

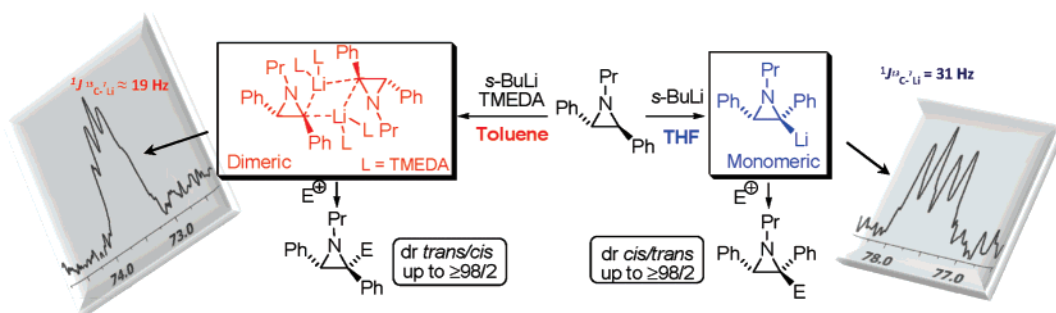
Regio- and Stereoselective Lithiation of 2,3-Diphenylaziridines: A Multinuclear NMR Investigation

Vito Capriati,[†] Saverio Florio,^{*,†} Renzo Luisi,^{*,†} Andrea Mazzanti,[‡] and Biagia Musio[†]

Dipartimento Farmaco-Chimico, Università di Bari, Consorzio Interuniversitario Nazionale Metodologie e Processi Innovativi di Sintesi C.I.N.M.P.I.S., Via E. Orabona 4, I-70125 – Bari, Italy, and Dipartimento di Chimica Organica “A. Mangini”, Università di Bologna, Viale Risorgimento 4, I-40136 – Bologna, Italy

florio@farmchim.uniba.it; luisi@farmchim.uniba.it

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The α -lithiation-trapping sequence of *trans*-*N*-alkyl-2,3-diphenylaziridines (*s*-BuLi or *s*-BuLi/TMEDA), taking place with a stereochemistry which dramatically depends on the solvent coordinating ability (inversion of configuration in THF and retention in toluene), has been carefully investigated. ^1H , ^{13}C , and ^7Li multinuclear NMR investigations at low temperature suggest that two differently configured lithiated aziridines (monomeric *cis*-**1-Li** in THF and dimeric *trans*-**1-Li** in toluene) are involved.

Introduction

In a recent paper from our lab, we reported that *trans*-*N*-alkyl-2,3-diphenylaziridines undergo exclusively α -lithiation with a stereochemistry that proved to be solvent-dependent¹ (retention of configuration in toluene and inversion in THF). To explain this solvent-dependent stereochemistry, we assumed that two differently configured organolithiums could be involved, likely a *cis*- in THF and a *trans*-aziridinyl lithium in toluene, although starting from the same diphenylaziridine (Scheme 1).

To prove the validity of such an assumption, a detailed multinuclear NMR investigation of the neutral and lithiated *N*-propyl-2,3-diphenylaziridine *trans*-**1** (Figure 1) has been carried out in both THF-*d*₈ and toluene-*d*₈.

Results and Discussion

Lithiation of *trans*-*N*-Propyl-2,3-diphenylaziridine **1 in THF-*d*₈ in an NMR Tube.** Aziridine *trans*-**1** in THF-*d*₈ at 195

K shows two slowly equilibrating topomers (Figure 1a).² Upon treatment of *trans*-**1** with *s*-Bu⁷Li, a fast deprotonation occurs, giving the corresponding α -lithiated intermediate (Figure 1b). Comparing the ^1H NMR spectra of the neutral and lithiated aziridine, a strong shielding of all the aromatic protons of the phenyl ring directly bonded to the lithiated carbon atom (C_α) testifies that a change in its electronic distribution has occurred. A complete assignment of the above protons has been made possible by a DQF-gCOSY analysis (see the Supporting Information), disclosing that the two H_o of the lithiated intermediate have completely different chemical shifts (5.80 and 7.10 ppm) and the H_p proton is less shielded than expected (6.20 ppm).³ The different chemical shifts of the two *ortho* protons of the phenyl ring bonded to the C_α carbon may be ascribed to a reduced mobility of this phenyl ring which rotates slowly around the C_α - C_i bond.⁴

(2) For a definition of topomer, see Binsch, G.; Eliel, E. L.; Kessler, H. *Angew. Chem., Int. Ed.* **1978**, *10*, 570–572.

(3) (a) Peoples, P. R.; Grutzner, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 4709–4715. (b) Hogan, A.-M. L.; O’Shea, D. F. *J. Org. Chem.* **2007**, *72*, 9557–9571.

[†] Università di Bari.

[‡] Università di Bologna.

(1) Luisi, R.; Capriati, V.; Florio, S.; Musio, B. *Org. Lett.* **2007**, *9*, 1263–1266.

