

UNIVERSITY OF PARDUBICE

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**Synthesis and characterization of non-, dis- and asymmetric
lithium amidinates**

Thesis of the Doctoral Dissertation

Pardubice 2018

Study program: Inorganic Chemistry

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Year of defence: 2018

The Ph.D. degree thesis was created at the Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice during years 2010-2018

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The Ph.D. degree thesis will be defended at the University of Pardubice in the face of commission for defending Ph.D. thesis chaired by Prof. Zdeněk Černošek, CSc. on 12. 9. 2018.

The Ph.D. degree thesis will be available in the Library of the University of Pardubice.

Keywords:

N-chelating ligand; amidinate; diiminoisindole; lithium; amide; NMR; XRD; structure

Klíčová slova:

N-chelatující ligand; amidinát; diiminoisindol; lithium; struktura; amid; NMR; XRD

Table of Contents

1. Introduction.....	6
2. Objectives.....	8
3. General methods	8
3.1. Synthesis	8
3.2. NMR spectroscopy.....	8
3.3. Crystallography	9
3.4. Elemental analysis.....	9
3.5. Melting point.....	9
4. Experimental part.....	10
4.1. Asymmetric amidinates.....	10
4.1.1. <i>General method for preparation of asymmetric amidinates</i>	10
4.2. Non- and Dis- symmetric amidinates.....	11
4.3. General method for preparation of nonsymmetric diiminoisoindoles ..	12
5. Results and discussion	13
5.1. Asymmetric amidinates.....	13
5.1.1. Synthesis	13
5.1.2. NMR spectroscopic studies in solution	13
5.1.3. Solid state studies.....	14
5.2. Dissymmetric and asymmetric amidinates	18
5.2.1. Synthesis	18
5.2.2. NMR spectroscopic studies in solution	19
5.2.3. Solid state studies.....	19
5.3. Nonsymmetric isoindoles.....	25
6. Conclusion	27
List of papers published by author	28
References	29

List of abbreviations:

<i>n</i> -Bu (ⁿ Bu)	butyl
<i>t</i> -Bu (^t Bu)	1,1-dimethylethyl
<i>i</i> -Pr (ⁱ Pr)	1-methylethyl
Bz	benzyl
Cy	cyklohexyl
Et	ethyl
Ln	lanthanoid
M	metal
Me	methyl
My	myrthanyl
py	pyridin
THF	tetrahydrofuran
TMEDA	tetramethylethyldiamine
Ph	phenyl
Dmp	2,6-dimethylphenyl
Dipp	2,6-diisopropylphenyl

1. Introduction

Deeper exploration of organometallic and coordination chemistry of main group metals in lower oxidation states is a phenomenon of approximately last two decades. Most research is focused on ligands that are able to stabilize metals in its lower oxidations states by the help of steric and electron-donating properties.

Amidates are formally derivatives of carboxylic acids. Their general formula is $[R^1NC(R^2)NR^3]^-$ where $R^1, R^3 \sim C$, or Si substituent, $R^2 \sim C$ substituent, or H; Figure 1) and they possess formal charge 1-. Due to their bonding possibilities (see Figure 2) they can act as monodentate (A), bidentate (B), bridging (C), $\eta^1:\kappa^2$ bimetallic (D) a $\kappa^2:\kappa^2$ bimetallic (E) ligands.¹ There are easy way to modify all substituents bonded directly to an amidinate central motif. By the substituent modification, steric and electron properties can be tuned and this particular feature led to massive development in the field of amidinate chemistry.²

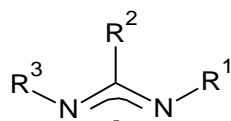


Figure1: General structure of amidinate

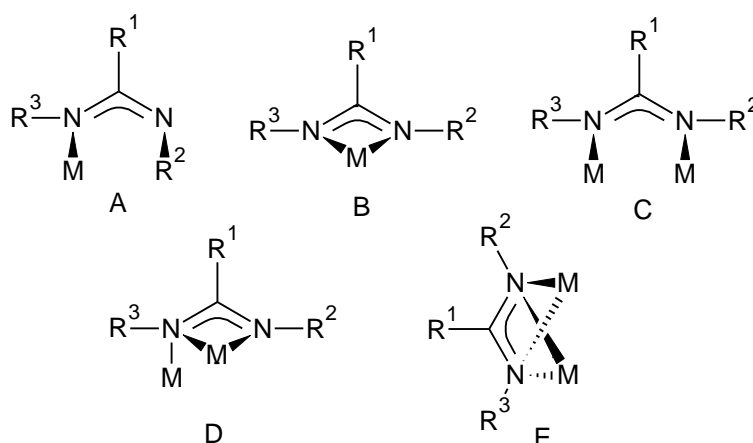


Figure 2: Bonding modes of amidinate ligands

Apart from these basic bonding modes, special cases can be observed. Examples of the special bonding modes can happen in the presence of aryl group³ or by formation of clusters or aggregates⁴ (Figure 3).

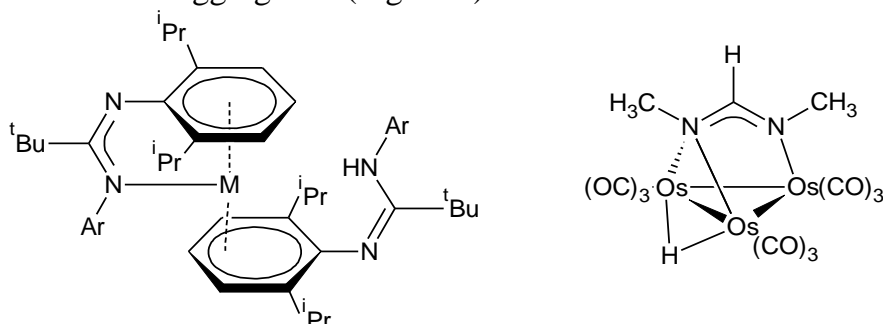


Figure 3: Special amidinate bonding modes

Although first mention about amidinate bonded to metal originates in 1951, when Bradley and Leete prepared first amidinate compound with copper,⁵ deeper interest in

amidates began, when a possibility to alternate cyclopentadiene with amidinate was discovered.⁶

Amidates are isoelectronic with carboxylates, allyl anions and others. Due to their similarity with allyls, amidates are sometimes classified as pseudoallyls (Figure 4).

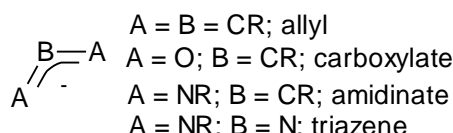


Figure 4: Pseudoallyls

Compared to allyl group, amidinate prefers bidentate bonding mode upon formation of a system with delocalized π -electrons. Results published by Kilner⁷ and Vriez⁸ show that amidinate is more similar to carboxylate than allyl. Similar results were obtained by Cotton, who used amidates to stabilize metal-metal bonds (Figure 5).⁹

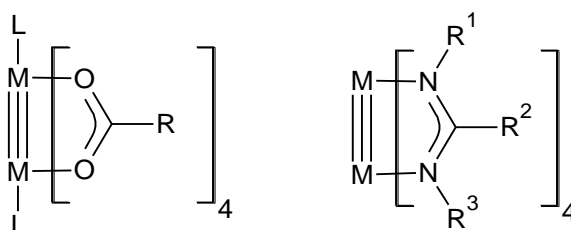


Figure 5: Metal-metal bonds stabilization by pseudoallyl ligands

When amidinate is bonded to a transition metal, stabilization metal-metal bond for two different metals is possible (Figure 6).¹⁰

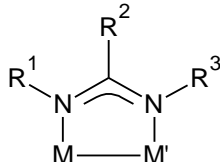


Figure 6: Metal-metal bond of two different metals stabilized by an amidinate

Most common bonding mode of C_1 symmetric amidinates of general formula $M[R^1NC(R^2)NR^3]$ is four-membered metalacycle with κ^2 -bonded metal. This metal is usually in the plane formed by amidinate central NCN motif. (Figure 7)

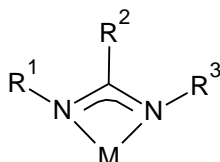


Figure 7: Most common bonding mode of amidinate to the metal

Steric demand of each substituent on N and C amidinate atoms determines properties of the whole molecule. While substituents bonded to the nitrogen atoms have impact on steric demands in the plane of amidinate, substituent on carbon atom affects steric properties above and below amidinate NCN plane.^{11,12}

Even though amidinate shown in figure 8 is C_2 symmetric from the point of propyl group its amidinate central motif has different substituents on each nitrogen atom which classifies it as C_1 symmetric amidinate. In this thesis C_2 symmetric molecules of bisamidinates are also classified as C_1 symmetric amidinates (e.g. in Figure 8)

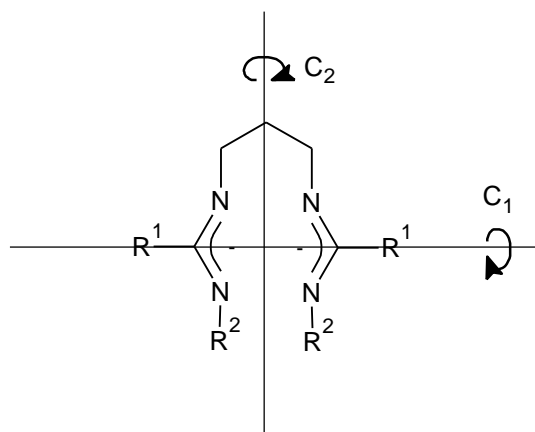


Figure 8: C_2 symmetric amidinate molecule

2. Objectives

The main aim of this thesis is to give a reader basic knowledge about amidinates and their coordination possibilities. The practical part of this thesis is focused on preparation and characterization of lithium amidinates and diiminoisindoles and their characterization by NMR and XRD techniques.

