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Note

Quest for lithium amidinates containing adjacent amino donor group at the central carbon atom

Jana Nevoralová, Tomáš Chlupatý, Zdeňka Padělková, Aleš Růžička*

Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic

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ABSTRACT

Lithium amidinate complexes bearing different peripheral substituents on both nitrogen atoms (*i*Pr and Dipp (2,6-di(isopropyl)phenyl-) and pendant, potentially coordinating group originated from the 2-(*N*,*N*-dimethylaminomethyl)phenyl moiety, at the central carbon atom were prepared by addition of the 2-(*N*,*N*-dimethylaminomethyl)phenyllithium to the appropriate carbodiimides. The structure of the isopropyl group substituted lithium amidinates is dimeric with bidentate amidinate unit and four-coordinated lithium atom. On contrary the Dipp group substituted lithium amidinate is monomeric with trigonal planar geometry of the lithium atom, monodentately bound amidinate unit and coordinated pendant arm.

1. Introduction

Metal complexes containing amidinate ligands, or its variations, are frequently tested as catalysts of various organic chemistry transformations in the present time. [1,2] Moreover the application of these complexes as precursors of new materials [3] together with stabilization of unusual [4], generally lower, oxidation states of metals in its complexes opened new areas of chemistry. The essential step of synthesis of metal amidinates is the preparation of lithium amidinate precursors, which in contrary to the target compounds are rarely described in the literature [5]. Lithium amidinates reveal usually three different types of structures [6] (Scheme 1) monomeric isobidentate with extra coordination of two donor atoms from such as THF or TMEDA molecule(s) (Scheme 1A), dimeric isobidentate with one donor on both of lithium atoms (Scheme 1B), or higher aggregates (Scheme 1C).

One of the goals in the metal amidinate chemistry is the modification of the amidinate skeleton and a fine tuning of the electronic and steric properties of the ligand. Except the usual transformations or modifications of nitrogen atom substituents, a substituent with an adjacent neutral flexible donor group could be attached to the central carbon atom of the amidinate ligand. This ligand arrangement would probably lead to a hemilabile connection of an extra donor to the metal centre, and creation of so called metal heteroscorpionate complex. Only preliminary attempts to prepare this type of complexes were performed, and therefore these are still rare (except of guanidinates and phosphaguanidinates) in the literature. Chronologically, the first attempt is the use of the amidinate containing the pyrazole heterocycle [7] in the Li, Ti and Zr complexes (Scheme 2A), and then the incorporation of 2-pyridyl- [8] or 2-furyl- [6b] groups to Li, Y or rare earth metal complexes (Scheme 2B and C). To the best of our knowledge the most recent examples of the real monoanionic system came from work published by Braunstein et al. (Scheme 2D) [9] where the amidinatomethylene bridged –NHC complexes of K, Ag and Cr are reported. An *o*-carboranyl substituted amidine ligand [10] which reveals a H-atom transfer from the carborane to the amidinate part (Scheme 2E), and related Ir complexes were published during last two years. The last example is the dianionic ligand reported by Trifonov and Carpentier [11] which combines a rare earth metal complexation by a bulky phenoxide substituted amidinate (Scheme 2F).

On the basis of the fact that none of above mentioned ligands has a monoanionic tridentate bonding fashion to the metal centre, we started to investigate the synthesis, as well as the structure, of amidinates, which could fulfil such a demand, prepared from 2-(*N*,*N*-dimethylaminomethyl)phenyllithium [12] and isopropyl- and 2,6-di(propan-2-yl)phenyl- (Dipp) disubstituted carbodiimides, respectively, in solution and in the solid state.

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* Corresponding author. Fax: +420 466037068.
E-mail address: ales.ruzicka@upce.cz (A. Růžička).