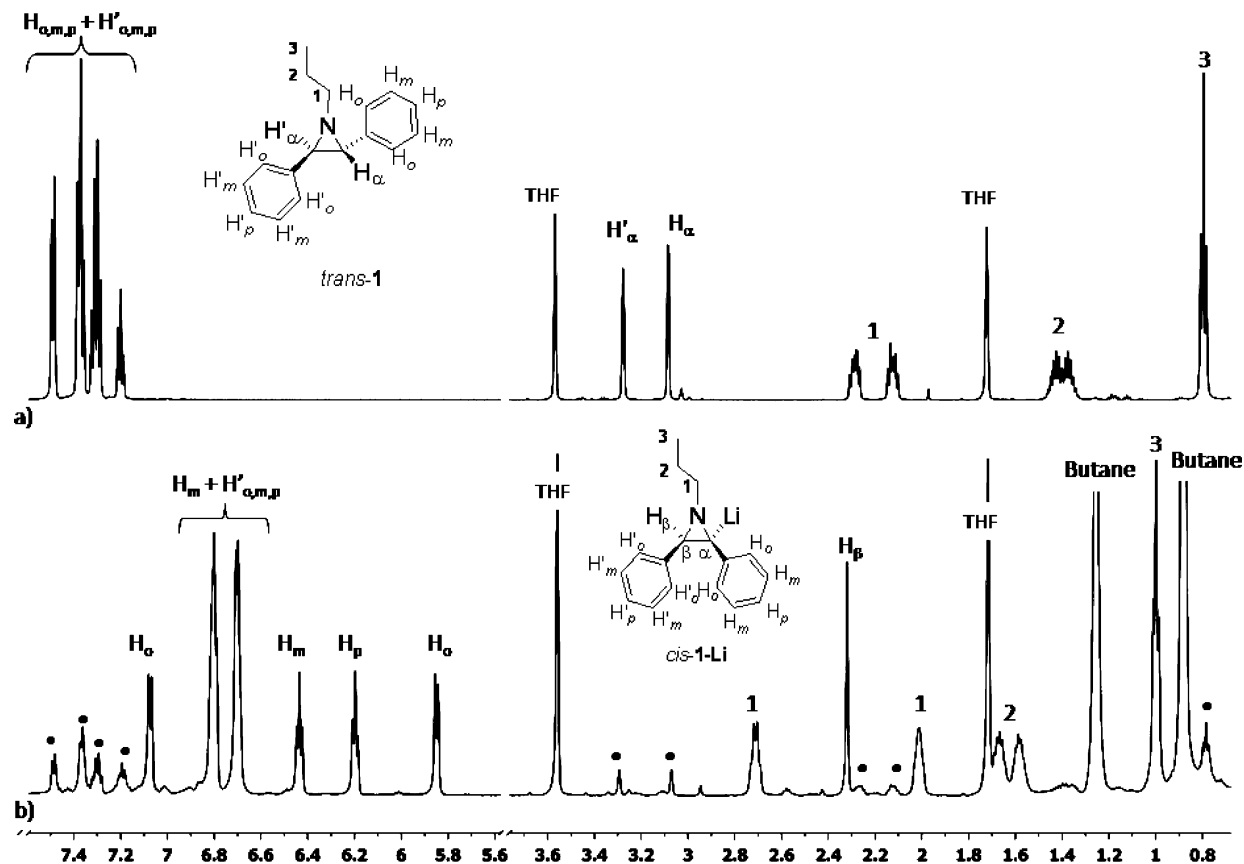
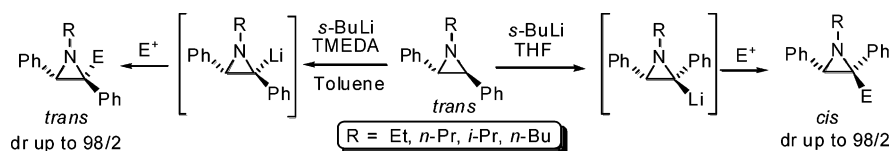


FIGURE 1. ^1H NMR (599.944 MHz) spectra of the neutral *trans*-2,3-diphenylaziridine **1** (a) and the α -lithiated intermediate (b) obtained upon treatment of *trans*-**1** with *s*-Bu 7 Li in THF- d_8 at 195 K (• = unreacted starting material).

SCHEME 1



The other phenyl ring bonded to the C_β carbon in the lithiated aziridine displays a less marked shielding of all the aromatic protons in the range 6.65–6.85 ppm, likely as a result of an anisotropic effect (Figure 1b).⁵

1D- and 2D-NOESY experiments, performed on the lithiated species, provided hints on the relationship between spatially close protons. In particular, a selective preirradiation of the proton H_β (2.32 ppm), within a double pulsed field gradient spin–echo (DPFGSE-NOE) sequence,⁶ showed an enhancement of the NCH_2 and the *ortho* protons (H'_o) of the phenyl ring linked to C_β (Figure 2). Moreover, NOESY experiments confirmed that the lone pair on the aziridine nitrogen is probably in a *trans* relationship with respect to the C_α -Li bond.⁷ Such spatial correlations and the upfield shift of the aromatic protons seem to suggest a *cis* configuration of the lithiated intermediate, namely, *cis*-**1-Li**. It was also interesting to find, in the 2D-NOESY experiment, that the two pairs of protons H_o and

H_m gave exchange peaks, confirming that this phenyl ring rotates slowly, with respect to the NMR time scale, around the C_α - C_i bond likely due to an increased double bond character (Figure 2).⁴

Additional information on the nature of the lithiated aziridine and its aggregation state can be obtained from ^{13}C NMR analysis.⁸ The ^{13}C NMR spectrum of the lithiated aziridine in THF- d_8 at 195 K shows sharp and well-resolved signals (Figure 3): the *ipso* (C_i) and *para* (C_p) carbons of the phenyl ring, directly bonded to the C_α , are upfield (116.0 ppm) and downfield (160.7 ppm) shifted, respectively, according to an enhanced π charge density in this phenyl ring, as found for other benzylic anions.⁹

(4) Kuhen, M.; Gunther, H.; Amoureux, J.-P.; Fernandez, C. *Magn. Reson. Chem.* **2002**, *40*, 24–30.

(5) Hoell, D.; Lex, J.; Mullen, K. *J. Am. Chem. Soc.* **1986**, *108*, 5983–5991.

(6) Neuhaus, D.; Williamson, M. *The nuclear Overhauser effect in structural and conformational analysis*; VCH: New York, 1989; p 264.

(7) Analogous conclusions have been reported for other lithiated aziridines; see (a) Haner, R.; Olano, B.; Seebach, D. *Helv. Chim. Acta* **1987**, *70*, 1676–1693. (b) Hine, J.; Hahn, S. *J. Org. Chem.* **1982**, *47*, 1738–1741. (c) Boche, G.; Lohrenz, J. C. W.; Opel, A. In *Lithium Chemistry*; Sapse, A.-M., Schleyer, P. von R., Eds.; Wiley: New York, 1995; p 195. (d) Bordwell, N. R.; Vanler, R.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9856.

(8) Bauer, W. In *Lithium Chemistry – A Theoretical and Experimental Overview*; Sapse, A. M., Schleyer, P. von R., Eds.; Wiley: New York, 1995; p 125.