3. General methods

3.1. Synthesis

All reagents and solvents were obtained from commercial sources (Sigma-Aldrich ABCR GmbH & Co. KG). All solvents were dried by the help of device PureSolv MD7 (Inovative Technology, Inc.) and after degassing stored over potassium or sodium mirror respectively. All reactions were carried out under argon atmosphere (argon 5.0, Linde Gas) using standard Schlenk techniques.

3.2. NMR spectroscopy

The NMR spectra were recorded from solutions in THF-d8 on a BrukerAscendTM 500 spectrometer (equipped with Z-gradient 5mm Prodigy cryoprobe) at frequencies ^1H (500.13 MHz), $^{13}\text{C}\{^1\text{H}\}$ (125.76 MHz) and $^7\text{Li}\{^1\text{H}\}$ (194.37 MHz) at 295 K. The solutions were obtained by dissolving of approximately 5-20 mg of each compound in 0.6 ml of deuterated solvent. The values of ^1H chemical shifts were calibrated to residual signals of THF-d8 ($\delta(^1\text{H}) = 3.58$ ppm). The values of ^{13}C chemical shifts were calibrated to signal of THF-d8 ($\delta(^{13}\text{C}) = 67.57$ ppm). The ^7Li chemical shift values are referred to external 1M solution of LiCl in D_2O ($\delta(^7\text{Li}) = 0.0$ ppm). For the measurement of CP/MAS NMR spectra BrukerAvance 500 spectrometer was used. ^{13}C CP/MAS NMR shifts were calibrated to adamantane ($\delta(^{13}\text{C}) = 37.85$ ppm)

3.3. Crystallography

The X-ray data for colorless crystals were obtained at 150 K using Oxford Cryostream low-temperature device on a NoniusKappaCCD diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.¹³ The absorption was corrected by integration methods.^{14,15} or multi-scan methods - SADABS.¹⁵ Structures were solved by direct methods (Sir92)¹⁶ and refined by full matrix least-square based on F^2 (SHELXL-97, SHELXL2014 or Olex2).¹⁷ Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{pivot atom})$ or of $1.5U_{\text{eq}}$ for the methyl moiety with C-H = 0.96, 0.97, 0.98 and 0.93 \AA for methyl, methylene, methine and hydrogen atoms in aromatic rings, respectively. The dynamic disorders of coordinated solvents (Et₂O or THF) as well as of the *n*-butyl group and parts of Dipp moieties were treated by standard methods.¹⁷⁻²⁰ Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

3.4. Elemental analysis

The compositional analyses were determined under an inert atmosphere of argon on the automatic analyzer EA 1108 by FISON'S Instruments.

3.5. Melting point

Melting points were measured on the devices Boetius (NAGEMMA) or Stuart MP3 and have not been corrected. Air sensitive compounds were analyzed in fused capillary or in perfluoralkylether.

4. Experimental part

4.1. Asymmetric amidinates

4.1.1. General method for preparation of asymmetric amidinates

To a solution of appropriate amine in hexane at -50°C , the hexane solution of $n\text{-BuLi}$ was added and the reaction mixture was slowly warmed to the room temperature providing a suspension. Into the suspension of prepared amide, the appropriate amount of trimethylsilylchloride was added. Reaction mixtures were stirred overnight, then filtered and the filtrate was treated with solution of $n\text{-BuLi}$ in hexanes. The precipitate was filtered off, washed with hexane and dried in *vacuo*. Prepared trimethylsilyl-substituted amide was dissolved in THF and appropriate nitrile was slowly added at -50°C . After the reaction was completed (monitored by ^1H and ^{13}C NMR spectroscopy), THF was removed in *vacuo*, product was washed with hexane and crystallized from THF or Et_2O .

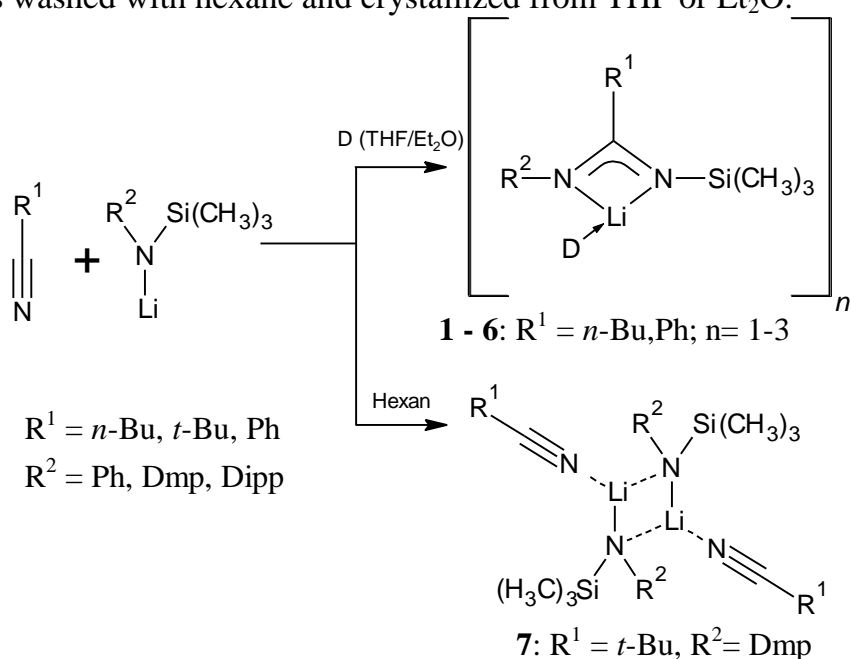


Figure 9: Reaction routes to compounds **1 - 7**.

4.2. Non- and Dis-symmetric amidinates

Into the suspension of prepared amide, the appropriate amount of trimethylsilyl chloride was added. Reaction mixtures were stirred overnight, then filtered and the filtrate was treated with solution of *n*-BuLi in hexanes. The precipitate was filtered off, washed with hexane and dried in *vacuo*. Prepared trimethylsilyl-substituted amide was dissolved in THF and appropriate amount of appropriate dinitrile in THF was slowly added at -50°C . The reaction mixture was allowed to warm to room temperature. After the reaction was completed (monitored by ^1H and ^{13}C NMR spectroscopy), THF was removed in *vacuo*, product was washed with hexane and crystallized from THF or Et_2O .

