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Lithium and Dilithium Guanidinates, a Starter Kit for Metal Complexes Containing Various Mono- and Dianionic Ligands

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ABSTRACT: Comparative studies of the synthesis of lithium guanidinates via nucleophilic addition of lithium amides to carbodiimides were performed. Four combinations of small or sterically crowded carbodiimide and sterically crowded lithium amide or lithium amide containing an adjacent amino donor group give ten different types of complexes. In particular, 2,6-[(CH₃)₂CH]₂C₆H₃NHLi (DipNHLi, 1) reacts with (CH₃)₂CHN=C=NCH(CH₃)₂ upon the formation of the dissymmetric dimeric complex 2 with four-coordinate Li atoms. In contrast, 1 with DipN=C=NDip gives the mononuclear lithium guanidinate 3 with two-coordinate lithium by κ^1 -guanidinate, solvent molecule, and additional interaction with a π -electron cloud of one of the Dip groups. Analogous reactions of 2-[(CH₃)₂NCH₂]-C₆H₄NHLi (7) yield complexes 8 and 9, where the adjacent amino donors are always coordinated. Further deprotonation of 2, 3, 8, and 9



leads to dilithium guanidinates(2–)—4, 5, 10, and 11, among which only 5, containing three Dip groups, is monomeric with contacts to two π -electron systems of Dip groups. The rest of the complexes are tetranuclear with different structural patterns. In the central parts of molecules, toward which the nitrogen atoms of the guanidinates are oriented, lithium atoms are usually pseudotetrahedral, but trigonal in peripheral parts. Adjacent solvent molecules, chelating amino groups, and π -electron systems of Dip groups are coordinated in order to complete coordination polyhedra. Complexes 4 and 5 deoligomerize in solution upon the formation of fluxional monomeric dilithium species. Conversely, 11 is a dimer in solution due to the strong donation of an amino group. The silylated lithium amide {2-[(CH₃)₂NCH₂]C₆H₄}[(Si(CH₃)₃]NLi (12) reacts with both carbodiimides to give dinuclear 13 obtained from diisopropylcarbodiimide and monomeric 14 from the second carbodiimide. Complexes 13 and 14 structurally resemble 8 and 9, with the highest degree of the localization of π -electron density within the N₃C guanidinate system, η^3 -contact to the Dip ring, and a lack of the solvent molecule in 14.

■ INTRODUCTION

Several amidines and guanidines as formal derivatives of carbonic or carbamic acids have found many applications in their neutral and neutral-condensed forms (biguanides). For example, they appeared in organic chemistry as catalysts or bases, in the production of plastics, biochemistry, natural products or drugs, and as propellants in car air bags.¹ Protonated forms (of amidinium or guanidinium type) can serve as organocatalysts, ionic liquids, drugs, in protein folding, and nonlinear optics.²

The preparation of guanidines mostly proceeds by direct addition of an amine to cumulated double bonds of carbodiimides.³ This atom-economic protocol called guanylation of an amine requires harsh conditions; in a remarkable number of cases, it is driven catalytically. The guanylations of secondary, aromatic, or sterically crowded amines cannot be achieved satisfactorily without a catalyst, owing to their decreased nucleophilicity.⁴ The d- and f-block metal complexes,⁵ as well as the coordination compounds of electron-deficient main-group metals (Li, Al, Mg, and Al)⁶

and nanoparticles prepared from transition metal oxides⁷ are reported to catalyze most of the guanylation reactions.

The deprotonation of amidines and guanidines by one equivalent of a strong base leads to amidinates and guanidinates, systems with an electron-rich chelating arrangement^{8,9} (Figure 1A,B),¹⁰ frequently used for the complexation of nearly all metals and metalloids of the Periodic Table of the Elements. Specifically N,N',N''-triscarbyl-substituted guanidinato ligands, which are also the subject of the present study, exhibit a higher basicity than amidinates, more bonding modes, and, last but not least, the ability to be also doubly deprotonated (Figure 1C). Metal complexes containing

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Figure 1. Examples of the structural motifs of lithium guanidinates. R^1 = H or an organic or silyl group; $R^{2,3}$ = an organic or silyl group; D = a donor/solvent. Data sources: refs 9e; 15a,d-p; and 16a,b.

various types of guanidinato ligand are habitually tested as catalysts of various organic reactions,¹¹ as precursors of new materials,¹² and for the stabilization of unusual,¹³ generally lower, oxidation states of metals. Very recently, these highly basic building blocks have been used as stabilizing substituents for the synthesis of phosphorus dications, which have superacidic character and are able to activate for example such strong C–F bonds.¹⁴

Nevertheless, most of these metal complexes are prepared from the starting lithium compounds followed by transmetalation with metal halides. The number of the studies dedicated to the preparation, structure, and reactivity of the mentioned lithium precursors is still limited. Generally, the chemistry of the monolithium guanidinates(1–) is more frequent¹⁵ (Figure 1B), and there are only two reports dealing with dilithium guanidinates(2–) (Figure 1C).¹⁶ In addition, related structures of dianionic guanidinates compensated by one lithium and another metal atom¹⁷ or dilithium boraamidinates/boraguanidinates,¹⁹ the known structures of lithium guanidinates range from only two monomeric examples, with an extra donor as an aromatic π -system^{15e} or a chelating methoxy group,²⁰ through several different symmetric or asymmetric dimers,^{15a,d,f-j,17a} to the sole example of a higher aggregate (tetranuclear)²¹ or an adduct.²² Two examples of lithium bis-guanidinates with a dimeric structure have been found as well.²³

Syntheses and comparative solution and solid-state studies of corresponding lithium amidinate complexes containing both aliphatic and aromatic substituents as well as substituents with potentially chelating groups²⁴ have revealed a great diversity of structures, behavior, and potential use.