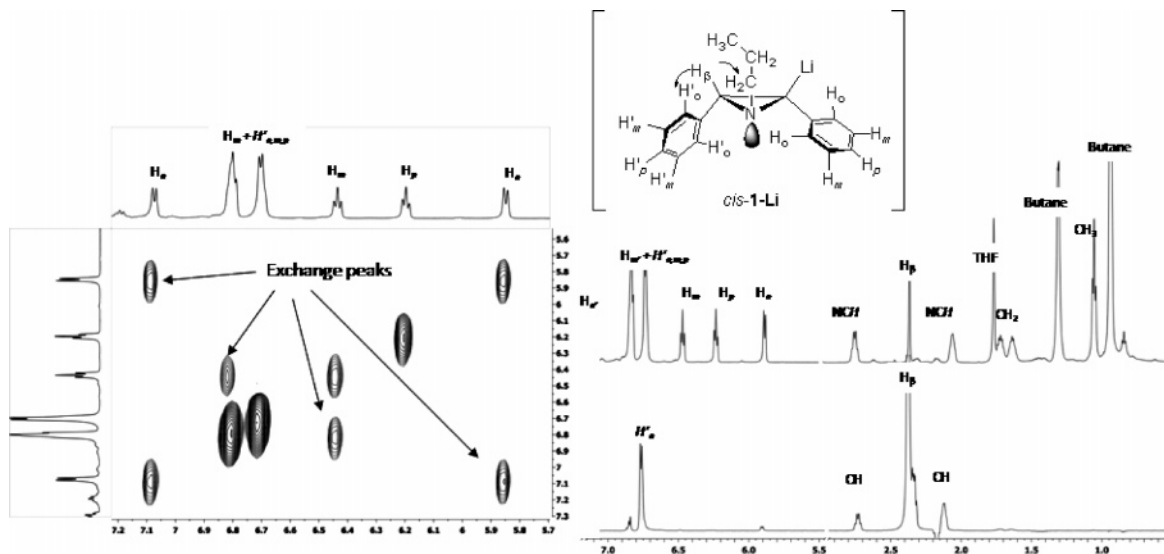


FIGURE 2. 2D- and 1D-NOESY on α -lithiated aziridine *cis*-1-Li in THF- d_8 at 195 K.

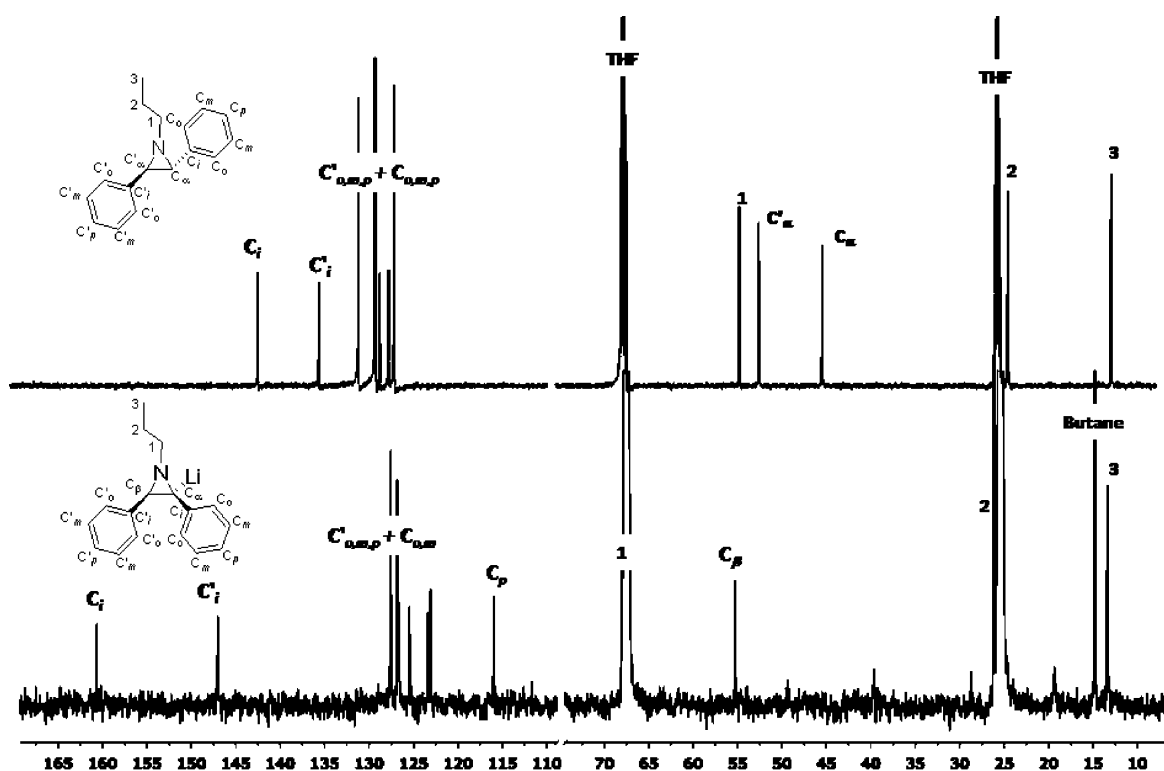


FIGURE 3. ^{13}C NMR (150.856 MHz) spectra of neutral *trans*-1 and lithiated aziridine *cis*-1-Li in THF- d_8 at 195 K.

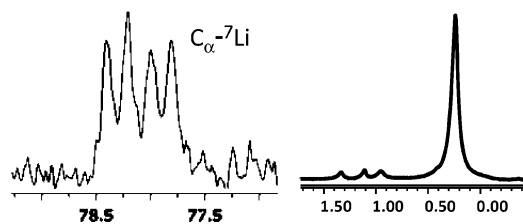
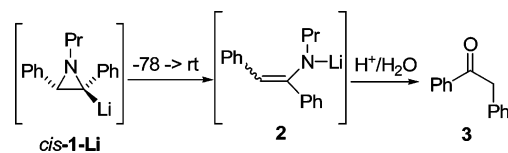


FIGURE 4. ^{13}C - ^7Li coupling and ^7Li (233.161 MHz) NMR spectrum of the lithiated aziridine *cis*-1-Li in THF- d_8 at 195 K.