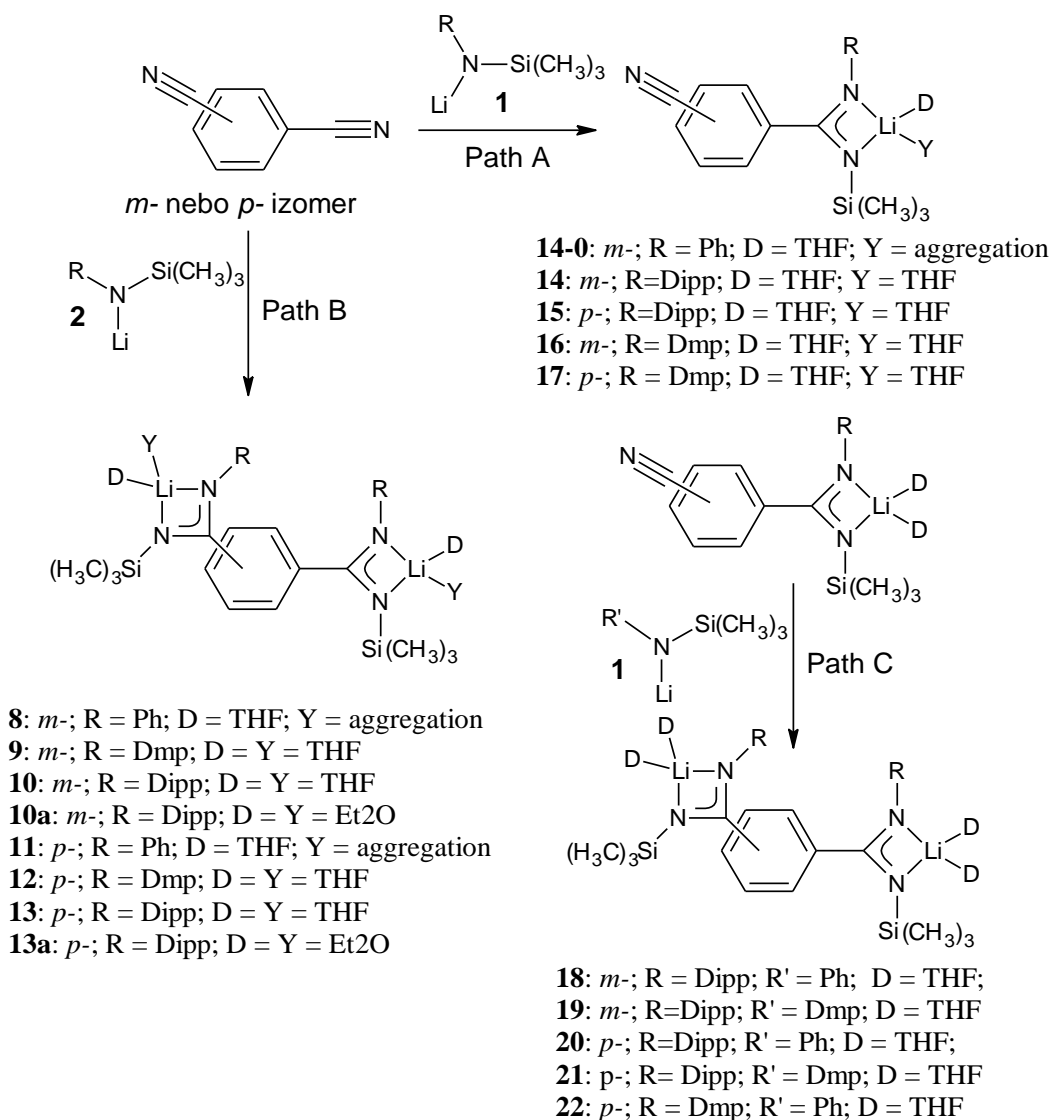


Figure 10: Reaction routes to compounds **8** - **22**.

4.3. General method for preparation of nonsymmetric diiminoisoindoles

Into the suspension of prepared amide, the appropriate amount of trimethylsilyl chloride was added. Reaction mixtures were stirred overnight, then filtered and the filtrate was treated with solution of *n*-BuLi in hexanes. The precipitate was filtered off, washed with hexane and dried in *vacuo*. Prepared trimethylsilyl-substituted amide was dissolved in THF and 1,2-dicyanobenzene in THF was slowly added at -50°C . The reaction mixture was allowed to warm to room temperature. After the reaction was completed (monitored by ^1H and ^{13}C NMR spectroscopy), THF was removed in *vacuo*, product was washed with hexane and crystallized from THF.

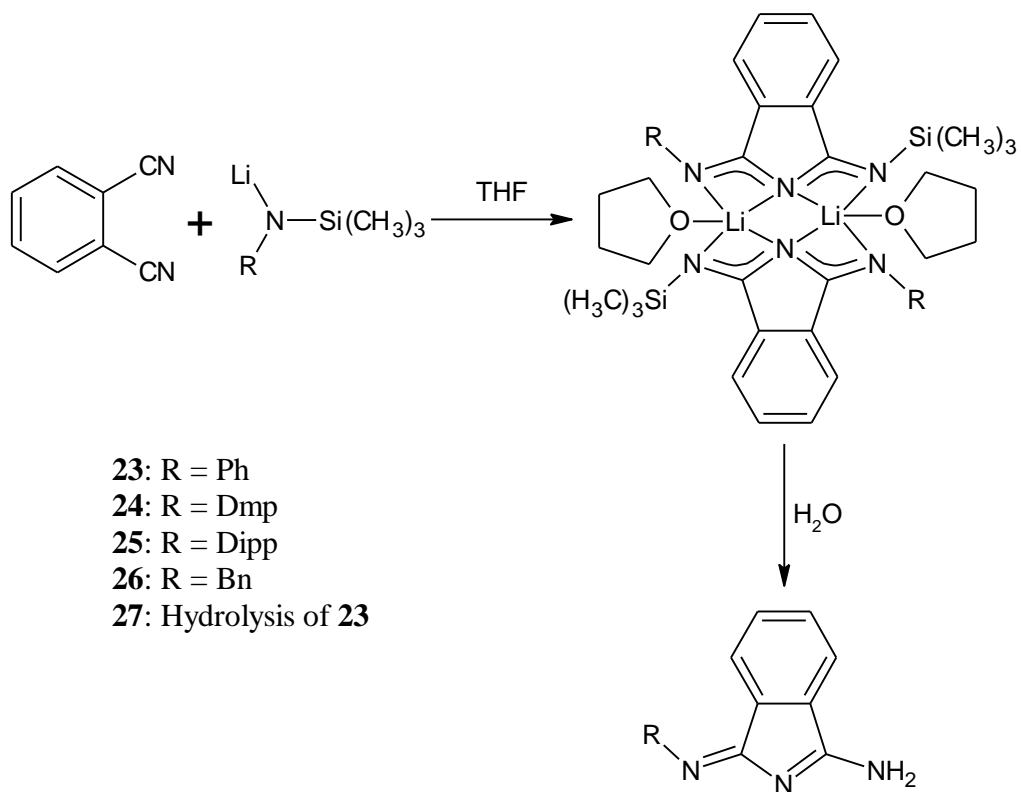


Figure 11: Reaction routes to compounds **23-27**

5. Results and discussion

5.1. Asymmetric amidinates

5.1.1. Synthesis

All lithium amidinates in forms of differently solvated molecules were prepared by the same procedure from appropriate trimethylsilylated lithium anilide and nitrile in moderate yields (**1** - **6**; isolated yields of 30-70%, Figure 9). In order to increase these yields, especially in cases of reactions of sterically crowded lithium amides, significant prolongation of reaction times is necessary. In this respect, one should take into the account that starting lithium amides decompose in coordinating solvents at elevated temperature ($> 30^{\circ}\text{C}$).

All the attempts to use other functional groups than the trimethylsilyl, various silicon or germanium based substituents failed, and no migration of these particular substituents (triethylsilyl-, triphenylsilyl- or triphenylgermyl-) groups to the nitrogen of a nitrile group has been observed. Moreover, the increase of the steric hindrance of the nitrile group could lead to the failure of demanded reaction pathway, as proven for reactions of *t*-BuCN with all lithium amides.

A short period of time increase of reaction temperature to 80°C led to the formation of small amount of *t*-Bu-substituted lithium amidinate - characteristic signal for the central carbon atom was detected by ^{13}C NMR spectroscopy (*vide infra*) - unfortunately along with a decomposition of starting lithium amides. The absolute prerequisite for conducting the process successfully is the use of a coordinating solvent. When hexane or toluene is used instead of Et_2O or THF, virtually no conversion to the lithium amidinate is observed in all cases. The crystallization of crude products from diethylether or THF usually led to the isolation of pure complexes in form of white powders or single crystals.

Adduct of *t*-BuCN with lithium trimethylsilyl-2,6-dimethylphenylamide (**7**) was obtained when these reagents were stirred in hexane for 10 hours. Exactly the same chemical shifts for appropriate nuclei of pure starting compounds were recorded both in ^1H and ^{13}C NMR spectra of **7** redissolved in THF-d_8 indicating the adduct **7** is stable only in the solid state.

5.1.2. NMR spectroscopic studies in solution

The purity as well as structure of prepared compounds was studied by the multinuclear NMR spectroscopic approach (^1H , ^7Li , and ^{13}C) in saturated THF-d_8 solutions. Surprisingly, only one set of relatively narrow signals was observed for most of the complexes suggesting a mononuclear character with two THF molecules being coordinated to the lithium centre and an isobidentate bonding mode of the amidinato ligands in solution.

When the compound with the combination of smallest substituents (*n*-Bu and Ph - compound **4**) is dissolved in the THF-d_8 and the NMR spectra measured, only sets of broad signals were observed probably due to an association of complexes to species with higher nuclearity, as shown in the solid state - *vide infra*, and an observation of its mutual concentration dependent equilibrium in solution.