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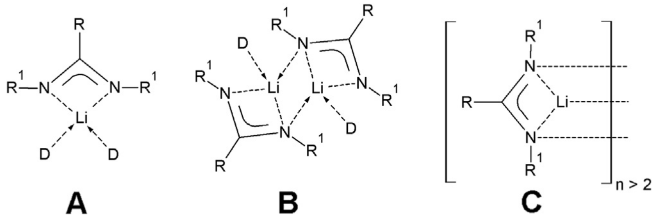


Scheme 1.

2. Results and discussion

2.1. Synthesis

All lithium compounds were prepared by the same way from the lithium precursor – *C*,*N*-chelated organolithium compound **1** and appropriate carbodiimide in high yield (Fig. 1). A smaller isopropyl group containing carbodiimide compounds **2** and **4** in diethylether and THF, respectively. Compound **5** can be obtained by a hydrolysis of **4** by water or air moisture. The use of bigger carbodiimide substituent – 2,6-di(isopropyl)phenyl- instead of the isopropyl one, has nearly no influence to the yield of the target molecule **3**.

2.2. NMR spectroscopic studies in solution

The purity as well as structure of prepared compounds was studied by the multinuclear NMR spectroscopic approach (^{1}H, ^{7}Li, and ^{13}C) in solutions of both non-coordinating and coordinating deuterated solvents (C_6D_6 and THF-d_8).

There are some similarities to the recently described lithium *n*-butylamidinates [5a] but the general comparison of these groups of compounds is not made because of the presence of an adjacent donor group and complexity of some spectral patterns in **2**–**4**. All spectra can be compared to the same type of spectra of precursors (carbodiimides [5a] and **1**) and a hydrolysis product (**5**). When **1** is reacted with carbodiimide, the significant upfield shift is detected for CH_2 group in ^{13}C NMR spectra: from 72.6 ppm (for **1**) to 62.2 (for **2** in THF-d_8), 63.5 (for **3** in C_6D_6) and 64.9 ppm (for **3** in THF-d_8); and in ^{1}H NMR spectra: 4.52, 2.86 ppm (AX spin system for **1** in C_6D_6) and 3.48 ppm (for **1** in THF-d_8) to 3.44 ppm (for **2** in THF-d_8) and 4.70, 2.85 ppm (AX spin system for **3** in C_6D_6) and 4.68, 2.97 ppm (AX spin system for **3** in THF-d_8). Analogous change of chemical shift values is found for the *ipso* carbon bound to the lithium atom in **1** (164.3 ppm) transformed to the *ipso* carbon (~140 ppm in **2** and **3**, respectively) bound to the central carbon atom of the amidinate NCN skeleton in ^{13}C NMR spectra. Similar upfield shift trend is seen also when chemical shifts in ^{7}Li NMR spectra for **1** (3.6 and 2.6 ppm) and **2** and **3** (1.6, −0.3 for **2**, 0.9 and 0.2 ppm for **3** in different solvents – see Supporting information) are compared. On the other hand, the opposite but solvent independent trend is found for the signal of the central carbodiimide carbon atom when