The main target of this particular study is the synthetic and structural investigation of groups of lithium and dilithium guanidinates substituted by a combination of both aliphatic, bulky aromatic group, and a potentially chelating group in order to create a tool for the preparation of guanidinates of various metals.

RESULTS AND DISCUSSION

In order to avoid the problems of the separation of the desired guanidines from the starting material and various catalysts, attention has been focused on the direct reactions of the respective lithium amides with carbodiimides, presumably yielding the desired lithium guanidinates. It is worth mentioning here that the direct noncatalyzed reactions of selected anilines with carbodiimides to guanidines gave only mixtures of starting material with products even when a prolonged reflux in toluene solution was applied. Reliable candidates for this comparative study are a series of complexes made by a combination of both sterically demanding lithium anilide or anilide with the adjacent donor amino group (Schemes 1 and 2) and carbodiimides substituted by bulky aryl





or alkyl groups. For all complexes, ¹H, ¹³C, and ⁷Li NMR spectra were recorded in THF- d_8 or C₆D₆. When sufficient solubility in noncoordinating solvents such as C₆D₆ was achieved, the measurement was also performed in them in order to compare the same parameters, which could provide essential information on the association of complexes in solution.

The reaction of lithium anilide 1, prepared by the lithiation of 2,6-(diisopropyl)aniline (ArNH₂, Scheme 1), with one molar equivalent of *i*PrN=C=N*i*Pr, led almost exclusively to the desired compound 2 in diethyl ether solution at room temperature. The ¹H NMR spectra of **2** recorded both in C_6D_6 and THF- d_8 showed rather unsymmetrical behavior of both isopropyl and Dip groups. Apart from two signals for H-atoms of aromatic rings, one signal at 3.45 ppm (C_6D_6) or 3.29 ppm (in THF-d₈) was attributed to the NH group; three signals were found for methine and four doublets of equal intensity for methyl groups. Three methine signals have the integral intensity ratio of 2:1:1, where the intense signal resonates at a higher frequency, which indicates the equivalency of methines bound to the Dip substituent, while other isopropyls are inequivalent. On the basis of this, one can predict the structure with the bidentate bonding mode of the guanidinate to the lithium atom, to which nitrogen from the former aniline

Scheme 2. Reaction Pathways to Lithium and Dilithium N,N'-Disubstituted- $\{N''-[2-[(dimethylamino)methyl]phenyl\}$ guanidinates



Figure 2. Molecular structure of 2 (left) and 2a (right). Selected bond lengths are given along with atom connectors in angstroms. Full ORTEPtype plots with more bond distances and angles with standard uncertainties are given in the SI.

and the second one from the carbodiimide is bound. The migration of the hydrogen atom from the former aniline/ lithium anilide to the starting carbodiimide (formal amination or addition to an unsaturated system) is another consequence of the presence of this structural motif. Moreover, the characteristic signals for coordinated diethyl ether, coming from the synthetic procedure, are also present in the spectrum measured in deuterated benzene. Only a two- and three-fold (for $-OCH_2CH_3$) intensity of these signals as compared to the integral value of the signal for the N-H group must be associated with coordination of the diethyl ether molecule per the dimeric structure of 2, which is not known in the lithium guanidinate family. The ¹³C NMR spectra of 2 in C_6D_6 and THF- d_8 resemble each other. The difference is admittedly seen in chemical shifts for the middle carbon of the guanidinate unit and the carbons bound to nitrogen atoms, but these are only 1-2 ppm. On the other hand, a major change is observed in ⁷Li NMR spectra, where the distinction in C_6D_6 and THF- d_8 is about 2.5 ppm. This particular shift could be virtually

connected to the structural changes in the dimeric one with only one coordinated diethyl ether molecule in C₆D₆, and thus two distinct lithium atoms, one four-coordinated by two bidentate guanidinates and the other one three-coordinated by only one nitrogen atom from both guanidinates and an oxygen atom from the diethyl ether molecule. Such a structure is most likely a product of the deficiency of the coordinating solvent, and the explanation of this structural arrangement requires the presence of a fast equilibrium between both coordination motifs, as ⁷Li NMR observes only one signal at 2.0 ppm. Unfortunately, all attempts to perform a low-temperature measurement in a noncoordinating solvent such as toluene- d_8 have nearly no influence on the spectral patterns or failed due to low-solubility issues at the lowest temperature. On the other hand, similar changes in chemical-shift values connected to the structural ones have been observed for lithium amidinates,² the structure of dissymmetric dinuclear lithium guanidinate reported by Jones^{15e} (Figure 1E, δ_{Li} 2.6 in C₆D₆) and in the solid state (see below). The second structure of 2 in THF- d_8