5.1.3. Solid state studies

Four independent molecules were found within the unit cell of **7**, where two pairs of them having mutually different orientation of the Dmp substituents of bridging amido groups - *syn* (Figure 10A) and *anti* (Figure 10B). The dimeric structural arrangement is further composed of lithium atoms which are three coordinated by two amides and one nitrile group. The trigonal geometry of lithium atoms vary from planar to pyramidal (extreme deviations of the Li atom from its parent N₃ plane are: 0.286 and 0.344Å in *syn* and 0.081 and 0.479Å in *anti* isomer) depending on the nature of the isomer. Nevertheless, the existence of these isomers has surprisingly only minor influence to the values of interatomic distances and the rest of the angles defining the central ring. The central four membered rings are heavily distorted from a planar arrangement with bridging amido ligands where the Li-N separations are nearly equidistant. In **7**, practically no elongation of the C≡N bonds is found upon its coordination to appropriate lithium atom in comparison to the parent nitrile which is also in accord with appropriate parameters found for lithium complexes containing organic nitriles.^{21,22} However, based on quite short separation between Li and N atoms one can assign them as strong coordination bonds.

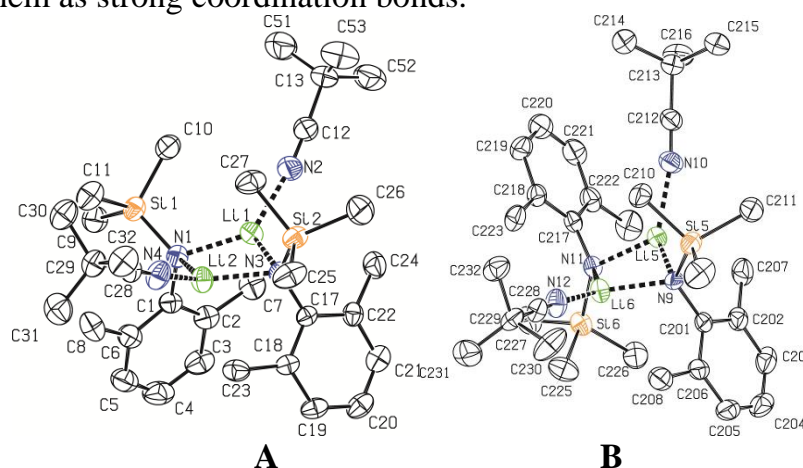
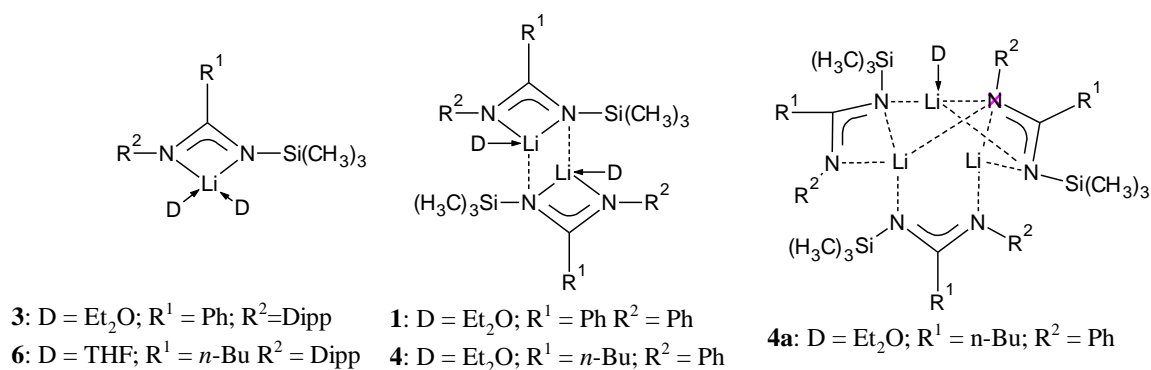


Figure 12: Molecular structure (ORTEP 50% probability level) of **7**, two independent molecules are shown, hydrogen atoms are omitted for clarity.



Scheme 1: Observed types of lithium amidinate structures

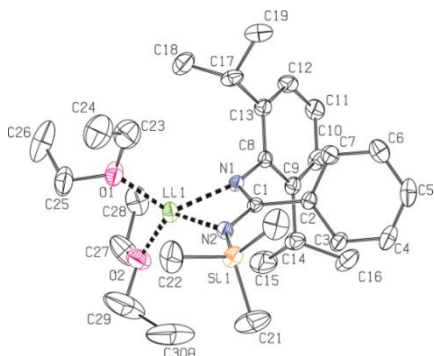


Figure 13: Molecular structure of **3** (ORTEP view, 30% probability level). Hydrogen atoms and disorder from Et₂O molecules are omitted for clarity.

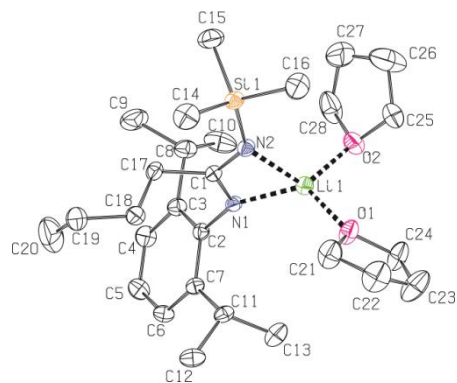


Figure 14: The molecular structure (ORTEP 40% probability level) of **6**.

Compounds **3** and **6** (Figures 13 and 14, Scheme 1), containing bulkiest peripheral groups (Dipp), reveal monomeric structures with four-coordinate lithium atom with (pseudo)tetrahedral geometry and similar interatomic distances between the nitrogen and lithium atoms. The isobidentate bonding fashion of the amidinate ligands is documented by equidistant C1-N bonds with a delocalized character. The nature of other substituents of the amidinate moiety located on the central carbon atom (Ph in **3** vs. *n*-Bu in **6**) as well as the presence of the nature of adjacent solvent molecule - THF vs. diethylether - has virtually no influence to the geometry of both molecules as reflected in interatomic distances and angles around the lithium atoms. In comparison of the geometry of **3** and **6** with mononuclear lithium *n*-butylamidinate containing two Dipp groups^{23,24} or lithium benzoylamidinate with one trimethylsilyl and Dipp groups,²⁵ the N2-C1-N1 angle in **3** and **6** is wider by ~3° and the C1-Li distance slightly shorter, with respect to previously reported analogues, which in general led to the planar fashion of the central four membered rings. On the other hand, the direct comparison of structures of phenyl-substituted **3** and analogous lithium amidinate with two Dipp groups in peripheral positions and phenyl group with adjacent nitrogen donor in the central position is not relevant because of monodentate bonding fashion of the amidinato unit in the latter case.²⁶

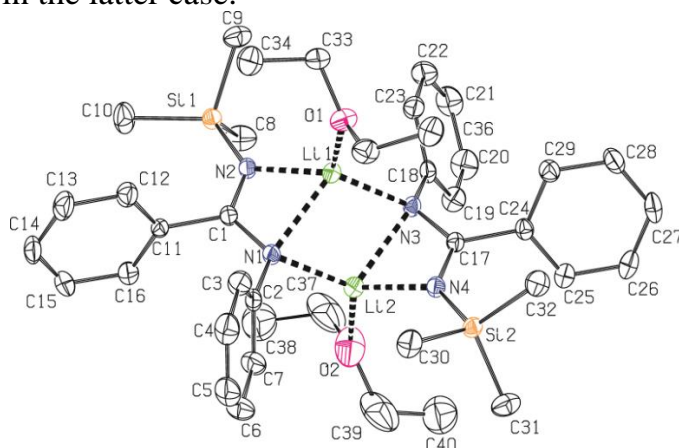


Figure 15: Molecular structure of **1** (ORTEP view, 40% probability level). Hydrogen atoms and disorder from Et₂O molecules are omitted for clarity.

The presence of smaller peripheral group - phenyl - in **1** and **4**, caused the formation of centrosymmetric dimers similarly to trimethylsilyl-substituted complexes of Lappert²⁷ and a couple of other complexes bearing smaller peripheral substituents.²⁴

Compounds **1** and **4** along with structures of all other reported dinuclear complexes reveal very close structures reflected in similar interatomic distances and angles (Figs. 15 and 16). The common feature of these structures are heavily distorted tetrahedral coordination geometries of the lithium atoms, with the largest deviations from the ideal shape in N1-Li1-N2 angles which are only about 66°. The Li-Li distances (~2.52 Å) are detected for these

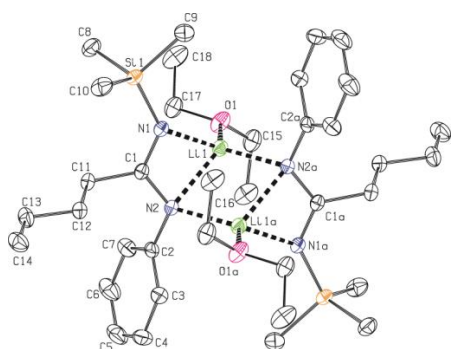


Figure 16: Molecular structure of **4** (ORTEP view, 40% probability level). Hydrogen atoms and disorder from Et₂O molecule are omitted for clarity.