Phase-sensitive heterocorrelation experiments (gHSQC-DEPT) allow also a complete assignment of each carbon atom to the corresponding directly bonded proton (see the Supporting

SCHEME 2



Information). The aziridine carbon atoms are both shifted downfield, but the C_α -Li is the most shifted one (78.2 ppm), exhibiting a quartet with a relative intensity of approximately 1:1:1:1, consistent with one lithium coupled to a single ^{13}C , and a coupling constant of $^1J_{^{13}\text{C}-^7\text{Li}} = 31.0$ Hz (Figure 4).⁸ Such multiplicity and the value of this coupling constant suggest that the lithiated

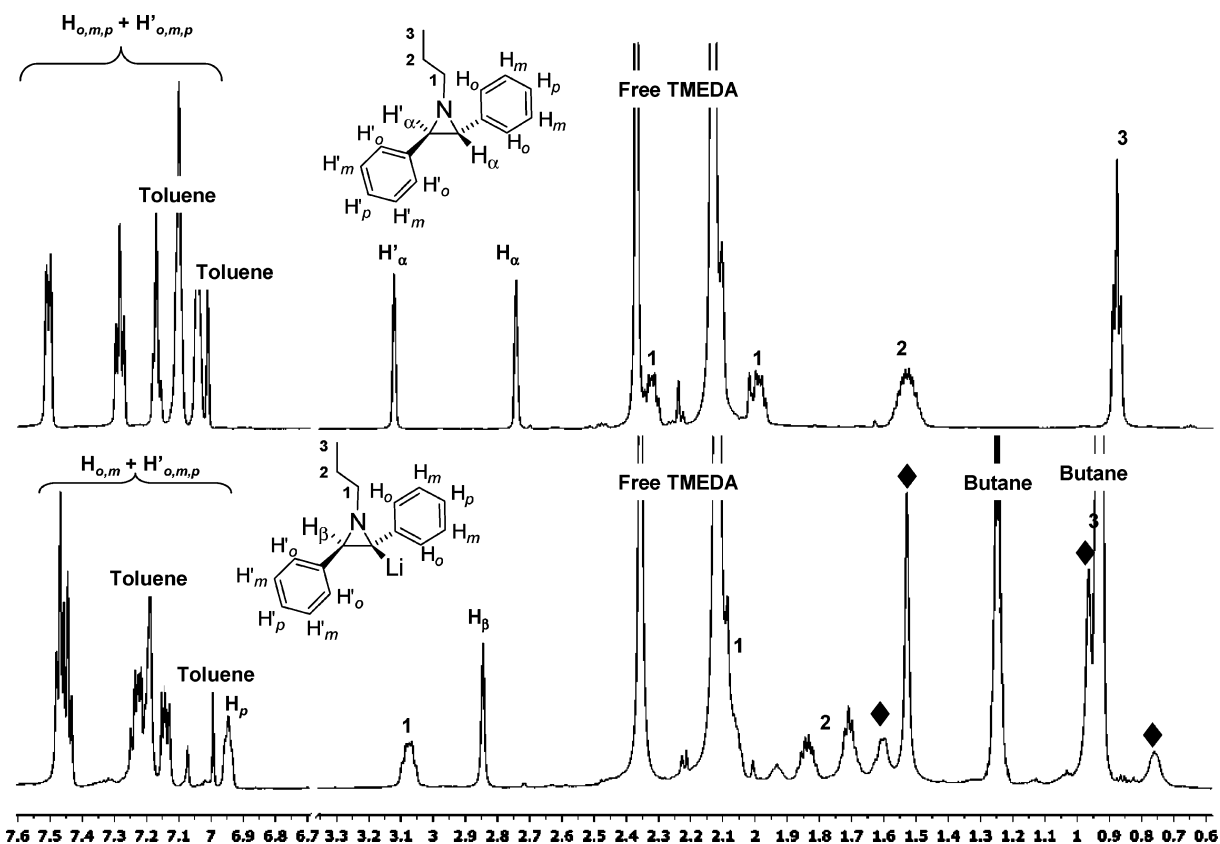


FIGURE 5. ^1H NMR spectra of the neutral *trans*-2,3-diphenylaziridine **1** and the α -lithiated intermediate obtained upon treatment with *s*-BuLi/TMEDA in toluene- d_8 at 195 K (◆ = signals of bonded TMEDA).

aziridine may be monomeric in THF solution with the lithium ion, likely, tightly bonded to the carbanionic carbon.¹⁰

Accordingly, only one signal was observed in the ^7Li NMR spectrum as expected for a single aggregation state. A change in concentration has no effect, and the above results are reproducible. Attempts to perform dynamic experiments failed because, in THF, the lithiated aziridine is unstable above 213 K, undergoing ring opening to give deoxybenzoin **3** presumably from lithiated enamine **2** (Scheme 2).¹¹

To summarize, all the data above seem to suggest a *cis* configuration for the lithiated aziridine in THF and a monomeric structure. Therefore, excluding that neutral aziridine *trans*-**1** isomerizes to the *cis*-isomer,¹ we must conclude that it is the *trans*-**1-Li** isomer that, as soon as it is generated, isomerizes to the *cis*-**1-Li** counterpart.

Lithiation of *trans*-*N*-Propyl-2,3-diphenylaziridine **1 in Toluene- d_8 at 195 K in an NMR Tube.** A similar investigation

(9) (a) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 7427–7429. (b) Oakes, F. T.; Sebastian, J. F. *J. Organomet. Chem.* **1978**, *159*, 363–371. (c) Ahlbrecht, H.; Harbach, J.; Hauck, T.; Kalinowski, H. O. *Chem. Ber.* **1992**, *125*, 1753–1762. (d) Ahlbrecht, H.; Harbach, J.; Hoffmann, R.; Ruhland, T. *Liebigs Ann.* **1995**, 211–216. (e) Ahlbrecht, H.; Harbach, J.; Kalinowski, H.-O.; Lang, A.; Maier, G. *Chem. Ber./Recl.* **1997**, *130*, 683–686.

(10) Attempts to perform ^1H - ^7Li HOESY experiments [as reported in (a) Bauer, W. *Magn. Reson. Chem.* **1996**, *34*, 532–537; (b) Alam, T. M.; Pedrotty, D. M.; Boyle, T. J. *Magn. Reson. Chem.* **2002**, *40*, 361–365] failed, likely because of a too short relaxation time of the ^7Li nuclei under the experimental conditions.

(11) (a) Luisi, R.; Capriati, V.; Florio, S.; Ranaldo, R. *Tetrahedron Lett.* **2003**, *44*, 2677–2681. (b) Troisi, L.; Granito, C.; Carlucci, C.; Bona, F.; Florio, S. *Eur. J. Org. Chem.* **2006**, 775–781. (c) O'Brien, P.; Rosser, C. M.; Caine, D. *Tetrahedron* **2003**, *59*, 9779–9791.

like that just described for neutral and lithiated aziridine *trans*-**1** in THF, has been performed in toluene- d_8 at 195 K. Lithiated aziridine has been generated in an NMR tube by treating a solution of aziridine *trans*-**1** in toluene (~ 0.1 M) with *s*-BuLi in the presence of TMEDA, which proved to be crucial for the deprotonation to occur.

