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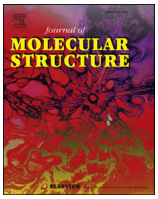

# Synthesis and structural characterization of novel amidinolithium compounds by the insertion reaction of $CO_2$ into the Li–N bond

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## ABSTRACT

Insertion of $CO_2$ into the Li–N bond of two amidinolithium compounds $[\{LiN(2,6\text{-}Me_2C_6H_3)C(H)N(2,6\text{-}Me_2C_6H_3)\}_2(THF)_3]$ and $[\{LiN(4\text{-}CH_3C_6H_4)C(H)N(4\text{-}CH_3C_6H_4)\}_2(THF)_3]$ have been studied, and two lithium carbamate compounds $[Li\{O_2C(N(2,6\text{-}Me_2C_6H_3)C(H)N(2,6\text{-}Me_2C_6H_3))\}\cdot THF]_4$ (**1**) and $[Li\{O_2C(N(4\text{-}CH_3C_6H_4)C(H)N(4\text{-}CH_3C_6H_4))\}\cdot THF]_6$ (**2**) were obtained. The molecular structure of **1** shows a novel cage structure containing four eight-membered (LiOCOLiOCO) rings and two four-membered (LiOLiO) rings with the $[Li_4(CO_2)_4]^{4+}$ cluster in central. And an unusual and novel structure of **2** was obtained with a "wheel" cage structure including six six-membered (LiOLiOCO) rings surrounding the $[Li_6(CO_2)_6]^{6+}$ cluster. Both of **1** and **2** were fully characterized by elemental analysis, NMR spectroscopy, and X-ray structural determinations.

## 1. Introduction

Carbon dioxide is a useful reagent due to its ease of handling and widespread availability [1]. For purpose of the synthesis and preparation on more valuable and novel organic products, the activations of $CO_2$ by reaction with organometallic compounds have been gained widespread attention [2]. For instance, the preparation and characterization of the alkali-metal carbamates ($MO_2CNR_2$) appear to be as a convenient precursor to isocyanates in industrial chemistry [3] and as a useful intermediate in diverse areas such as agricultural [4] and medicinal chemistry [5].

In addition, the insertion reactions of $CO_2$ into the metal–N bond of aluminum compounds [6] and magnesium compounds [7] have been reported and gained considerable attention, but the lithium compounds obtained by inserting $CO_2$ into a pre-formed Li–N bond were less studied. Snaith's group reported a TMEDA-solvated structure with the diphenylamido carbamate $LiO_2CNPh_2$ [8] and a THF-solvated structure with the indole-based lithium carbamate [9], and Kennedy et al. reported two compounds, $[(TMPCO_2)Li\cdot TMEDA]_2$ with a central eight-membered $(LiOCO)_2$ ring and $[Li_{12}(\mu_8\eta^8\text{-}CO_3)_2(O_2CTMP)_8\cdot 4THF]$ containing a pair of central carbonato $CO_3$ groups in the structure [1]. Although di(aryl) formamidinate [ArNCHNAr] ligands have been extensively used in transition metal chemistry [10], there are no papers about the reaction of amidinolithium compounds with $CO_2$ have been published. Herein, we report two novel lithium compounds based on the insertion of $CO_2$ molecule into the Li–N bond of di(aryl)formamidinatolithium compound, and their details of the syntheses and the structural characterizations are presented and discussed.

## 2. Experimental

### 2.1. Materials and methods

The amidinolithium compounds $[\{LiN(2,6\text{-}Me_2C_6H_3)C(H)N(2,6\text{-}Me_2C_6H_3)\}_2(THF)_3]$ and $[\{LiN(4\text{-}CH_3C_6H_4)C(H)N(4\text{-}CH_3C_6H_4)\}_2(THF)_3]$ have been synthesized according to the literature procedures [10,11]. The lithium carbamate compounds **1** and **2** were prepared in good yields from the reaction of amidinolithium compounds with $CO_2$ in THF solution via a balloon filled with dry $CO_2$ gas (Scheme 1). Both of **1** and **2** were all characterized by satisfactory C, H and N microanalysis, $^1H$, $^{13}C\{^1H\}$, $^7Li$ spectra in $C_6D_6$ at ambient temperature, and single crystal X-ray structural data.