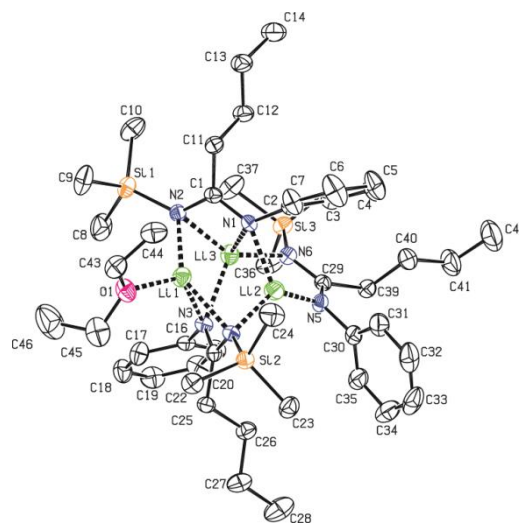


Figure 17: Molecular structure of **4a** (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity.

compounds which is slightly longer than in the amidinates bearing the same peripheral substituents (~2.42 Å)²⁸. The degree of conjugation within the amidinate moiety reflected in separations of the carbon and nitrogen atoms within the amidinate unit is also lower than in symmetrical lithium amidinates and mononuclear **3** and **6**. The nearly equidistant Li-N separations are only slightly longer than the sum of the covalent radii of both atoms (2.04 Å).^{29,30} The third and fourth coordination place is occupied by the nitrogen of the second amidinate unit, and the oxygen atom of the diethylether molecule, respectively. The interplanar angle of the NCN amidinate planes in **1** is 5.4(2)° which is in strong contrast to the situation found in **4** and the rest of the molecules reported in the literature where these planes are always parallel. This fact might indicate the boarder-line case of arrangement of these groups in **1** which is supported by the fact that both quarternary carbon atoms of the phenyl ring and the silicon atom lie in the NCN plane which is typical for monomeric structures and reveal higher degree of conjugation within these units. The distance between NCN planes in **4** is 0.397(3)Å, which is dependent on the steric repulsion of the substituents and a donor ability of the coordinated solvent, is slightly longer than in the lithium amidinates containing adjacent donor group²⁶ but still shorter than in remaining dimeric structures (0.471 Å for [*n*-BuC(NCy)₂Li(THF)]₂³¹, 0.652(3) Å for [*n*-BuC(N-*i*Pr)₂Li(Et₂O)]₂ and 1.028 Å for a lithium triphenylamidinate adduct with HMPA³²). Lithium atoms are located above the NCN amidinate planes by 0.761(2)Å and

0.810(3)Å for **1** and 0.701(3)Å for **4**, respectively, which is similar to dimeric lithium amidinates containing adjacent donor group²⁶ but a bit over the values found for remaining compounds in the literature.^{24,23,33}

Several crystals of trinuclear adduct **4a** are formed along the dimer **4** in the same flask. The structure of **4a** (Figure 17) is best described as an adduct of the common dimer (fragments containing N1, N2, C1 and Li3 and N3, N4, C15 and Li1 atoms) from which one molecule of the diethylether was extruded, and a monomer without any coordinated solvent, where the last amidinate ligand altered the isobidentate to bidentate-bridging fashion to Li2 and Li3 atoms. All three lithium atoms reveal different coordination geometry, going from Li1 which is in an immediate neighborhood as found in dimers - heavily distorted tetrahedral with three nitrogen atoms and oxygen from diethylether molecule, through the Li2 being in nearly perfect trigonal vicinity of N1, N2 and N5 atoms (Li atom is only 0.227(2) Å above the plane) to four-coordinate Li3 which has the geometry between seesaw and heavily distorted tetrahedron. The Li-N distances vary from 1.95 to 2.25Å where the shortest ones were found in the triangle of Li2 atom as well as in the bidentate-bridging amidinate. On the other hand, the high degree of π -electron density conjugation over all amidinates is documented in the middle carbon to nitrogen distances being 1.33Å.

5.2. Dissymmetric and asymmetric amidinates

5.2.1. Synthesis

In this Ph.D. thesis, all the lithium nitriloamidinates **14** - **17** and dilithium bisamidinates **8-13a** and **18-22**, are air and moisture sensitive white solids which were prepared according to Figure 10 from appropriate trimethylsilylated lithium anilide and 1, 3- or 1, 4-dicyanobenzene by the addition of amide to the nitrile function with subsequent migration of trimethylsilyl group in moderate to excellent yields (complete conversion, isolated yields of single crystalline material - 40 - 90%). In order to complete the conversion of the starting dinitriles, especially in cases of reactions with sterically crowded lithium amides, significant prolongation of reaction times is necessary. In the Table 1, time necessary to complete reactions is presented, where the clear match between the steric bulk of the amide substituent and the type of dinitrile used is recognized. For example, when the amide with the smallest substituent - Ph - is reacted with the 1, 4-dicyanobenzene the time necessary for complete conversion to lithium nitriloamidinate is almost negligible, for completing the reaction of the same reactants in a stoichiometric ratio 2:1, about four hours are needed for essentially quantitative yield of **11**. The reaction of phenyl substituted lithium amide with 1, 3-dicyanobenzene in 2:1 ratio demands about 12 hours for formation of **8** because of less space around the nitrile function in the case of *meta* substitution. The total extreme is the synthesis of *meta*-substituted dilithium bisamidinate **10** containing the most sterically demanding Dipp groups where the reaction time is more than 40 days. Similarly as for reactions of benzonitrile and valeronitrile described in the previous chapter, reactions should proceed at room temperature or below because decomposition of starting lithium amides in coordinating solvents at elevated temperature (> 30°C). The use of smallest lithium anilide in the series, phenyl - (**8** and **11**), led to relatively fast and complete conversion of starting dinitriles, but presumably differently solvated higher nuclearity species were formed in the solution which is in line with our previous observations of equilibrium of mono- to oligomeric complexes in solution and in the solid state for lithium amidinates bearing small peripheral substituents. Slow reaction progress detected for bulkier amides led us to the idea to isolate lithium nitriloamidinates as potential hybrid ligands. Surprisingly all the lithium nitriloamidinates **14** - **17** were crystallized in a very pure form from reactions of dinitriles with one equivalent of appropriate lithium anilide containing bulkier groups as Dmp or Dipp (Figure 10, Path A). In cases of reactions of phenyl-substituted anilides, only a mixture of species with both partially and completely reacted nitrile groups is obtained. Due to this reason, **14-0** could not be isolated as a pure product. The addition of two equivalents of lithium anilides (Fig. 10; Path B) gave dissymmetric dilithium bisamidinates where the complexes bearing the phenyl group (**8** and **11**) reveal only a limited solubility in solvents used because of aggregation (vide infra). When the path C (in Fig. 10) is followed, starting from lithium nitriloamidinates with Dmp or Dipp and another molar equivalent of the lithium anilide containing different substituent, one can isolate asymmetric dilithium bisamidinates **18** - **22**.

Table 1: Duration of reactions for complete conversion of starting material^a

Isomer ^c /Stoichiometry ^d	Substituent reaction time ^b /product		
	Ph	Dmp	Dipp
<i>m</i> -/ 1:1	-/1	24/2	24/3
<i>p</i> -/ 1:1	-	12/4	12/5
<i>m</i> -/ 2:1	12/6	24/7	1008/8
<i>p</i> -/ 2:1	4/9	12/10	24/11

^amonitored by ¹H and ¹³C NMR spectroscopy - based on integration of aliphatic groups in ¹H and/or quantitative ¹³C NMR spectra for signal of unreacted nitrile group, ^b[hours], ^cstarting dinitrile, ^dstarting lithium amide to dinitrile ratio

5.2.2. NMR spectroscopic studies in solution

The progress of reactions performed was monitored along with purity as well as structure of prepared compounds by the multinuclear NMR spectroscopic approach (¹H, ⁷Li, and ¹³C) in saturated THF-d₈ solutions and for insoluble complex **11** by solid state ⁷Li, and ¹³C CP-MAS NMR spectroscopy. The ¹H NMR spectra of all complexes, except for insoluble **11** and the rest of complexes containing phenyl substituent (**8** and **11**) which allows an aggregation, reveal one set of relatively sharp signals suggesting isobidentate bonding mode of the amidinato ligands in solution²³. In the case of asymmetric dilithium bisamidinates, one set of well resolved signals is attributed to each geometrically independent part of molecule.