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Figure 3. Molecular structure of 3. Selected bond lengths are given along with atom connectors in angstroms. Full ORTEP-type plots with more bond distances and angles with standard uncertainties are given in the SI.

connected to the N1 atom, and the lithium coordinated to nitrogen N3 and O1 atoms from the diethyl ether molecule. Although the contacts are slightly closer than found for 2, the lithium-coordination sphere is not saturated enough and requires extra electron density from the π -system of the phenyl ring (Li–Cg, 2.444(3) Å). For comparison with other complexes in this study and some of the literature-reported separations for other types of lithium-aryl complexes,²⁵ the centroid of the phenyl ring is depicted showing the η^6 -type of coordination, but the η^1 - to η^3 -type would be more appropriate in the case of 3 (Li–Cg(η^3), 2.293(3) Å). Direct literature comparison is available with the lithium guanidinate of Jones et al.^{15e} (Figure 1E), which, however, resembles the dissymmetric complex 2, but when synthesis was conducted in THF instead of hexane, a mononuclear complex with η^1 -guanidinato- η^3 -aryl and coordinated THF molecule has been isolated. All of the structural parameters of the mononuclear lithium guanidinate of Jones et al.'s work and 3 seem to be the same including the separations of the Li-phenyl ring and Li-O of THF or diethyl ether molecule (Figure 3), respectively. The only exception is thus the difference between the chemical shifts in the ⁷Li NMR spectra recorded in C_6D_6 solution (1.6^{15e} vs -1.0 ppm for 3).

According to Scheme 1, monolithiated complex 2 gave dilithiated guanidinate(2-) 4 by a simple addition of an appropriate amount of *n*-butyllithium. Once crystallized after the synthesis, 4 became only sparingly soluble in coordination solvents. That is why in this case only the ¹H and ⁷Li NMR spectra were recorded in THF- d_8 . The ¹H NMR spectrum shows one set of broad signals and the disappearance of any signal attributable to the NH group. In ⁷Li NMR spectrum just one signal at -1.0 ppm was observed. In the solid state, the associated species of 4 probably deoligomerize in the THF solution upon the formation of a highly dynamic molecule with both lithium atoms coordinated by the guanidinato(2-) unit in a more or less bidentate bonding mode. The coordination sphere of distorted tetrahedra is completed by additional molecules of THF. In the solid state, the situation differs dramatically. Although two different structures of 4 have been obtained from THF and diethyl ether solutions (see Figure 4 for the THF adduct 4; for Et₂O adduct (4a), see Figure S5 in the SI), these have an essentially identical pattern and are also very close in all of the interatomic distances and angles. The structure from the THF solution displayed in Figure 4 is composed of two perpendicularly oriented distinct guanidina-

symmetric lithium guanidinates or amidinates, or dimeric with one coordinated THF molecule per one lithium atom as also reported earlier (see Figure 1D). The solid-state structures of 2, determined on the single crystal material obtained from both solvents, correspond to the structure predicted from solution NMR spectroscopic investigations. Both are dimers with a dissymmetrical arrangement of planar ligands, which coordinate two lithium atoms by the nitrogen atoms bearing smaller substituents (isopropyl), while nitrogen atoms substituted by Dip groups are prone to coordinate only one lithium atom. In the centrosymmetric structure of the THF complex (Figure 2 (right)) with coplanar and nearly isobidentate ligands (Li-N distances differ by less than 0.15 Å), each lithium atom is four-coordinated in the pseudotetrahedral environment by three nitrogen donors originating from both ligands and the THF molecule. In the diethyl ethersolvated complex (Figure 2 (left)), there are two different lithium atoms, the one that is three-coordinated by two nitrogens from two ligands, and the other, four-coordinated by two nitrogen atoms from each mutually twisted and nearly perpendicularly oriented ligand. Such a structural arrangement is similar to the solvent-free structures depicted in Figure 1E, where the coordination polyhedra of the lithium atom are completed by agostic interactions with the C-H moieties of the ligands instead of diethyl ether in 2 (see Figure 2). Although the Li-N and Li-O separations seem to be similar in both structures of 2, slightly bigger discrepancies are recognized in the dissymmetric (1.975(3)-2.182(3) Å) and a more strained structure with diethyl ether (2.054(4)-2.108(3))Å) (see Figure 2 and Supporting Information (SI) Figures S1 and S2).

solution could be monomeric with two THF molecules (see Figure 1F) coordinated to the lithium center as described for

