
15. B. Conway, A. R. Kennedy, R. E. Mulvey and S. D. Robertson, *Angew. Chem. Int. Ed.*, 2010, **49**, accepted DOI: 10.1002/anie.201000181.
16. (a) D. J. Woodcock, *Chem. Commun.*, 1968, 267-268; (b) D. C. D. Butler and H. Alper, *Chem. Commun.*, 1998, 2575-2576.
17. T.-T. Wu, J. Huang, N. D. Arrington and G. M. Dill, *J. Agric. Food Chem.*, 1987, **35**, 817-823.
18. I. Vauthey, F. Valot, C. Gozzi, F. Facche and M. Lemaire, *Tetrahedron Lett.*, 2000, **41**, 6347-6350.
19. M. Aresta, A. Dibenedetto and E. Quaranta, *J. Chem. Soc. Dalton Trans.*, 1995, 3359-3363.
20. A. Belforte and F. Calderazzo, *J. Chem. Soc. Dalton Trans.*, 1989, 1007-1009.

21. D. B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti and G. Pampaloni, *Chem. Rev.*, 2003, **103**, 3857-3897.
22. A. R. Katritzky, M. Black and W.-Q. Fan, *J. Org. Chem.*, 1991, **56**, 5045-5048 and references therein.
23. (a) A. Otero, J. Fernández-Baeza, J. Tejeda, A. Antiñolo, F. Carrillo-Hermosilla, E. Díez-Barra, A. Lara-Sánchez, M. Fernández-López, M. Lanfranchi and M. A. Pellinghelli, *Dalton Trans.*, 1999, 3537-3539; (b) A. Otero, J. Fernández-Baeza, J. Tejeda, A. Antiñolo, F. Carrillo-Hermosilla, E. Díez-Barra, A. Lara-Sánchez and M. Fernández-López, *Dalton Trans.*, 2000, 2367-2374; (c) A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, L. Sánchez-Barba, M. T. Expósito and A. M. Rodríguez, *Dalton Trans.*, 2003, 1614-1619.
24. S. Inoue and Y. Yokoo, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3651-3653.
25. D. B. Dell'Amico, F. Calderazzo, M. Dell'Innocenti, B. Güldenpfennig, S. Ianelli, G. Pelizzi and P. Robino, *Gazz. Chim. Ital.* , 1993, **123**, 283.
26. U. Abram, D. B. Dell'Amico, F. Calderazzo, S. Kaskel, L. Labella, F. Marchetti, R. Rovai and J. Strähle, *Chem. Commun.*, 1997, 1941-1942.
27. K. Knabel, I. Krossing, H. Nöth, H. Schwenk-Kircher, M. Schmidt-Amelunxen and T. Seifert, *Eur. J. Inorg. Chem.*, 1998, 1095-1114.
28. K. Knabel and H. Nöth, *Z. Naturforsch., Teil B*, 2005, **60**, 1027-1035.
29. C.-C. Chang, B. Srinivas, M.-L. Wu, W.-H. Chiang, M. Y. Chiang and C.-H. Hsiung, *Organometallics*, 1995, **14**, 5150-5159.
30. T. Habereder, H. Nöth and R. T. Paine, *Eur. J. Inorg. Chem.*, 2007, 4298-4305.
31. S. C. Ball, I. Cragg-Hine, M. G. Davidson, R. P. Davies, A. J. Edwards, I. Lopez-Solera, P. R. Raithby and R. Snaith, *Angew. Chem. Int. Ed.*, 1995, **34**, 921-923.
32. R. P. Davies, P. R. Raithby and R. Snaith, *Organometallics*, 1996, **15**, 4355-4356.
33. O. Feier-Iova and G. Linti, *Z. Anorg. Allg. Chem.*, 2008, **634**, 559-564.
34. U. Köhn and E. Anders, *Tetrahedron Lett.*, 2002, **43**, 9585-9589.
35. Y. Tang, L. N. Zakharov, A. L. Rheingold and R. A. Kemp, *Organometallics*, 2004, **23**, 4788-4891.
36. J. R. Hagadorn, L. Que Jr. and W. B. Tolman, *J. Am. Chem. Soc.*, 1998, **120**, 13531-13532.
37. P. C. Andrews, N. D. R. Barnett, R. E. Mulvey, W. Clegg, P. A. O'Neil, D. Barr, L. Cowton, A. J. Dawson and B. J. Wakefield, *J. Organomet.Chem*, 1996, **518**, 85-95.
38. K. Hyvärinen, M. Klinga and M. Leskelä, *Polyhedron*, 1996, **15**, 2171-2177.
39. K.-C. Yang, C.-C. Chang, C.-S. Yeh, G.-H. Lee and S.-M. Peng, *Organometallics*, 2001, **20**, 126-137.
40. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

TOC entry



CO_2 insertion into M-N bonds (M = Li, Al) gives carbamato derivatives of the utility amide 2, 2, 6, 6 – tetramethylpiperidide. Salt metathesis of the Li derivative with the parent aluminium chloride provides an alternative route to the group 13 carbamate. The TMEDA solvated lithium carbamate and the unsolvated aluminium carbamate are both $(MOCO)_2$ dimers in the solid state.