5.2.3. Solid state studies

When the peripheral group of the amidinate ligand is sufficiently bulky, as for example Dipp, the structural arrangement of lithium amidinates in the solid state leads to the formation of mononuclear species (Figure 18A)^{1,34-37} with nearly isobidentate bonding fashion of the amidinate ligand. The coordination geometry of the central lithium atom can be described as a distorted tetrahedral where the deviations from the ideal shape are strongly dependent on the presence of adjacent donor atom or chelating groups (Et₂O, THF, TMEDA, etc.). The second, nearly equally populated structural group of lithium amidinates, are the dinuclear centrosymmetric complexes (Figure 18B)^{23,37,38} where the bridging character of one of the nitrogen atoms is pronounced.

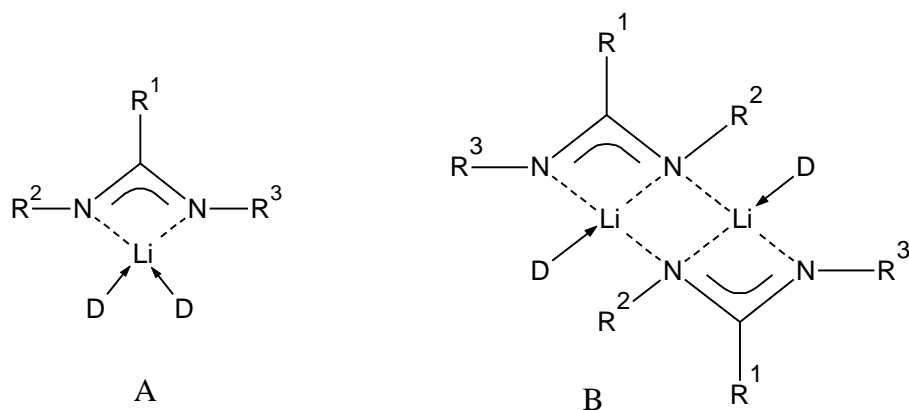


Figure 18: Most frequent structural motifs of lithium amidinates.

In this respect, the prepared lithium nitrilo amidinates (**14** and **17**, Figures 19 and 20) and dilithium bisamidinates (**10**, **10a**, **12**, **13**, **13a** and **21** - Figures 21-26) crystallize exclusively in the form of complexes where one amidinate group is able to complexate one lithium atom in nearly isobidentate bond fashion and the coordination polyhedra is completed by two diethylether or tetrahydrofuran molecules.

The lithium nitriloamidinate complexes **14** and **17** reveal similar arrangement and interatomic distances of the nitrile group to parent dinitriles. Non-negligible changes of geometries of mentioned compounds can be seen in slightly different orientation of each of amidinate groups and phenyl ring, where nitriloamidinate complexes reveal almost perpendicular orientation of both planes, while in the most sterically hindered *meta*-substituted bisamidinate complex **10** the same type of interplanar angles is sharpened by $\sim 25^\circ$ similarly to *para*-substituted bisamidinates. In all the bisamidinates, mutual *anti*-orientation of the silyl groups is found. The structure of asymmetric complex **22** reveals almost the same structure as the rest of *para*-substituted bisamidinates **12** and **13**. When compared with the literature data, all these complexes containing isobidentate amidinate ligands are structurally similar to previously reported non-symmetric lithium amidinates **1** and **4**, mononuclear lithium *n*-butylamidinate containing two Dipp groups^{23,24} or lithium benzoylamidinate with one trimethylsilyl and Dipp groups³⁹.

On the other hand, the arrangement with bidentate-bridging amidinate ligand providing thus the polymeric array is detected only for the complex **11** (Figure 27) which is comparable with reported trimethylsilyl-substituted centrosymmetric dimeric complexes of Lappert²⁷ and a couple of other complexes bearing smaller peripheral substituents²⁴.

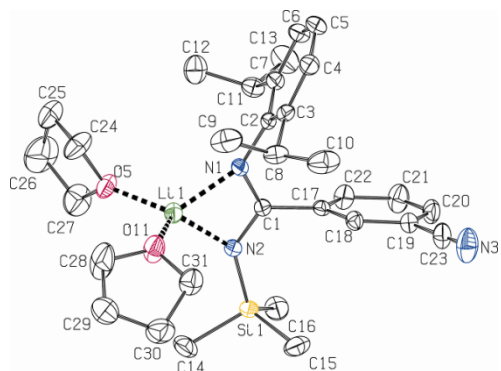


Figure 19: Molecular structure (ORTEP 50% probability level) of **14**, hydrogen atoms are omitted for clarity.

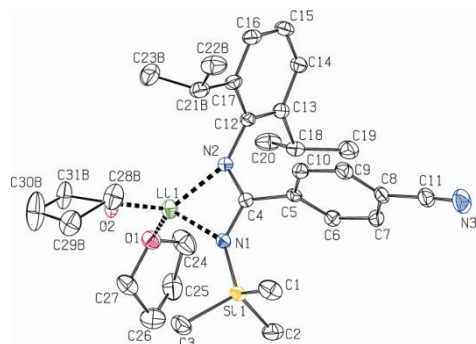


Figure 20: Molecular structure (ORTEP 40% probability level) of **15**, hydrogen and second positions of disordered atoms are omitted for clarity.

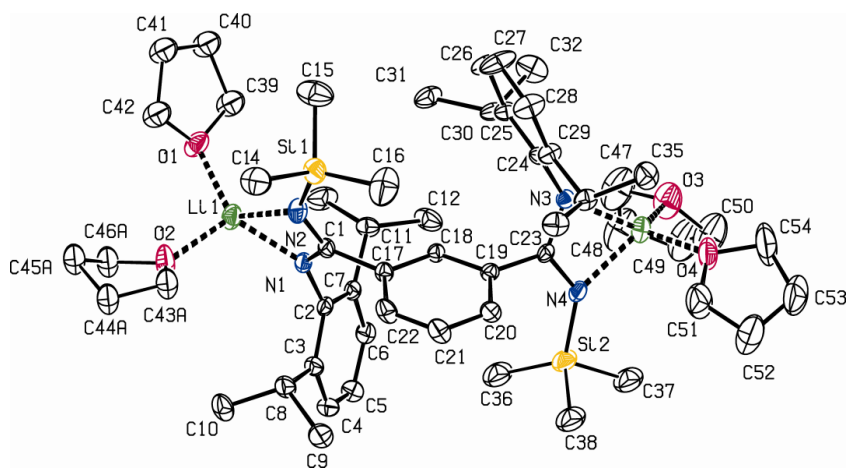


Figure 21: Molecular structure (ORTEP 50% probability level) of **10**, hydrogen and second positions of disordered atoms are omitted for clarity.

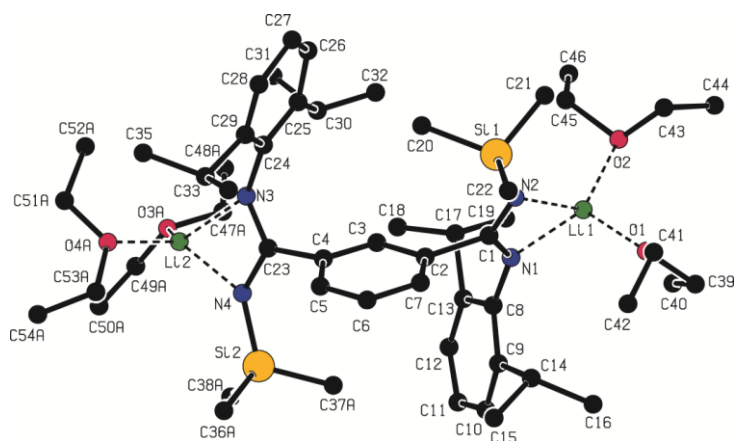


Figure 22: Molecular structure of **10a**.