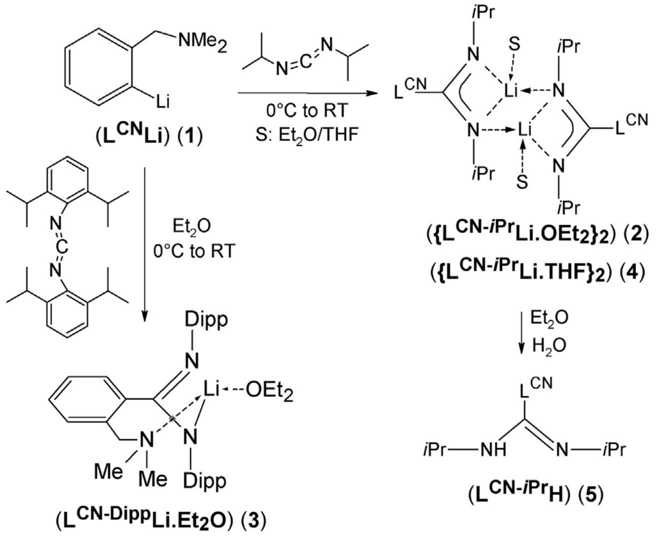
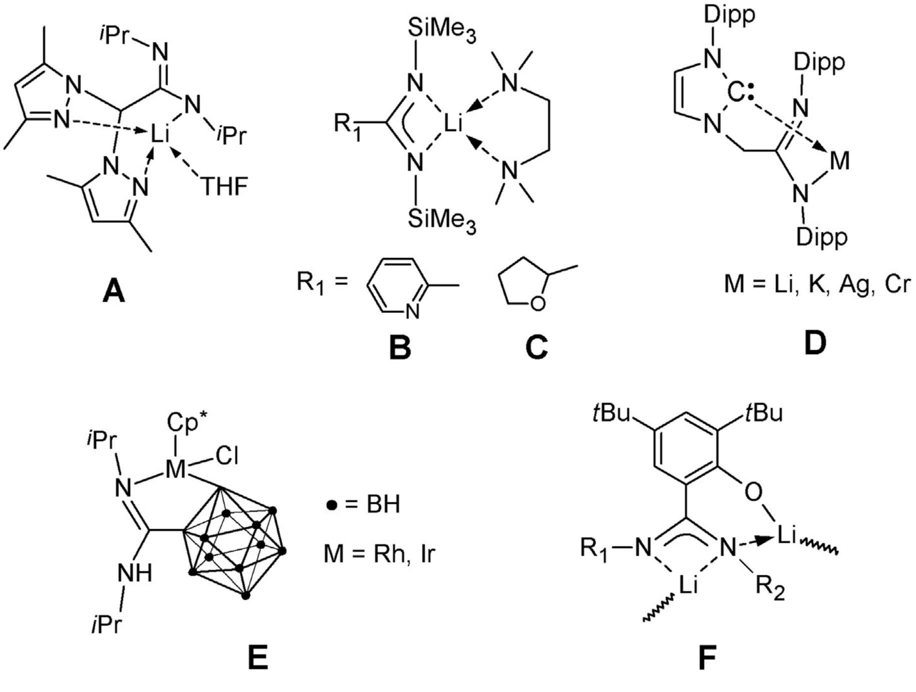


Fig. 1. Reaction routes to compounds **2**–**5** – reagents and conditions.



Scheme 2.

a carbodiimide (∼ 140 ppm) is reacted with **1** (167.4 ppm for **2** and ∼ 159 ppm for **3**). Upfield shifted signal attributed to the same carbon atom is detected when **2** is treated with water giving amidine **5** (155.1 ppm). This change is already seen in ^{1}H NMR spectrum of **2**, where the methylene group resonates as a sharp singlet but for the same group of **5** an AX spin pattern is detected indicating a free rotability of this group in **2**. All these changes are connected to the formation of lithium amidinates from starting compounds or a further hydrolysis.

Significant differences were found also within the group of lithium amidinates containing additional donor group (**2** and **3**). While very broad signals were detected in the ^{1}H NMR spectrum of **2** in benzene solution and one set of well resolved signals is measured in each ^{1}H and ^{13}C NMR spectrum in THF-d_8, all spectra of **3** in both solvents are complex revealing AX spin patterns for methylene groups and two signals for aminomethyl groups in ^{13}C NMR spectrum in benzene. Good indicia for the structural diversity between these two structures are the chemical shift values for the central carbon atom of the NCN skeleton of **2** and **3**. For **2** the value of 167.4 ppm was detected which is slightly lower (∼ 171 ppm) than was found for dimers of lithium *n*-butylamidinates [5a] coordinated by Et_2O and THF molecules, respectively, which is most likely caused by a change of the aliphatic chain for aromatic ring substituent of the central carbon atom. Tremendous shift is observed going from **2** to **3** being 159.3 ppm. Moreover the value of this parameter in **3** is nearly the same in both solvents used which is a further proof of structural similarities.