^1H NMR spectra of the neutral and lithiated aziridine in this solvent are reported in Figure 5. Contrary to what was observed in THF, no strong upfield shift for the aromatic protons of the phenyl ring directly bonded to the C_α has been observed, with the exception of H_p at 6.95 ppm which was slightly shifted upfield, as expected.³

The chemical shifts of the aromatic protons in the neutral and lithiated aziridine (7.0–7.5 vs 6.9–7.5 ppm) suggest that, in this case, probably there is no deep change in the arrangement of the phenyl rings. In the upfield part of the ^1H NMR spectrum, four new signals have been detected: gHSQC-DEPT experiments (see the Supporting Information) suggest that the two broad multiplets at 0.75 and 1.6 ppm are due to the CH_2 groups, whereas the two large singlets at 0.94 and 1.53 ppm are due to the CH_3 groups of TMEDA. The above signals are present in the spectrum together with the free TMEDA signals at 2.1 ppm (CH_3) and 2.4 ppm (CH_2) and do not change their chemical shifts upon changing the equivalents of TMEDA for the deprotonation. At 195 K, it seems as though the exchange between bonded and free TMEDA may occur slowly with respect to the NMR time scale; raising the temperature up to 225 K, the signals become broader, thus testifying that a faster exchange is now underway (see the Supporting Information).

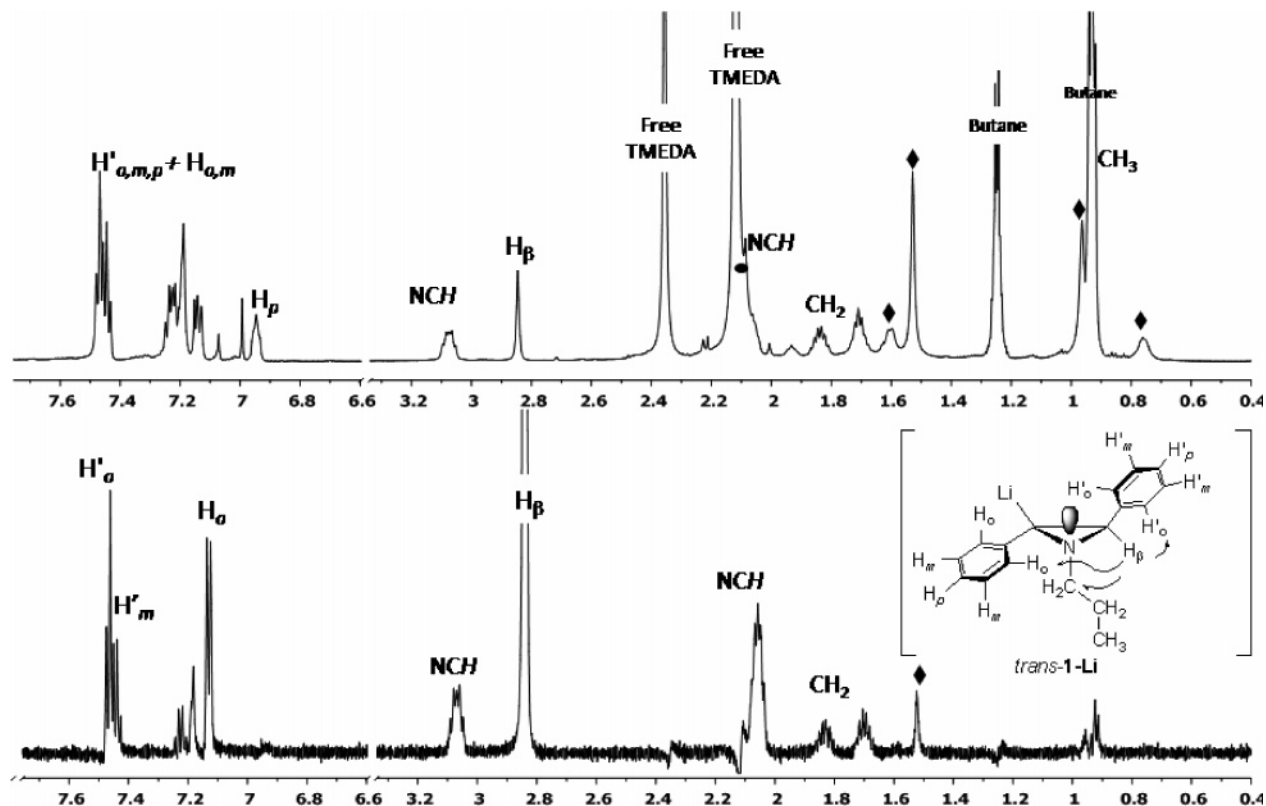


FIGURE 6. 1D NOESY on α -lithiated aziridine *trans*-1-Li in toluene- d_8 at 195 K (\blacklozenge = bonded TMEDA).

A 1D-NOESY experiment was performed by selective preirradiation of the benzylic proton H_β : the corresponding NOEs interactions are depicted in Figure 6. The enhancement of the *ortho* protons (H_o and H'_o) of both phenyl rings is a clear evidence of a *trans* relationship between them. The above evidence suggests that, in toluene, the lithiated aziridine exists as *trans*-1-Li.

All the above considerations have been confirmed by ^{13}C NMR and HSQC-DEPT experiments (see the Supporting Information). In the ^{13}C NMR spectrum (Figure 7), the C_i and C_p of the phenyl ring directly bonded to the lithiated carbon atom are downfield (154.3 ppm) and upfield shifted (120.3 ppm), respectively. Signals of the free TMEDA and those of the bonded TMEDA (two singlets at 56.2 and 56.9 ppm for the CH_2 and two singlets at 43.7 and 46.9 ppm for the CH_3) are also in the range 40–60 ppm.

Lithiated carbon at 73.5 ppm is a poorly resolved septet (Figure 8b) ($^1J_{^{13}\text{C}-^7\text{Li}} = 19$ Hz) reminiscent of a dimeric structure.^{12,13} The ^7Li NMR spectrum shows only one signal likely due to two equivalent lithium ions linked to a single ^{13}C .

The question that rises at this point is about the structure of the dimeric lithiated intermediate in toluene (homochiral or heterochiral) and its “architecture” with reference to how the TMEDA should strongly solvate such a dimer.