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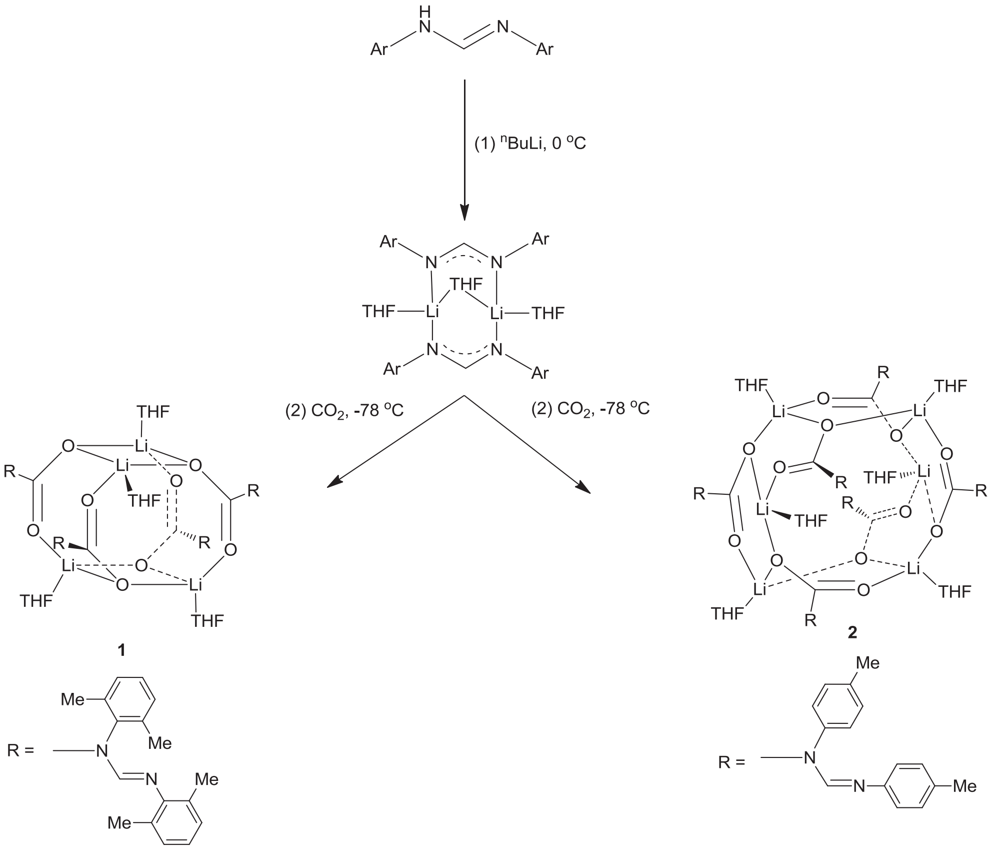