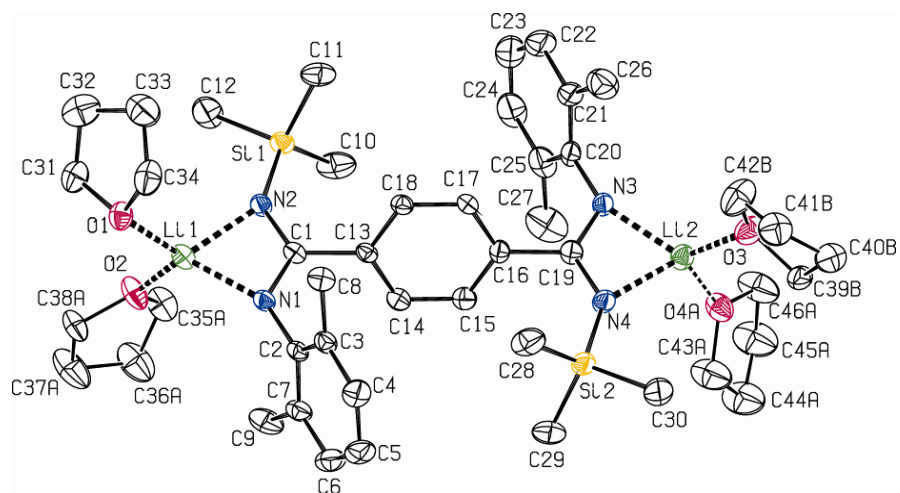


Figure 23: Molecular structure (ORTEP 40% probability level) of **12**, hydrogen atoms are omitted for clarity..

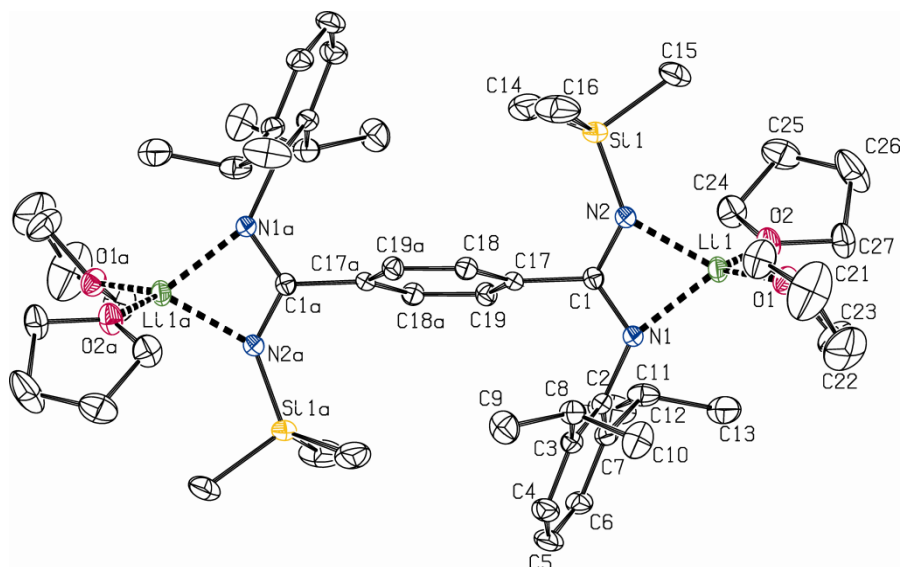


Figure 24: Molecular structure (ORTEP 40% probability level) of **13**, hydrogen atoms are omitted for clarity.

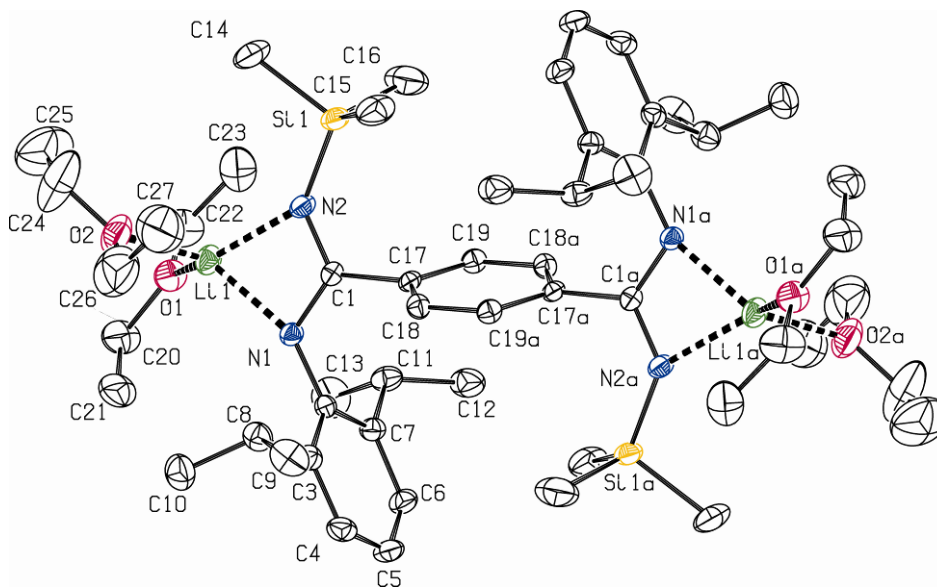


Figure 25: Molecular structure (ORTEP 40% probability level) of **13a**, hydrogen atoms are omitted for clarity.

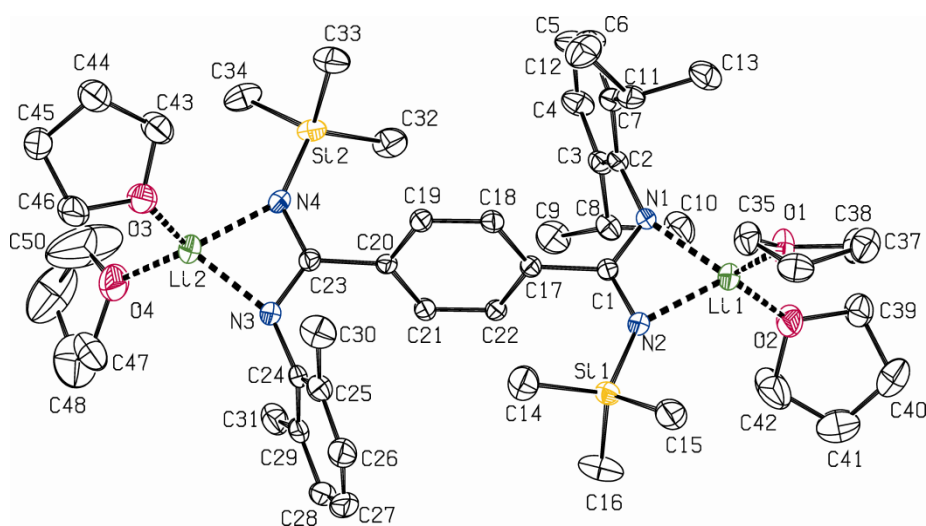


Figure 26: Molecular structure (ORTEP 40% probability level) of **21**, hydrogen and second positions of disordered atoms are omitted for clarity.

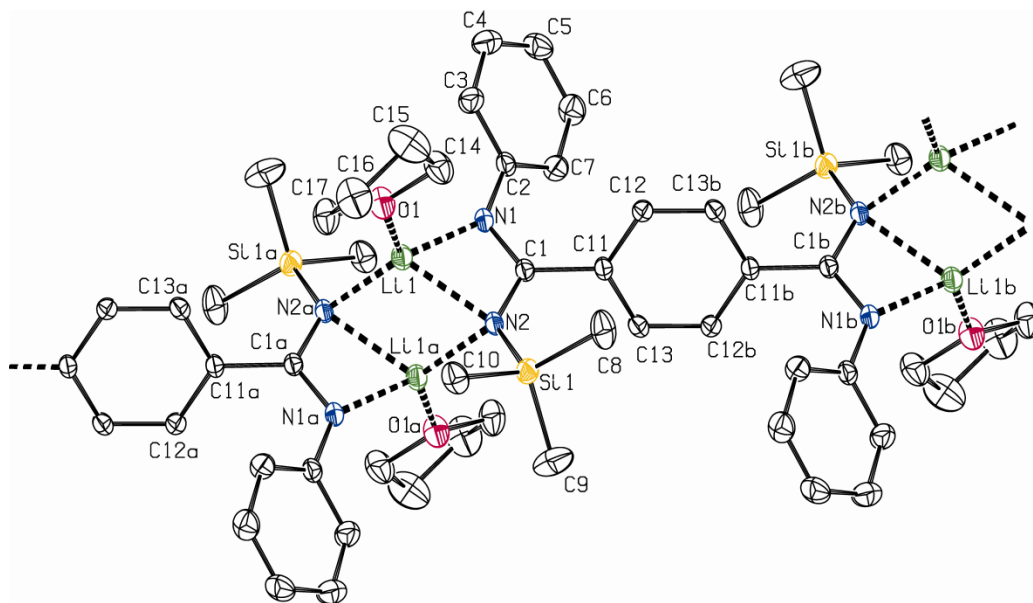


Figure 27: Molecular structure (ORTEP 40% probability level) of **11**, hydrogen and disordered atoms are omitted and the independent part of the polymeric chain is shown for clarity.