To demonstrate the stereochemistry of *trans*-1-Li into the dimeric structure, lithiation of the chiral nonracemic aziridine (*S,S*)-*trans*-1, simply prepared from the commercially available (*R,R*)-2 (Scheme 3),¹⁴ has been examined.

Lithiation in toluene- d_8 of (*S,S*)-*trans*-1 gives a species which shows spectra (^1H , ^{13}C , and ^7Li NMR) identical to those obtained from racemic aziridine *trans*-1, thus supporting the homochiral hypothesis (see the Supporting Information). Concerning the structure of the dimer, ^1H NMR analysis reveals a 2:1 ratio between *trans*-1-Li and bonded TMEDA. Assuming that a slow exchange between free and bonded TMEDA takes place, the structure of the lithiated aziridine in toluene- d_8 may be the one depicted in Figure 9A, that is, an endless polymer of homochiral dimeric units with TMEDA acting as a bridging ligand, as proposed for other lithiated TMEDA-solvated intermediates.¹⁵ However, at present, a dimeric structure with two solvating molecules of TMEDA cannot be ruled out (Figure 9B).¹⁶

Regardless of the solution structure A or B, it can be stated that in toluene aziridine *trans*-1-Li should be a *trans*-configured homochiral dimer.

The proposed model that accounts for the *trans*-1-Li to *cis*-1-Li isomerization mentioned above (in THF) could be the one depicted in Scheme 4. THF should solvate the lithium ion of *trans*-1-Li as soon as it is formed, thus promoting a quick

(12) Dynamic reasons or fast quadrupolar-induced relaxation of the ^7Li nucleus could account for the low resolution of the septet-like signal of C_α which, however, is similar enough to the signal simulated (Figure 10) using WINDNMR (Reich, H. J. *J. Chem. Educ. Software* **1996**, 3D, 2; <http://www.chem.wisc.edu/areas/reich/plt/windnmr.htm>).

(13) By using *s*-Bu ^6Li (prepared as analogously described for *n*-Bu ^6Li ; see Hilmersson, G.; Davidsson, Ö. *Organometallics* **1995**, 14, 912) to accomplish the deprotonation, no improvement in the resolution of the C_α - ^6Li signal was observed obtaining a featureless lump (see the Supporting Information).

(14) Lohray, B. B.; Gao, Y.; Sharpless, K. B. *Tetrahedron Lett.* **1989**, 30, 2623–2626.

(15) Examples of polyamine solvation and TMEDA effects have been investigated; see (a) Schade, S.; Boche, G. *J. Organomet. Chem.* **1998**, 550, 359–379. (b) Schade, S.; Boche, G. *J. Organomet. Chem.* **1998**, 550, 381–395. (c) Collum, D. *Acc. Chem. Res.* **1992**, 25, 448–454. (d) Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J. A.; Bauer, W.; Pi, R.; Schleyer, P. v. R.; Schollhorn, H.; Thewalt, U. *Organometallics* **1989**, 8, 1688–1696.

(16) The reaction is extremely slow without TMEDA. All attempts to generate the lithiated intermediate without TMEDA by transmetalation from the corresponding tributyltin aziridine were unsuccessful.

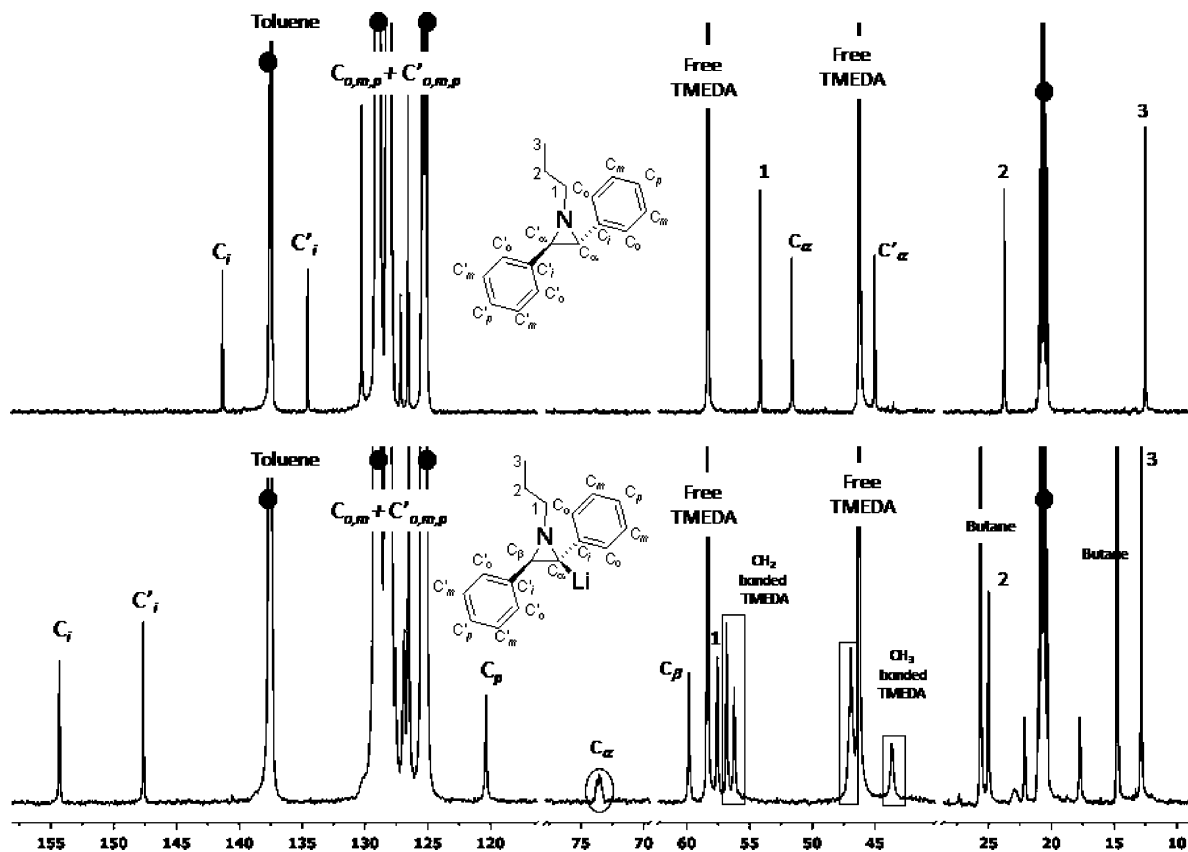


FIGURE 7. ^{13}C NMR spectra of the neutral and lithiated aziridine *trans*-1 in toluene- d_8 at 195 K.