In the case of the DipN=C=NDip, the same reaction pathway that led to 2 provided 3. According to the studies in solution of both solvents, all NMR spectra are much easier to read than in the case of 2 (as a result of the presence of the same substituents at all three nitrogen atoms). One set of broader signals is found in THF, which makes it possible to suggest the monomeric structure with a higher degree of molecular dynamics, probably the exchange of the lithium and hydrogen atoms between all three possible positions within the plane of the guanidinato unit. The NH group resonates at a much higher frequency (4.94 ppm for 3 in benzene vs 3.45 ppm for 2), which is caused by the presence of the hydrogen on the nitrogen atom connected to the phenyl instead of the isopropyl group. In the ¹H NMR spectrum in deuterated benzene, four different signals were assigned to the methyl groups with the integral ratio 18:6:6:6 due to the less dynamic process in this solvent. Both ¹³C NMR spectra exhibit a highfield shift of the middle guanidinate (N_3C) atom by ca. 8 ppm in comparison to 2, which is a sign for the lower delocalization of π -electrons within the guanidinato system. The chemical shifts in ⁷Li NMR are rather distant (-1.0 in benzene and -2.8ppm in THF- d_8), probably as a result of the structure with one coordinated diethyl ether molecule, originating from the synthesis, in deuterated benzene, and very strongly coordinated or easily accessible THF molecules. Unfortunately, the measured variable temperature NMR spectra did not provide any additional information on these structures in the range of -80 to 60 °C. The solid-state structure of 3 (Figure 3), crystallized from diethyl ether, is monomeric with the localized double bond between the C1 and N2 atoms, hydrogen



Figure 4. Molecular structure of **4**. Selected bond lengths are given along with atom connectors in angstroms. Full ORTEP-type plots with more bond distances and angles with standard uncertainties are given in the SI.

to(2-) ligands bridged by three lithium atoms. All of these central lithium atoms have different stereochemistry. The first (Li1) exists in the neighborhood of a heavily distorted tetrahedron with out-of-plane isobidentate guanidinate coordination by N2 and N3 atoms, N4 atom from the next guanidinate, and the oxygen of the THF close to the polyhedra. The second case is the pyramidal three-coordinated atom Li2, which is coordinated analogously to Li2 by the N4 and N5 atoms of first and the N2 atom of the second guanidinato unit. Contrary to Li1, the coordination of an adjacent solvent molecule is missing in the case of Li2. These two lithium guanidinates form a U-shaped unit instead of the staircase-like arrangement, the most typical for lithium amidinates and guanidinates ${}^{15a,d,f-j,17a}$ and observed for 2. This unusual composition is probably caused by the presence of the third lithium atom Li3, which has enforced the closing of this system by coordination with N3 and N5 atoms. The vicinity of this ion is trigonal, completed by an O2 atom. Nevertheless, both guanidinates exhibit, according to the planar shape and N-C separations, a similar type of delocalization of the electron density-two longer (1.370(3) and 1.398(2)Å) and one shorter (1.336(3)Å). The order of the nitrogen-atom substituents is different. The guanidinate with the pivotal atom C1 has smaller substituents on the nitrogen atoms routed to the center of the structure, and the Dip substituent of the N1 atom indicates the center. On the contrary, the C26 and N6 atoms, where the π -electron density is concentrated, are in an outer location. The N6 atom bears the isopropyl substituent and the additional lithium atom Li4. The N4 and N5 atoms confined to the center of the structure are bound to the Dip and isopropyl groups as in 2 and 3. The Li4 atom is two-coordinated by the N6 atom and O3 from the THF molecule with a rather obtuse angle of $146.7(4)^{\circ}$. Additional contact with the π -system of the Dip ring should be taken into account as well, approaching the same distance of the Li4 atom to the centroids (2.492(4)Å) as in 3 (2.444(4)Å)

When another equivalent of *n*BuLi is added to 3, complex 5 is isolated quantitatively. The same solubility and dynamics issues are valid for this complex as those for dilithium guanidinate(2–) (4). The absence of the NH resonance, one set of broad signals in the ¹H NMR spectrum, together with only one broad resonance at -2.6 ppm observed in the ⁷Li

NMR spectrum in THF- d_{sy} indicate once again the monomeric structure of the species in solution. One can expect a rather high degree of molecular motion and low hapticity of the guanidinato ligand toward the lithium atoms, which are additionally connected to the solvent donor molecules. In the solid state, the molecule is monomeric–dinuclear (Figure 5) with the all-in-plane arrangement of the guanidinate(2–).



Figure 5. Molecular structure of 5. Selected bond lengths are given along with atom connectors in angstroms. Full ORTEP-type plots with more bond distances and angles with standard uncertainties are given in the SI.

The Dip ligands are perpendicularly oriented, thus forming the paddle-wheel structure of the whole molecule. The lithium atoms are indeed two-coordinated, but each of them has additional noncovalent contact with the close π -system of the Dip group (2.374(3) and 2.479(4) Å), which resembles the pattern already found in 3 or 4 (~2.4–2.5 Å). Although the separations of all coordinated atoms from lithium atoms are slightly shorter (Li–N, 1.892(3) and 1.907(3) Å; Li–O, 1.925(3) and 1.938(3) Å) than in other more associated structures, the O–Li–N angles seem to be sharper by ~5 or 20° than those found in 3 and 4, respectively. Also the C1–N distances are slightly closer to each other (1.338(3) – 1.378(4) Å) than in 3, which indicates a higher degree of π -electron conjugation within the central system.