In contrary to the ^{1}H and ^{13}C NMR spectra which are quite indicative for the evaluation of structural changes and concentration independent, the ^{7}Li NMR spectra parameters reveal chaotic changes of values even in cases of a preparation of more diluted sample of the same compound (see Supporting information). Except the evaluation of the reaction of **1** with carbodiimides no additional relevant information can be obtained from this parameter.

2.3. Solid state study

The structures of centrosymmetric dimers of **2** and **4** were determined by X-ray diffraction techniques. Although different donor solvent molecule is present in both compounds, they reveal very close structures reflected in unit cell parameters, interatomic distances and angles one to each other (Fig. 2 and Fig. S1). The coordination geometries of the lithium atoms in **2** and **3** are distorted tetrahedral, with the largest deviations from ideal shape in N1–Li1–N2 angles which are only about 66°. The Li–Li distance (∼2.45 Å) is in line with previously described dimeric lithium amidinates [5a]. Although the dimethylamino group is a very good donor, the formation of the dimer is preferred over its coordination in **2** and **4**. A high degree of conjugation within the amidinate moiety is detected for these compounds (see Fig. 2 and Fig. S1 captions). The Li–N distances are nearly equivalent with separations only slightly longer than the sum of the covalent radii of both atoms (2.04 Å) [13] and the closest contact of each lithium atom to the outer non-bridging N2 atom. The NCN amidinate planes are mutually parallel in both molecules with interplanar distances of 0.309(3) Å for **2** and 0.102(3) Å for **4**, respectively, which are the closest in cases of dimeric lithium amidinates and are dependent on the steric repulsion of the substituents and a donor ability of the solvent (0.244 Å for $[n\text{-BuC(N-}i\text{Pr)}_2\text{Li(THF)}]_2$ [5a], 0.471 Å for $[n\text{-BuC(NCy)}_2\text{Li(THF)}]_2$ [6i], 0.652(3) Å for $[n\text{-BuC(N-}i\text{Pr)}_2\text{Li(Et}_2\text{O)}]_2$ [5a] and 1.028 Å for a lithium triphenyl amidinate adduct with HMPA [6g]), while this parameter is always bigger when the Et_2O is coordinated to the lithium atom of the same compound than the THF molecule. Lithium atoms are located out of the NCN amidinate planes by 0.797(2) Å for **2** and 0.837(3) Å for **4**, respectively, which is a bit over the values found for similar compounds in the literature [6j]. Parallel planes defined by lithium and nitrogen atoms of the amidinate (N1–Li1–N2) ligand are perpendicularly oriented to the planes defined by the phenyl ring, Li and oxygen atoms.