Complex **11** reveals very close structure to these non-symmetric lithium amidinates reflected in similar interatomic distances and angles (Figure 27). The common aspects of such arrangements are represented mainly by heavily distorted tetrahedral coordination geometries of the lithium atoms, with N-Li-N angles about 66° . The Li-Li distance ($2.473(3)\text{\AA}$) is in line with the same type of parameter established for these compounds ($\sim 2.42\text{\AA}$)²³. The degree of conjugation within the amidinate moiety reflected in separations of the carbon and nitrogen atoms within the amidinate unit is also lower than in symmetrical lithium amidinates and the rest of lithium amidinates revealing the isobidentate bonding mode of the ligand. The coplanar arrangement of amidinate NCN planes in **11** is in good agreement with the geometry of the rest of respective molecules reported in the literature. The separation of neighboring NCN planes which is dependent on the steric repulsion of the substituents and flexibility of ligand in **11** is $1.108(3)\text{\AA}$. This value is much higher than in similar dimeric lithium amidinates ($0.397(3)\text{\AA}$ for **4**, 0.471\AA for $[n\text{-BuC}(\text{NCy})_2\text{Li}(\text{THF})]_2$ ³¹ or $0.652(3)\text{\AA}$ for $[n\text{-BuC}(\text{N-}i\text{Pr})_2\text{Li}(\text{Et}_2\text{O})]_2$ ²³).

5.3. Nonsymmetric isoindoles

Last but not least important part of this thesis is devoted to the reactivity of 1,2-dicyanobenzene. Similarly as in previous chapters reaction of this particular nitrile with selected trimethylsilylated anilides leads to the migration of trimethylsilyl group from nitrogen it was originally bonded to. In contrast to previously described reactions, the close vicinity of another nitrile group enables it to join the reaction and leads to formation of isoindole and further migration of trimethylsilyl group to the second nitrogen of dicyanobenzene as can be seen in figure 11.

No matter the steric demands of anilide substituent, prepared diiminoisoindolides exclusively crystallize in the form of dimeric structures. In these structures lithium is in the center of tetragonal pyramid. Base of the pyramid in this motif is formed by four nitrogen atoms and top position in this pyramid is occupied by oxygen from coordinating solvent.

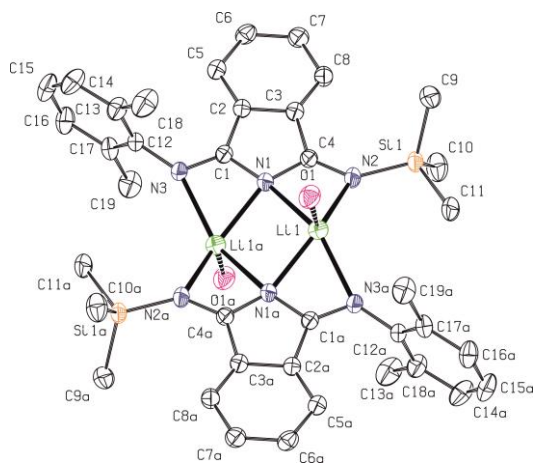


Figure 28: Molecular structure (ORTEP 50% probability level) of **24**, hydrogen atoms and carbon atom of coordinating solvent are omitted for clarity.

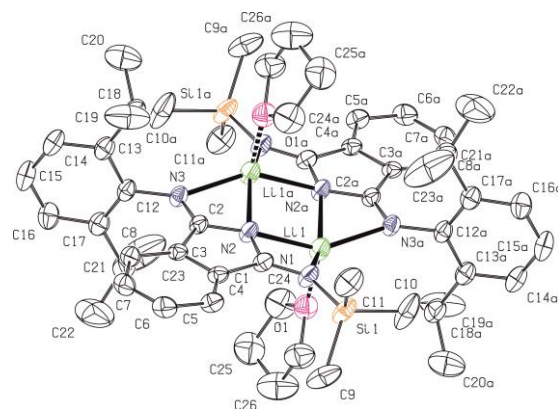


Figure 29: Molecular structure (ORTEP 50% probability level) of **25**, hydrogen atoms and carbon atom of coordinating solvent are omitted for clarity.

After hydrolysis 1-arylimino-3-aminoisoindolin was obtained. XRD of **27** shows, that both hydrogen atoms are bonded to terminal nitrogen forming primary amine. This structure is similar to structures published by Tamagi.⁴⁰

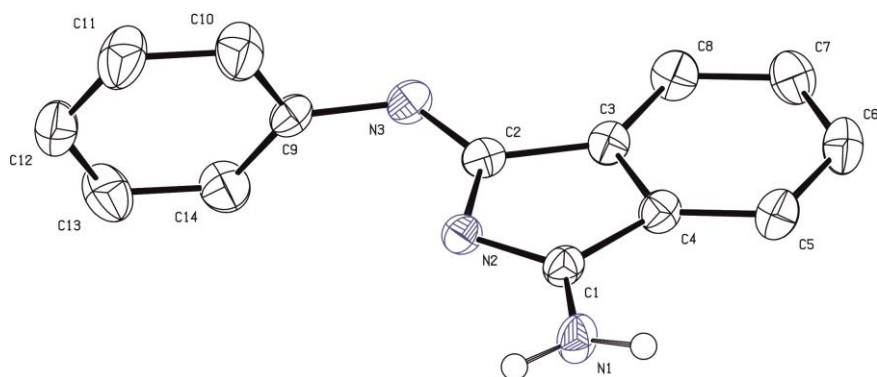


Figure 30: Molecular structure (ORTEP 50% probability level) of **27**. Carbon bonded hydrogen atoms are omitted for clarity.

When more than one molar equivalent of starting lithium amide was added to a reaction mixture with 1,2-dicyanobenzene only mixture of **23-25** and starting amide was obtained according to NMR spectra which supports the fact that no further addition reactions to the lithium 1-(trimethylsilylimino)-3-(alkyl- or arylimino)isoindolines are possible at specified conditions. Unfortunately these reactions cannot be performed at elevated temperature due to thermal instability of starting amides.

6. Conclusion

In summary five series of new complexes (nonmetric amidinates, nonsymmetric nitriloamidinates, dissymmetric bisamidinates, asymmetric bisamidinates and nonsymmetric isoindolines) have been prepared and structurally characterized both in solution and solid state.

All new complexes have been prepared in forms bearing peripheral groups of different steric bulk, lower steric demands of the nitrogen as well as the central carbon atom substituents. Due to high variety of steric demands of substituents on nitrogen and carbon atoms different structural motifs were observed. While in simple amidinate with highly steric demanding substituents (Dipp) monomer structure was observed, in amidinates with lower sterically demanding substituents (Dmp) mostly dimers were formed. Quite interesting form of polymer crystal was revealed in linear bisamidinate with phenyl groups. Another interesting form of trinuclear aggregate with three different bonding modes was also observed. In all these complexes four-coordinated lithium atom was found.

On the contrary, nonsymmetric 1,3-diiminoisoindolines form dimers in solid state no matter of steric demands of peripheral groups. In these dimers lithium atom is five-coordinated with two bidentateisoindolie units and the fifth coordination position is occupied with oxygen from coordinating solvent.

Acknowledgement

The author would like to thank prof. Ing. Aleš Růžička, Ph.D. for advices and kind help over the years, Ing. Zdeňka Růžičková, Ph.D. for the X-ray diffraction analysis and Ing. Petr Švec for NMR spectroscopy consultations. This work was supported by Czech Science Foundation (projects P207/12/223 and 17-10377S).

List of papers published by author

Milan Erben, Jan Merna, Ondřej Hylský, Jana Kredatusová, Antonín Lyčka, Libor Dostál, Zdeňka Padělková, Martin Novotný; Synthesis, characterization and styrene polymerization behavior of alkoxy-silyl-substituted monocyclopentadienyltitanium(IV) complexes; *J. Organomet. Chem.* 725, **2013**, 5-10

Martin Novotný, Zdeňka Padělková, Jaroslav Holeček, Aleš Růžička; O,N-Chelated germanium, tin and lead compounds containing 2-[N,N-(dimethylamino)methyl]phenolate as ligand; *J. Organomet. Chem.* 733, **2013**, 71-78

Martin Novotný, Petr Švec, Zdeňka Růžičková, Aleš Růžička; Structure of non-symmetric lithium amidinate complexes prepared by addition of lithium amides to various nitriles; *J. Organomet. Chem.* 828, **2017**, 68-74

Martin Novotný, Petr Švec, Zdeňka Růžičková, Aleš Růžička; Direct access to non-symmetric lithium nitriloamidinate and disymmetric dilithium bisamidinate complexes from 1,3- or 1,4- dicyanobenzene and lithium amides; *J. Organomet. Chem.* 849-850, **2017**, 88-97.

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