The trimethylsilylated compound **6** was selected for further reactivity studies as the representative lithiated amide prepared from secondary amine with a Dip substituent in order to confirm the presumption that the reactivity of lithium amides is influenced by the steric demands of the amide. The NMR spectra of **6** in both solvents of choice along with the molecular structure (see Figure S7) of the mononuclear complex with two diethyl ether molecules are given in the SI. The molecular structure of **6** in the form of the dimer crystallized from a noncoordinating solvent is reported elsewhere.²⁶ Reactions of **6** with both carbodiimides in various solvents do not proceed at room temperature (Scheme 1). Unfortunately, it is not possible to increase the temperature because amide **6** becomes unstable in solution at a slightly elevated temperature.

In fact, the list of reaction pathways given in Scheme 2 is a replica of the above-described reactivity and structures mentioned in Scheme 1 with only one important difference—aniline $L^{NN}H_2$ with the adjacent donor group is used instead of bulky ArNH₂.

Lithium amide 7 (see the SI for its characterization and dimeric structure with one coordinated diethyl ether molecule

per one lithium atom) reacts smoothly with smaller carbodiimide *i*PrN=C=N*i*Pr to give complex 8 (Scheme 2). The ¹H, ⁷Li, and ¹³C NMR spectra recorded in both coordinating and noncoordinating deuterated solvents exhibit essentially the same traces and patterns. A common feature of the ¹H NMR spectral patterns of compounds containing a structure with the [N, N-(dimethyl)] aminomethyl] phenylgroup is the existence of an AX-spin system for methylene and two distinct signals for methyl groups. This is only possible when the nitrogen atom from this group is intramolecularly connected rigidly to the metal center, expressing the properties of the diastereotopic methylene group. Exactly this phenomenon occurs in 8, where also two different signals for CH groups and four doublets for the methyl groups of the guanidinate substituents are visible. The resonance of the NH group found at a lower frequency (4.00 ppm in ¹H NMR in THF- d_{8} , while in C₆D₆ it is not detected) and the sole signal at 2.0 ppm in ⁷Li NMR spectra indicate the migration of the hydrogen atom from amide to the former carbodiimide nitrogen atom, also observed for complex 2. This allows a dissymmetric orientation of the guanidinate toward the lithium atom in an anisobidentate bonding mode and the formation of a dimer where the lithium atom is four-coordinated with pendant arm coordination. The structure of this complex has been confirmed to be similar in solid state (Figure 6) to a U-



Figure 6. Molecular structure of 8. Selected bond lengths are given along with atom connectors in angstroms. Full ORTEP-type plots with more bond distances and angles with standard uncertainties are given in the SI.

shaped lithium guanidinate dimer 4. The presence of two L^{NN} chelating fragments is evident in the lower part of the structure, thus completing unusual κ^2 -guanidinato (to the first lithium atom) and κ^1 -guanidinato- κ^1 -amino (to the second lithium atom) bonding modes. The cumulation of π -electron density between C10-N3 (1.296(3) Å) and C26-N7 atoms (1.301(3) Å), as reflected in their separations, is a common feature of a number of anisobidentately bonded guanidinates. Each of these nitrogen atoms substituted by isopropyl groups is very strongly coordinated to only one lithium atom in the upper part of the structure, which is in contrast to the structures of 2, where nitrogen atoms with smaller substituents are always bidentate. The remaining nitrogen atoms of guanidinates (N1 and N5) are bound to both lithium atoms asymmetrically, with the difference in the distances being \sim 0.25 Å. Tighter connection is similar to the surprisingly short connection of Li atoms to the amino nitrogen atoms-Li1-N2

(2.027(4)Å) and Li2–N6 (2.056(3)Å). The NH groups are located at the N4 and N8 atoms at the periphery of the molecule.

A moderate yield for complex 9 was achieved by analogous reactions to 2, 3, and 8. The ¹H NMR spectrum in benzene solution is characterized by relatively broad sets of signals, indicating fast exchange processes of Dip substituents as well as the methylene group of the L^{NN} part—typical of changes in the coordination modes of the amino pendant group. The NH group resonates at 5.92 ppm, which is a sign of the migration of hydrogen from the former amide to the carbodiimide part. The chemical shift (-1.9 ppm) in the ⁷Li NMR spectrum indicates the monodentate fashion of the guanidinato ligand plus an extra coordination of another donor such as the pendant amine and probably also the influence of the π -system. The ¹H NMR spectrum in THF- d_8 is different to some extent (less dynamic system). The presence of extra donor molecules caused sharpening of signals, while the NH group seems to be NMR silent. This is also reflected in the ⁷Li NMR spectrum with the 1.5 ppm resonance as a result of the higher coordination number of the lithium atom. It is worth mentioning that the signals for the central carbon atoms of the guanidinato ligand have not been detected in the ¹³C NMR spectra in either solvent, which is in line with the proposed fast exchange processes within the whole molecule. The solid-state structure of 9 (Figure 7) is mononuclear with the three-



Figure 7. Molecular structure of 9. Selected bond lengths are given along with atom connectors in angstroms. Full ORTEP-type plots with more bond distances and angles with standard uncertainties are given in the SI.

coordinated lithium atom in a pyramidal vicinity of tightly bound κ^1 -guanidinate (Li–N, 1.936(3) Å), the pendant amino arm (Li–N, 2.108(3) Å), and the oxygen (Li–O, 1.957(3) Å) of the diethyl ether molecule. The distance between the amino nitrogen N1 and Li1 is slightly longer than in 8 (2.028(4) and 2.056(3) Å). The contribution of the additional contact of the π -system of the Dip group completing the shape to a virtual tetrahedron is also significant, but much smaller (Li1–Cg1, 3.274(4) Å) than in 3–5, where the contact is ~0.8 Å closer. Distinct separations of C1 atom and nitrogen atoms of the guanidinato unit (1.296(3)–1.410(3) Å) imply less π -electron conjugation within this system.