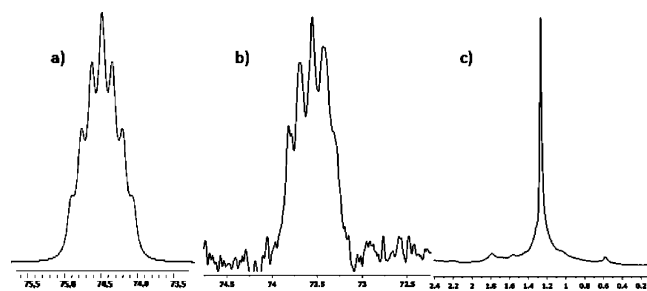
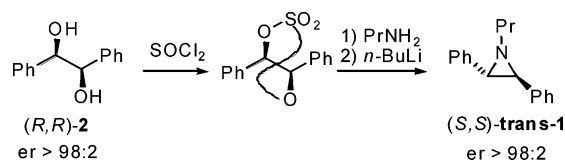


FIGURE 8. Simulated (a) and real (b) ^{13}C - ^7Li coupling and ^7Li NMR spectrum (c) for the lithiated aziridine *trans*-1-Li in toluene- d_8 at 195 K.

SCHEME 3



isomerization^{17,18} to the thermodynamically more stable *cis*-1-Li that exists as a contact ion pair as suggested by the ^{13}C - ^7Li coupling constant found.^{19,3a}

That the solvating property of the medium could promote such isomerization has been proved with the following experi-

(17) Assuming a *cis* relationship between the nitrogen lone pair and the C_α -Li bond, the solvent separated ion pair should suffer destabilizing interactions which should favor the isomerization (see ref 7).

(18) For examples of interconversion between the contact ion pair and solvent ion pair, see (a) Reich, H. J.; Sikorski, H.; Thompson, J. L.; Sanders, A. W.; Jones, A. C. *Org. Lett.* **2006**, *8*, 4003–4006; (b) Ruhland, T.; Hoffmann, R. W.; Schade, S.; Boche, G. *Chem. Ber.* **1995**, *128*, 551–556.

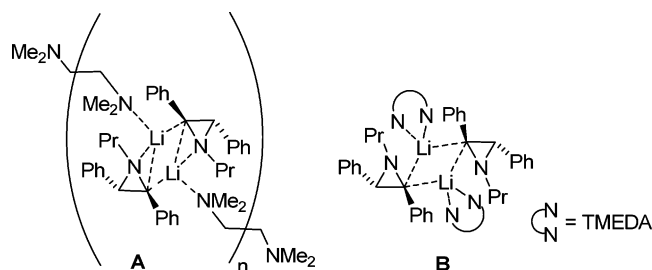
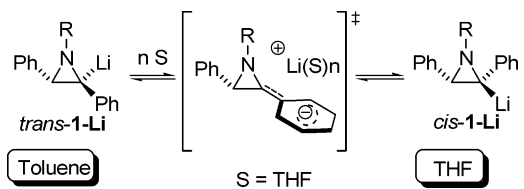


FIGURE 9.

SCHEME 4



ment performed in an NMR tube. To a solution of *trans*-1-Li in toluene- d_8 , 10 equiv of THF- d_8 was added, and the resulting mixture was spectroscopically monitored: the ^{13}C NMR spectra before and after the addition of THF are shown in Figure 10. As can be noted, the C_i and C_p of the phenyl ring directly bonded to the lithiated carbon (C_α) after the addition of THF- d_8 show the same chemical shifts observed for *cis*-1-Li in THF- d_8 . After

(19) (a) Hoell, D.; Schnieders, C.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 243–245. (b) McKeever, D.; Waack, R. *J. Organomet. Chem.* **1971**, *28*, 145–151.

(20) It has been reported that a crown-ether could also promote, in the flask, the same *trans*-1-Li to *cis*-1-Li isomerization (see ref 1).

