The First Aziridinylguanidinates: New Precursors for Potentially Volatile Metal Guanidinates*

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The first lithium-aziridinylamidinates, Li[(C₂H₄N)C(NR)₂], have been prepared by addition of N-aziridinylithium, C₂H₄NLi (2), to either N,N'-disopropylcarbodiimide or N,N'-dicyclohexylcarbodiimide. The cyclohexyl derivative 4 was crystallised from both diethyl ether (Et₂O) and THF to afford the crystalline solvent adducts [Li[(C₂H₄N)C(NR)₂]·S]₂ (4: S = THF; 4a: S = Et₂O) which were structurally characterised by X-ray diffraction. In the solid state, these lithium-aziridinylamidinates comprise ladder-type dimeric molecular structures.

Since the pioneering work by Gordon et al. and Winter et al., amidinate and guanidinate complexes of various metals have been successfully employed as atomic layer deposition (ALD) and metal organic chemical vapour deposition (MOCVD) precursors for thin layers of metals, metal oxides, and metal nitrides. Meanwhile, the chemistry and applications of metal amidinates and guanidinates have been addressed in several comprehensive review articles. Highly useful ligands that have been frequently employed in the preparation of volatile metal guanidinates are the N,N'- dialkyl-N,N'-dimethylguanidinate anions [Me₂NC(NR)₂]⁻ (R = isopropyl, cyclohexyl). These chelating, monoanionic guanidinate ligands have been proven to be extremely useful for the design of volatile early transition metal and lanthanide guanidinate precursors. In the course of our ongoing investigation of metal amidinates and guanidinates, we reasoned that the analogous anions containing an aziridinyl ring instead of the -NM₂ group would represent an interesting and potentially useful addition to the current library of guanidinate ligands. Herein, we report the synthesis and full characterisation of the first lithium-aziridinylguanidinates.

The most reliable and generally applicable synthetic route to guanidinates involves insertion of carbodiimides, R–N=C=N–R (R = alkyl, cycloalkyl), into M–N bonds. Lithium guanidinates are the most important starting materials for further metathetical reactions with other metal halides and related precursors. Aziridine (ethylenimine, C₂H₄NH) is commercially available, but it can also be easily prepared from β-aminoethylsulfuric acid and 40% sodium hydroxide solution following an established procedure. The required N-aziridinylolithium, C₂H₄NLi (2), was first reported by Gilman et al. and has been frequently employed as reagent in organic and organometallic syntheses. Its preparation according to Scheme 1 involves treatment of aziridine (1) with n-butyllithium in n-hexane/diethyl ether solution. Extraction with diethyl ether affords unsolvated 2 as a white, air- and moisture-sensitive powder.

Subsequent reactions of 2 with N,N'-disopropylcarbodiimide and N,N'-dicyclohexylcarbodiimide, respectively, were carried out in THF solution at 0°C followed by stirring for 12 h at room temperature (Scheme 2). During this time, the newly formed lithium-aziridinylguanidinates partially precipitated as white solids. Evaporation of the reaction mixtures to dryness followed by washing of the resulting solids with n-pentane yielded the mono-THF-solvated lithium-aziridinylguanidinates 3 and 4 as colourless, free-flowing powders, which are readily soluble in THF and 1,2-dimethoxyethane (DME), moderately soluble in diethyl ether, but virtually insoluble in hydrocarbon solvents. Isolated yields were 75% for 3 and 90% for 4. Hence, both new compounds are readily accessible in synthetically useful quantities.

The new lithium-aziridinylguanidinates 3 and 4 were characterised by infrared (IR) spectroscopy, NMR, mass spectrometry, and elemental analyses. The IR spectra of 3 and 4 did not show bands attributable to C≡N bonds (range of 2185–2120 cm⁻¹), indicating a normal chelating coordination mode of the guanidinate anions to lithium. Both the ¹H and ¹³C NMR
spectra of 3 and 4 were in good agreement with the expected aziridinylamidinate formation. In the $^1$H NMR spectra, the resonances of the aziridinyl protons were found at $\delta$ 1.81 (3) and $\delta$ 1.83 (4) ppm, respectively. Two solvate adducts of the cyclohexyl derivative 4 were structurally characterised by X-ray diffraction. X-ray-quality single-crystals of the THF adduct 4 were obtained by cooling a saturated solution in THF at 4°C for several days. Re-crystallisation of 4 from diethyl ether at $-32^\circ$C afforded colourless single-crystals of the diethyl ether (Et$_2$O) adduct 4a. Solubility of both 3 and 4 in DME was also very high, but single-crystals could not be obtained. The X-ray analyses of 4 and 4a revealed the presence of ladder-type dimeric structures (Chart 1).