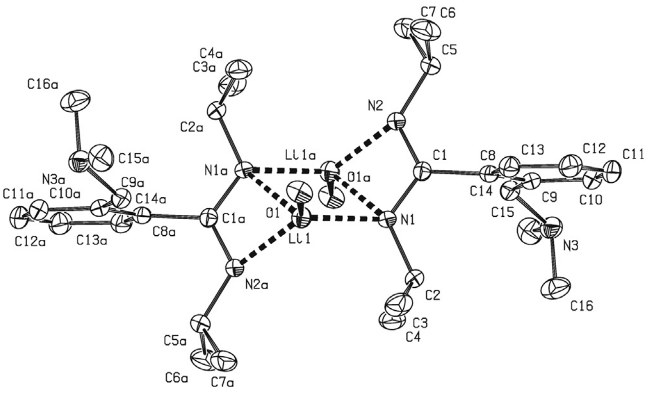


Fig. 2. Molecular structures of $\{L^{CN\text{-}iPr}Li.Et_2O\}_2$ (**2**) and $\{L^{CN\text{-}iPr}Li.THF\}_2$ (**4**) (ORTEP view, 40% probability level). Hydrogen atoms and methylene groups from Et_2O molecules are omitted for clarity. Selected interatomic distances [Å] and angles [°] for $\{L^{CN\text{-}iPr}Li.Et_2O\}_2$ (**2**) and $\{L^{CN\text{-}iPr}Li.THF\}_2$ (**4**, appropriate values are given in italics in parenthesis): C1a–Li1 2.373(5) (*2.369*(*4*)); N1–C2 1.468(3) (*1.467*(*3*)); N1a–Li1 2.134(5) (*2.162*(*4*)); N1–Li1 2.080(4) (*2.079*(*4*)); N2a–Li1 2.017(5) (*1.994*(*4*)); Li1–O1 1.974(4) (*1.942*(*5*)); C1–N2 1.321(3) (*1.323*(*3*)); C1–N1 1.337(3) (*1.342*(*3*)); C8a–C1a–N2a 121.04(18) (*121.23*(*7*)); C8a–C1a–N1a 121.67(18) (*121.52*(*17*)); N1–C1–N2 117.29(18) (*117.29*(*18*)); Li1–N1a–Li1a 72.26(16) (*70.45*(*15*)); N1a–Li1a–O1a 114.3(2) (*113.0*(*2*)); N2a–Li1–O1 120.62(19) (*118.76*(*19*)); C8–C1–N2 121.04(18) (*121.18*(*18*)); C8–C1–N1 121.67(18) (*121.52*(*17*)); N1–C1–N2 117.29(18) (*117.29*(*18*)); C2–N1–Li1 111.03(17) (*111.12*(*17*)); C5–N2–Li1a 147.12(19) (*145.2*(*2*)); Li1–N1–Li1a 72.26(16) (*70.45*(*15*)); N2–Li1a-O1a 120.62(19) (*118.76*(*19*)); N1–Li1–O1 114.3(2) (*113.0*(*2*)); N1a–Li1–N1 107.74(18) (*109.55*(*18*)).

In contrary to the dimeric **2** and **4** (Fig. 2 and Fig. S1), **3** (Fig. 3) reveals monomeric structure with very short distance between the nitrogen from dimethylaminomethyl group and the lithium atom which is similar as the sum of the covalent radii of both atoms. A high affinity of the pendant donor amino group to coordinate the lithium atom is further demonstrated in rather huge torsion angle

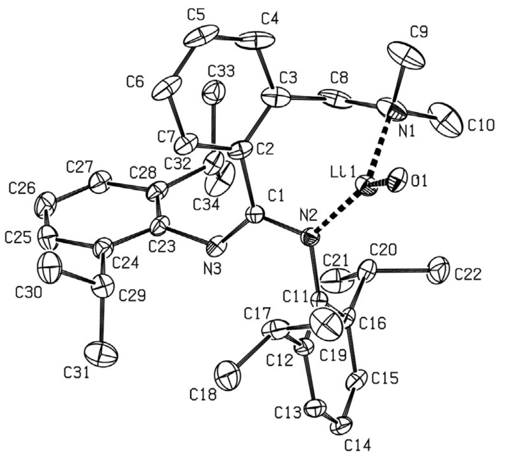


Fig. 3. Molecular structure of $L^{CN\text{-}Dipp}Li.Et_2O$ (**3**) (ORTEP view, 30% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°] for $L^{CN\text{-}Dipp}Li.Et_2O$ (**3**) which is consist of two independent molecules (appropriate values of second unit are given in italics in parenthesis): C2–C1 1.523(7) (*1.508*(*7*)); C1–N2 1.359(7) (*1.356*(*6*)); C1–N3 1.290(7) (*1.295*(*6*)); N2–Li1 1.930(10) (*1.944*(*11*)); Li1–O1 1.992(10) (*1.953*(*11*)); Li1–N1 2.073(11) (*2.056*(*11*)); C23–N3 1.411(6) (*1.412*(*6*)); C11–N2 1.425(6) (*1.430*(*6*)); C2–C1–N3 122.6(5) (*123.3*(*5*)); C2–C1–N2 113.8(4) (*114.0*(*4*)); N2–C1–N3 123.2(5) (*122.5*(*5*)); C11–N2–Li1 126.3(4) (*125.3*(*4*)); O1–Li1–N1 112.5(5) (*114.7*(*5*)); N2–Li1–N1 110.1(5) (*108.4*(*5*)); C1–N3–C23 126.8(5) (*129.0*(*4*)).