The second deprotonation of 8 (Scheme 2) led to the fairly insoluble complex 10 in good yield. This issue was managed to grow single crystals of suitable quality from a highly diluted THF solution. The structure of 10 (Figure 8) strongly



Figure 8. Molecular structure of **10**. Selected bond lengths are given along with atom connectors in angstroms. Full ORTEP-type plots with more bond distances and angles with standard uncertainties are given in the SI.

resembles 8 with respect to important parameters and shape. In fact, the same U-shaped core of 8, with two central lithium atoms pseudotetrahedrally coordinated by three nitrogen atoms from two guanidinates and the amino pendant arm, is further deprotonated at peripheral N3 atoms to give virtually 10. Two lithium atoms Li2 bear one nitrogen atom of guanidinate (Li2–N3, 1.927(3)Å) and two oxygen atoms from THF molecules in the trigonal neighborhood run out from the molecular core. The shape of this dilithium guanidinate(2–) dimer is fairly different from the similar type of complex reported by Reed et al.^{16a} (Figure 1H), which seems to be the staircase-like central part with two parallel ends, thus promoting an S-shaped structure.

The preparation of 11 is much easier in comparison with 10 because the solubility in coordinating solvents is better. The ¹H NMR spectrum in THF shows one set of relatively sharp signals with inequivalent signals only for the methyls of the Dip group. For the first time, two diverse signals of equal intensity have been found in the ⁷Li NMR spectrum at -0.2 and -3.0ppm. Surprisingly enough, the solid-state structure of 11 (Figure 9) exhibits a nearly planar arrangement of all nitrogen atoms, and thus also guanidinato units, in the centrosymmetric dimeric species. As for the structure published by Reed et al.^{16a} (Figure 1H) and 10, the complex is formed by two lithium guanidinates and two peripheral L^{NN}-Li fragments distributed to the opposite sides from the center. On the other hand, for the steric reasons of four Dip groups in the central part, the repulsion causes an unusual planar arrangement with both lithium atoms oscillating above and below this unit. The C-N distances within the guanidinate(2-) core are decently equilibrated, signifying a perfectly conjugated system. The shortest distance (of negligible difference of 0.015 Å) to the N4 atom could be associated with the N4-bearing Dip ring, which provides a noncovalent interaction to the peripheral lithium atom Li1 (2.172(4) Å). Apparent differences between the Li-N distances in the central part are once again caused by the repulsion of both ligands. The peripheral lithium atoms Li1 are strongly coordinated to the guanidinate and amino group in a bent fashion—the N1–Li1–N2 angle is 105.85(19)°. The extra supply of the electron density from the π -electron system of the Dip group is reflected in the very short separation of the



Figure 9. Molecular structure of 11. Selected bond lengths are given along with atom connectors in angstroms. Full ORTEP-type plots with more bond distances and angles with standard uncertainties are given in the SI.

Li1 from the Cg1. The L^{NN} parts are quite screwed out of the central plane of the molecule.

Reactions of potentially more reactive and soluble silvlated L^{NN} lithium amide 12 (Scheme 2) with both studied carbodiimides were investigated in spite of previous unsuccessful attempts in the case of the simpler silvlated lithium amide 6 because of low steric protection and, last but not least, also proposed chelating behavior of the ligand with an activation potential. Complex 12 seems to be dimeric in solution as well as in the solid state, where the classical centrosymmetric structure with bridging amide is observed. Moreover, the very strong intramolecular connection of the adjacent amino donor protects the lithium from the necessity of the further aggregation or accommodation of an additional donor solvent to the coordination sphere (see Figure S13 in the SI).

Complex 12 reacts nicely with both carbodiimides upon the formation of the desired lithium guanidinates substituted by the trimethylsilyl group, but their structures are greatly different. The complex originating from the smaller carbodiimide (Scheme 2; 13) has exactly the same NMR spectral patterns and chemical shifts as complex 2 in benzene. Of course, there are differences in the presence of the trimethylsilyl group instead of the hydrogen atom and in the presence of the L^{NN} fragment instead of the DipN one, but it is clear that the trimethylsilyl group has migrated (first described by Cole and Junk $^{\rm 27}$ on 2-aminopyridine) from the $L^{\rm NN}$ to the nitrogen atom of the former carbodiimide. The structure of 13 is suggested to be dimeric as the methylene group of the pendant arm is diastereotopic and the guanidinate ligand is isobidentate to one of the lithium atoms while monodentate to the other one, which is based on the increase if the ¹³C NMR chemical-shift value of the central atom of guanidinate to ~ 166 ppm from ~ 162 ppm for 8. The central core of the complex is suggested to have a staircase-like arrangement with two lithium atoms bound between dissymmetrically oriented guanidinato ligands. The fourth coordination place is occupied by the amino pendant moiety. The disappearance of the AX spin pattern and the coalescence of inequivalent signals for isopropyls in the ¹H NMR spectrum in THF-d₈ determining compound 13 to be monomeric. The disaggregation of the dimer with subsequent rearrangement of the guanidinate and

the employment of solvent donor to the coordination sphere of the three-coordinated lithium atom are predicted.