Related dimers. Previous studies had revealed that the dimeric structures are not maintained in solution. Polar solvents such as CDCl$_3$ and [D8]THF are able to destroy these aggregates, producing well resolved $^1$H NMR spectra with one set of signals as observed for the isopropyl protons in 3. A significant difference between amidinate and guanidinate is the possible delocalisation of the –NR$_2$ lone pair into the central CN 3 core in the latter. With an average bond length of 1.469(3) Å, the C–N bond lengths between the aziridinyl N atom and the carbon atom in the CN$_2$ Li ring are very similar to the C–N distances within the aziridine ring (average bond length of 1.451(3) Å). Moreover, the aziridine CNC$_2$ plane is rotated 36.1° in 4 and 38.1° in
out of the CN 2 Li chelate ring plane, and in both structures the aziridinyl nitrogen atom is distinctly pyramidal (distance from the plane C1–C2–C3: 0.6434 Å in 4 and 0.6353 Å in 4a).

Based on the findings, these structural features indicate that (C2H4N)–C\(\text{p}\)-bonding is significant in these new aziridinylamidinate anions.

In conclusion, the coordination chemistry of guanidinate anions is of significant current interest with respect to the synthesis of homogeneous catalysts and volatile metal precursors for ALD and MOCVD processes. Various substituted guanidinate anions are now available, and can be adjusted to different purposes (e.g. catalytic activity, volatility). In the present study, the first lithium-aziridinylamidinates have been synthesised in high yields using a straightforward synthetic protocol. These anions can be viewed as ring-closed derivatives of the well-established dimethylamino derivative \([\text{Me}_2\text{NC(NiPr)}_2]\)/C0.[4] The latter has already been proven to be highly useful for the synthesis of volatile ALD and MOCVD precursors of various transition metals and lanthanides. Future work will reveal if improved volatility can be achieved with the use of the new aziridinylamidinate ligands.

### Experimental

**Materials and Methods**

All reactions were carried out in oven-dried and flame-dried glassware under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques. Et2O and THF were
distilled from sodium/benzophenone under nitrogen atmosphere before use. All glassware was oven-dried at 120°C for at least 24 h, assembled while hot, and cooled under high vacuum before use. n-Butyllithium (BuLi), N,N'-diisopropylcarbodiimide, and N,N'-dicyclohexylcarbodiimide were purchased from Aldrich and used as received. Aziridine (ethylenimine, C₂H₄NH (1)) was purchased from ABCR, but samples were also prepared following the established procedure.[5] In both cases, the aziridine was freshly distilled from KOH pellets before use. Cautionary note:[5] Aziridine is strongly caustic and burns the skin. Inhalation of the vapours causes acute inflammation of the eyes, nose, and throat, with symptoms resembling those of bronchitis. Continued exposure to the vapour may cause an individual to develop extreme sensitivity to it. Also, aziridine is very inflammable and polymerises with explosive violence under certain conditions. It should be handled only in a well-ventilated hood, and the use of rubber gloves is advisable.

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Anal. Calc. for C₁₃H₂₆LiN₃O (247.31 g mol⁻¹): C 62.95, H 10.15, N 16.19 %.

The data were collected with the Stoe XAREA[-]THF, 400 MHz 3.95–3.99 (4H, m, THF), 3.81–3.75 (4H, m, THF).

Synthesis of Li[(C₅H₅)NC(NPr)₂]-THF (3)

A solution of N-aziridinyl lithium, C₅H₅NLi (2) (1.5 g, 30.6 mmol), in THF (120 mL) was cooled to 0°C and treated slowly with N,N'-diisopropylcarbodiimide (3.9 g, 30.6 mmol) and n-pentane (20 mL). The product was isolated by filtration and dried under vacuum at 40°C to give 3 as a moisture-sensitive, colourless solid (5.68 g, 75 %).

Synthesis of Li[(C₅H₅)NC(NCy)₂]-THF (4)

Compound 4 was prepared using the same procedure as that described for 3 by reaction of N-aziridinyl lithium, C₅H₅NLi (2) (1.0 g, 20.5 mmol), with N,N'-dicyclohexylcarbodiimide (4.2 g, 20.4 mmol) in THF (100 mL) (6.68 g, 90 %).

References


(g) S. Aharonovich, M. Kapon, M. Botoshansky, M. S. Eisen, *Organometallics* 2008, 27, 1869. doi:10.1021/OM801216P