(C2–C3–C8–N1) of 91.8(2)° which define the deflection of the nitrogen atom from the plane of the parent aromatic ring. Only one nitrogen atom of the amidinate skeleton is coordinated to the lithium atom with slightly shorter distance than is found for N2–Li in **2** and **4**. The bonding fashion is further reflected in different interatomic distances within the amidinate moiety (C1–N2 1.359(7) (*1.356*(*6*)); C1–N3 1.290(7) (*1.295*(*6*))) where the C1–N3 distance can be seriously attributed to a double bond and the angle N2–C1–N3 is slightly wider than in **2** and **4**. The coordination geometry of the Li atom is trigonal planar with the orientation of the plane 61.6(2)° from the plane defined by NCN amidinate moiety.

The structure of the amidine **5** (Fig. S2) has been determined in order to compare it with prepared lithium complexes where the amidine NCN unit is very similar to the same fragment in **3**. Surprisingly, no H-bridge promoted connectivity of the amidine N–H and dimethylaminomethyl group is detected.

3. Conclusions

In summary, we have prepared and structurally characterized two types of lithium amidinates, wearing peripheral groups of different steric and electronic properties and potentially chelating donor group, both in solution and the solid state. Although the smaller isopropyl substituent permit the formation of centrosymmetric dimers with bidentate amidinate unit and four-coordinated lithium atom, the use of bigger Dipp group directing the formation of the monomer with trigonal planar geometry of the lithium atom, monodentately bound amidinate unit and coordinated pendant arm. Both types of structures determined in the solid state most likely retain in solution.

4. Experimental

4.1. Synthesis

All syntheses were performed using the standard Schlenk techniques under an inert argon atmosphere. All solvents and starting carbodiimides were purchased from commercial sources (Sigma–Aldrich and VÚOS, a. s. Pardubice-Rybitví). Solvents were dried with the help of solvent purification system PureSolv MD 7 supplied by Innovative Technology, Inc., degassed and then stored under argon atmosphere. Single crystals suitable for X-ray analyses were obtained under argon from corresponding saturated solutions of products in Et_2O or THF cooled to −30 °C. Melting points were measured in an inert perfluoroalkylether and were uncorrected. Deuterated solvents for NMR spectra (C_6D_6 and THF-d_8) were distilled, degassed and stored over a K-mirror under argon atmosphere.

4.1.1. General procedure of preparation of etherate of lithium N,N′-disubstituted [1-(N,N-dimethylaminomethyl)-phen-2-yl]amidinates ({L^{CN-R}Li(solvent)}$_x$) (2–4)

To a suspension of 2-[(dimethylamino)methyl]phenyllithium (**1**) in Et_2O cooled to 0 °C, one equivalent of appropriate *N*,*N*′-disubstituted carbodiimide (a solution in Et_2O) was added. Heterogeneous reaction mixture was allowed to warm to the room temperature and stirred until all the solid particles of **1** disappeared. Colourless solution was filtered and Et_2O was evaporated under vacuo to give white solids. Crude products of **2**–**4** were washed with hexane and dried under vacuo to give pure white crystalline of lithium *N*,*N*′-disubstituted [1-(*N*,*N*-dimethylaminomethyl)-phen-2-yl]amidinates **2**–**4**.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.07.067.

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