The complex 14 in C_6D_6 solution reveals a monomeric nature with κ^1 -bonded guanidinate via the nitrogen from the L^{NN} part and strong contact of the pendant arm (formation of a diastereotopic methylene group). The spectral patterns in the THF- d_8 solution indicate the decoordination of the pendant moiety. The formation of an inverted structure where the lithium sits between two nitrogen atoms bearing the Dip and L^{NN} groups (bidentate fashion) and the additional coordination of solvent molecules most likely confirm this statement. Paradoxically, the combination of the Dip and trimethylsilyl groups reserves more place for coordination of four donors than the *i*Pr groups in 13 (for proposed structures see SI Scheme S1). In the solid state, the structure of 14 approaches the suggested structure in C_6D_6 solution (Figure 10), where, in



Figure 10. Molecular structure of 14. Selected bond lengths are given along with atom connectors in angstroms. Full ORTEP-type plots with more bond distances and angles with standard uncertainties are given in the SI.

addition, the structure has all-in-plane heteroatoms together with the central C1 atom and only the phenyl rings are deviated. At first sight, that structure resembles **8**, but it is made unique by significant differences: (i) lithium here interacts with the Dip group settled on the nitrogen group together with the trimethylsilyl group, while in **8** with the Dip group at imino nitrogen, (ii) absence of an additional donor induces the shortest $(1.922(4)\text{\AA})$ separation of π -electron cloud to lithium²⁵ (~1.3 Å shorter than in **8**).

CONCLUSION

To conclude, we have prepared and structurally characterized five different types of lithium guanidinato complexes by a combination of the reaction pathways of the following: bulky lithium anilide and both aliphatic and aromatic carbodiimides; lithium anilide with an adjacent amino donor group and both aliphatic and aromatic carbodiimides; and trimethylsilylated lithium anilide with an adjacent amino donor group and both aliphatic and aromatic carbodiimides. On the other hand, reactions of bulky trimethylsilylated lithium anilide with carbodiimides did not proceed under the desired conditions. Lithiated guanidinates, which contain an NH group, can further be easily deprotonated to give dilithium guanidinates(2-). From the structural point of view, the family of these complexes is very diverse, but some light has been shed

on this problem. For example, (i) the reaction of any lithiated amide with carbodiimide always proceeds with the subsequent migration of hydrogen or the trimethylsilyl group to the nitrogen atom originating from carbodiimide; (ii) the use of any combination of smaller/aliphatic carbodiimide and an amide always produces dissymmetric aggregated structures stable in the solution of a noncoordinating solvent and in the solid state, which deoligomerize upon the formation of monomeric species when the coordinating solvent is added; (iii) in contrast, the use of the combination of all three aromatic substituents of trisubstituted guanidinate in most cases yields monomeric species with an extra coordination of one of the aromatic groups to the lithium atom, which also occurs in the solid state (while in the coordinating solvents, the tendency to form monodentately bound guanidinates with an adjacent donor solvent at the lithium centers is explored); (iv) when the adjacent donor group capable of an intramolecular interaction with lithium atoms is used, this is always done in noncoordinating solvents and in the solid state; (v) trimethylsilylated lithium guanidinates exhibit different structural behavior from those having an NH group as a consequence of the higher basicity at the guanidinate core and the impossibility to form intra- or intermolecular Hbridges: (vi) it is possible to evaluate and predict the structures on the basis of the confrontation of the measurements of multinuclear NMR spectra in the solutions of different solvents—among other things, the higher π -electron conjugation of the guanidinate unit is reflected in the increase of the ¹³C NMR chemical shift of the central carbon atom.

We believe a starter kit for the preparation of structurally predictable metal guanidinates further usable in catalysis or material science has been explored. Moreover, the guanidinates containing an NH group, dilithium guanidinates(2-), or trimethylsilylated lithium guanidinates could open a new field for the preparation of bimetallic complexes mainly with regard to the heterobimetallic ones with cooperative behavior or properties. These are currently being investigated in our group.

EXPERIMENTAL SECTION

In the following paragraphs, only simplified and general procedures are presented. A detailed description of the synthesis and the characterization of all complexes are given in the SI.

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 by the PureSolv MD 7 solvent purification system supplied by Innovative Technology, Inc., degassed, and then stored under argon atmosphere. Single crystals suitable for X-ray analyses were obtained under argon from the corresponding saturated solutions of products in organic solvent(s) cooled to 7 or -30 °C. Melting points were measured in an inert perfluoroalkyl ether and were uncorrected. Deuterated solvents for NMR spectra were distilled, degassed, and stored over a K or Na mirror under argon atmosphere.