**Scheme 1.** Synthetic routes of compounds **1** and **2**.

### 2.2. Synthesis of [Li{$O_2C(N(2,6-Me_2C_6H_3)C(H)N(2,6-Me_2C_6H_3))$}·THF]$_4$ (**1**)

A colorless THF solution of *N*, *N*'-di(2,6-dimethylphenyl)formamidine (0.601 g, 2.38 mmol) was cooled to 0 °C, and an excess of $^n$BuLi (1.56 mL, 1.6 M, 2.50 mmol) was added dropwise, resulting in an immediate color change of the solution to light yellow. The solution was allowed to room temperature and stirred for 4 h, and then the mixture stirred at −78 °C for 10 min with $CO_2$ via the balloon filled with dry $CO_2$ gas. During this time, the color of the solution gradually changed to dark green from greenyellow. Then, the solution was allowed to warmed to room temperature gradually and stirred overnight. X-ray quality single crystals were grown from a concentrated Hex/THF solution. (0.568 g, 63.8% yield). Mp: 182–185 °C. Anal. Calc. for $C_{88}H_{108}Li_4N_8O_{12}$: C, 70.58; H, 7.27; N, 7.48. Found: C, 70.51; H, 7.39; N, 7.32%. $^1$H NMR (300 MHz, $C_6D_6$): δ(ppm) 1.42 (s, 4H, THF-**H**), 2.23 (s, 3H, C**H**$_3$), 2.35 (s, 6H, C**H**$_3$), 2.42 (s, 3H, C**H**$_3$), 3.46 (s, 4H, THF-**H**), 7.03–7.25 (m, 6H, Ar**H**), 8.75 (s, 1H, NC**H**N); $^{13}$C NMR ($C_6D_6$, 75 MHz): δ(ppm) 18.3, 19.0 ($CH_3$), 25.6 (THF-**C**), 67.6 (THF-**C**), 123.1, 130.8, 136.7, 138.9 (ArH-**C**), 151.6 (N**C**N), 159.1 (**C**O$_2$); $^7$Li NMR ($C_6D_6$, 117 MHz): δ(ppm) −0.342; 0.483.

### 2.3. Synthesis of [Li{$O_2C(N(4-CH_3C_6H_4)C(H)N(4-CH_3C_6H_4))$}·THF]$_6$ (**2**)

A colorless THF solution of *N*, *N*'- di(*p*-methyl phenyl) formamidine (0.507 g, 2.26 mmol) was cooled to 0 °C, and an excess of $^n$BuLi (0.90 mL, 2.5 M, 2.26 mmol) was added dropwise, resulting in an immediate color change of the solution to light yellow. The solution was allowed to room temperature and stirred for 4 h, and then the mixture stirred at −78 °C for 10 min with $CO_2$ via the balloon filled with dry $CO_2$ gas. During this time, the color of the solution gradually changed to colorless. Then, the solution was allowed to warmed to room temperature and stirred overnight. X-ray quality single crystals were grown from a concentrated Hex/THF solution at −30 °C. (0.586 g, 74.9% yield). Mp: 175–179 °C. Anal. Calc. for $C_{120}H_{138}Li_6N_{12}O_{18}$: C, 69.36; H, 6.69; N, 8.09. Found: C, 69.23; H, 6.79; N, 7.93%. $^1$H NMR (300 MHz, $C_6D_6$): δ(ppm) 1.40 (s, 4H, THF-**H**), 2.13 (s, 6H, C**H**$_3$), 3.56 (s, 4H, THF-**H**), 6.73–7.03 (m, 8H, Ar**H**), 7.91 (s, 1H, NC**H**N); $^{13}$C NMR ($C_6D_6$, 75 MHz): δ(ppm) 20.4 ($CH_3$), 25.5(THF-**C**), 67.5(THF-**C**), 119.3, 127.9, 129.8, 132.0 (ArH-**C**), 143.5(N**C**N), 149.5 (**C**O$_2$); $^7$Li NMR ($C_6D_6$, 117 MHz): δ(ppm) 1.56.

### 2.4. X-ray crystallography

Crystallographic measurements were performed with Mo−Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer at 173 K. Corrections were applied for Lorentz and polarization effects as well as absorption using multiscans (SADABS) [12]. Each structure was solved by direct methods and refined on $F^2$ by full matrix least-squares (SHELX97) [13] using all unique data. Then the remaining non-hydrogen atoms were obtained from the successive difference Fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained to parent sites, using a riding mode (SHELXTL) [14]. Experimental details for the structure determination are presented in Table 1. Selected bond lengths and angles for compound **1**and **2** are listed in Table 2 and Table 3.