NMR spectra of the starting lithium amides **1**, **6**, **7**, and **12** in THFd₈ and/or in C_6D_6 (see the SI for NMR data) were measured for comparison and for the studies of the chemical shifts of target compounds. The syntheses of **1**,²⁸ **6**,²⁹ **7**,³⁰ and **12**³⁰ are reported elsewhere. The NMR spectra were recorded from the solutions of appropriate compounds in deuterated solvent(s) on a Bruker Avance 500 spectrometer (equipped with a Z-gradient 5 mm probe) at 295 K at the frequencies of 500.13 MHz for ¹H, 125.76 MHz for ¹³C{¹H}, and 194.37 MHz for ⁷Li{¹H}. Solutions were obtained by dissolving approximately 40 mg of each compound in approximately 0.6 mL of deuterated solvents. The values of ¹H chemical shifts were calibrated to the internal standard—tetramethylsilane ($\delta({}^{1}\text{H}) = 0.00$) or to the residual signals of benzene ($\delta({}^{1}\text{H}) = 7.16$) and THF ($\delta({}^{1}\text{H}) = 3.58$ or 1.73), respectively. The values of ${}^{13}\text{C}$ chemical shifts were calibrated to the signals of THF ($\delta({}^{13}\text{C}) = 67.6$) or benzene ($\delta({}^{13}\text{C}) = 128.4$) and those of ${}^{7}\text{Li}$ to the external 1 M LiCl in D₂O ($\delta({}^{7}\text{Li}) = 0.0$, recalculated to the frequency ratio Ξ for a 500.13 MHz spectrometer –194.3695079361 MHz). All ${}^{13}\text{C}$ NMR spectra were measured using a standard proton-decoupled experiment, and CH and CH₃ vs C and CH₂ were differentiated using the APT method. 31

The X-ray data for the colorless crystals of 2–5, $6 \cdot [Et_2O]_2$, [7: Et₂O]₂, 8–11, [12]₂ and 14 (see Table S1 in the SI) were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K α radiation (λ = 0.71073 Å), a graphite monochromator, and the φ and χ scan mode. Data reductions were performed with DENZO-SMN.³² The absorption was corrected by integration methods.³³ The structures were solved by direct methods (Sir92)³⁴ and refined by full matrix least-squares method on the basis of F^2 (SHELXL97).³⁵ Hydrogen atoms were mostly localized on a difference Fourier map, but to ensure the uniformity of crystal treatment, all hydrogens were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$ (pivot atom) or $1.5U_{eq}$ (methyl). H atoms in methyl, methylene, and methane moieties and hydrogen atoms in aromatic rings were placed with C–H distances of 0.96, 0.97, 0.98, and 0.93 Å, and 0.86 Å for N–H bonds.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 1997777–1997791 for all complexes: 2-5, $6 \cdot [Et_2O]_2$, $[7 \cdot Et_2O]_2$, 8-11, $[12]_2$, and 14 and its solvatopolymorphs.

General Procedure of Preparation of Lithium N,N'-Disubstituted-{N''-[2,6-di(propan-2-yl)phenyl]}guanidinates ($L^{Dipp-R}HLi$) (2, 3). To a solution of lithium [2,6-di(propan-2yl)phenyl]azanide (1) in Et₂O cooled to 0 °C, one equivalent of starting N,N'-disubstituted carbodiimides (a solution in Et₂O) was added. The reaction mixtures were allowed to warm to room temperature and stirred overnight. After that, the Et₂O was evaporated in vacuo and crude products were washed with a small amount of hexane to give white crystalline products of 2 and 3.

General Procedure of Preparation of Lithium N,N'-Disubstituted-{N''-[2-[(dimethylamino)methyl]phenyl}guanidinates (L^{NN-R}HLi) (8, 9). To a solution of lithium 2-[(dimethylamino)methyl]phenylazanide (7) in Et₂O cooled to 0 °C, one equivalent of starting N,N'-disubstituted carbodiimides (a solution in Et₂O) was added. The reaction mixtures were allowed to warm to room temperature and stirred overnight. After that, the Et₂O was evaporated in vacuo and crude products were washed with a small amount of hexane to give white crystalline products of 8 and 9.

General Procedure of Preparation of Lithium N,N'-Disubstituted-{N''-trimethylsilyl-[2-[(dimethylamino)methyl]phenyl}guanidinates (L^{NN-R} (SiMe₃)Li) (13, 14). To a solution of lithium trimethylsilyl-2-[(dimethylamino)methyl]phenylazanide (12) in Et₂O cooled to 0 °C, one equivalent of starting N,N'-disubstituted carbodiimides (a solution in Et₂O) was added. The reaction mixtures were allowed to warm to room temperature and stirred overnight. After that, the Et₂O was evaporated in vacuo and crude products were washed with a small amount of hexane to give white crystalline products of 13 and 14.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01362.

Full experimental section and all molecular structures of tilted compounds in ORTEP views with selected interatomic distances and angles (PDF)

Accession Codes

CCDC 1997777-1997780 and 1997782-1997791 contain the supplementary crystallographic data for this paper. These

pubs.acs.org/IC

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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to Professor Dr. Antonín Lyčka on the occasion of his 70th birthday and enormous contribution to the field of NMR spectroscopy.

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