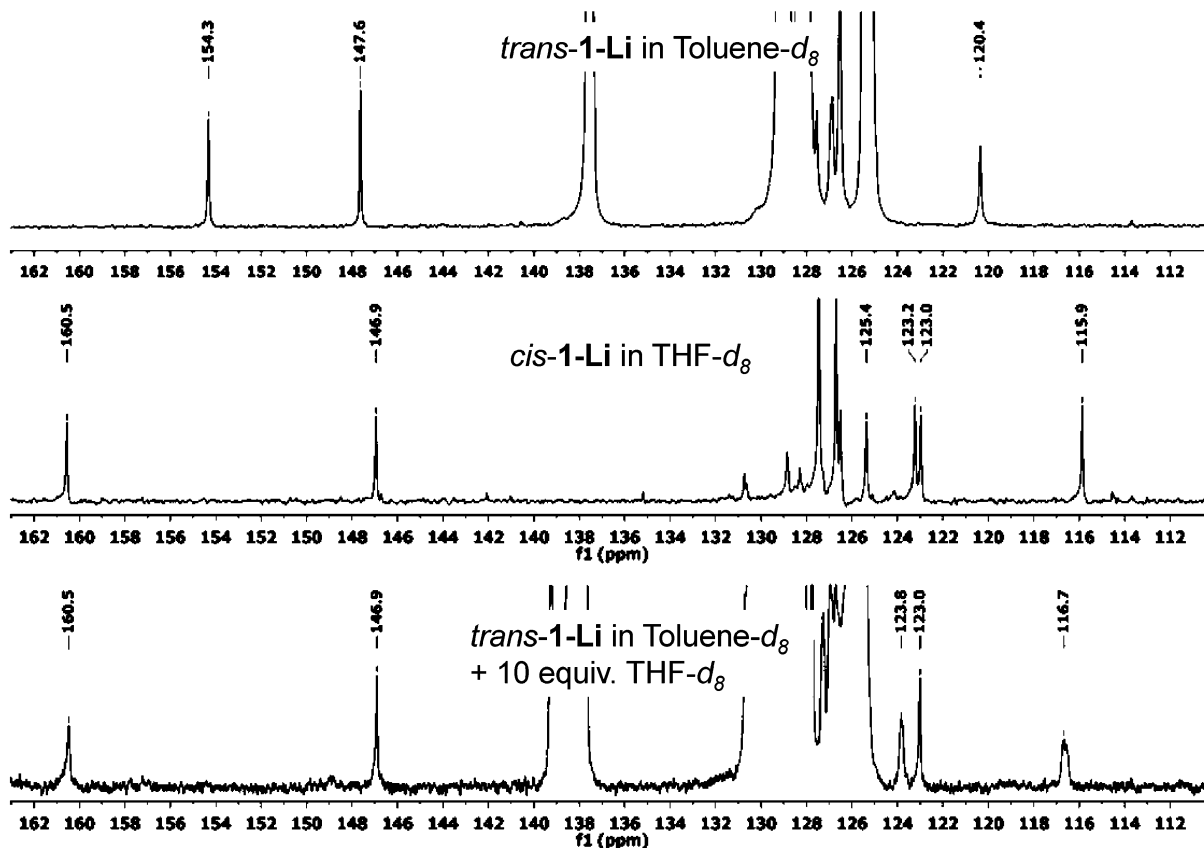


FIGURE 10. THF-promoted isomerization of *trans*-1-Li to *cis*-1-Li in an NMR tube.

quenching with a proton source, the *cis*-configured neutral aziridine has been recovered.²⁰

Conclusion

In conclusion, this work reports, for the first time, a detailed multinuclear NMR investigation of α -lithiated 2,3-diphenylaziridines. Strong spectroscopic evidence has been produced to prove that α -lithiated-2,3-diphenylaziridines have different configurations and aggregation states in different solvents (i.e., a monomeric *cis*-1-Li in a coordinating solvent such as THF and a TMEDA-solvated dimeric *trans*-1-Li in toluene), giving an explanation for the opposite stereochemical course observed in the reactions with electrophiles. Moreover, it has been demonstrated that the solvent polarity determines the nature and configuration of the lithiated intermediates, disclosing that a switch between two differently configured lithiated aziridines is possible. The knowledge of the structure of these lithiated intermediates can have an important repercussion on the synthetic applications of lithiated aziridines derived from parent enantiopure aziridines.²¹ These studies are at present under investigation.

Experimental Section

NMR Spectroscopy. All low-temperature multinuclear NMR experiments were conducted on a spectrometer equipped with a 5

mm autoswitchable broadband gradient (Z) probe and on a custom-built triple resonance 5 mm gradient (Z) probe working at the following frequencies: 599.944 MHz (¹H), 150.856 MHz (¹³C), and 233.161 MHz (⁷Li).

Typical Procedure²² for the Preparation of Lithiated Aziridine 1 in THF-*d*₈. In a 5 mm NMR tube equipped with an Omni-Fit valve, under Ar, a filtered (celite) solution of commercial *s*-BuLi (0.06 mmol) was added, and the solvent was removed under *vacuum*. The resulting oil was then precooled to -78 °C and dissolved in 350 μ L of solvent (THF-*d*₈ or toluene-*d*₈). In a separate vial, under Ar, 10 mg (0.04 mmol) of the aziridine **1** (with 0.06 mmol TMEDA for the experiment performed in toluene) was dissolved in 350 μ L of dry solvent (THF-*d*₈ or toluene-*d*₈). This solution was added to a precooled (-78 °C) 5 mm NMR tube containing the *s*-BuLi solution, and the resulting deep yellow mixture was quickly transferred into the NMR probe precooled to -78 °C. All the experiments were run without spinning.

Spectroscopic Data of *trans*-*N*-Propyl-2,3-diphenylaziridine 1 in THF-*d*₈. Two slowly equilibrating invertomers, dr: 50/50. ¹H NMR (600 MHz, THF-*d*₈, 195 K) δ 0.80 (t, J = 6.7 Hz, 3 H), 1.30–1.45 (m, 2 H), 2.09–2.16 (m, 1 H), 2.25–2.32 (m, 1 H), 3.08 (d, J = 2.8 Hz, 1 H), 3.28 (d, J = 2.8 Hz, 1 H), 7.20 (t, J = 7.7 Hz, 1 H), 7.27–7.34 (m, 3 H), 7.35–7.40 (m, 4 H), 7.49 (d, J = 7.2 Hz, 2 H). ¹³C NMR (150 MHz, THF-*d*₈, 195 K, assignment on the basis of HSQC-DEPT experiment) δ 12.5 (CH₃), 24.1 (CH₂), 45.0 (CH), 52.2 (CH), 54.4 (NCH₂), 126.7, 127.4, 128.4, 128.8, 128.9, 130.8, 135.2 (C_i), 142.1 (C_i).

Spectroscopic Data of Aziridine *cis*-1-Li in THF-*d*₈. ¹H NMR (600 MHz, THF-*d*₈, 195 K) δ 1.00 (t, J = 7.4 Hz, 3 H), 1.50–1.60 (m, 1 H), 1.61–1.71 (m, 1 H), 1.98–2.05 (m, 1 H), 2.30 (s, 1 H), 2.68–2.75 (m, 1 H), 5.85 (d, J = 8.0 Hz, 1 H), 6.20 (t, J = 7.3

(22) The procedure for an experiment with an aziridine/*s*-BuLi/TMEDA ratio of 1/1.5/1.5 and a sample concentration of 0.06 M is reported. Ratios and concentrations can be changed (0.05–0.2 M).

(21) (a) For a special issue on aziridinyl anions, see *Oxiranyl and Aziridinyl Anions as Reactive Intermediates in Synthetic Organic Chemistry*, Tetrahedron Symposia-in-Print; Florio, S., Ed.; Tetrahedron **2003**, 59, 9693–9864. (b) Hodgson, D. M.; Bray, C. D. In *Aziridines and Epoxides in Organic Synthesis*; Yudin, A. K., Ed.; Wiley-VCH: Weinheim, Germany, **2006**; pp 145–184. (c) Hodgson, D. M.; Bray, C. D.; Humphreys, P. G. *Synlett* **2006**, 1–22. (d) Luisi, R.; Capriati, V.; Di Cunto, P.; Florio, S.; Mansueto, R. *Org. Lett.* **2007**, 9, 3295–3298.

Hz, 1 H), 6.43 (t, $J = 7.3$ Hz, 1 H), 6.68–6.72 (m, 3 H), 6.78–6.85 (m, 3 H), 7.08 (d, $J = 8.0$ Hz, 1 H). ^{13}C NMR (150 MHz, THF- d_8 , 195 K, assignment on the basis of HSQC-DEPT experiment) δ 13.3 (CH_3), 25.0 (CH_2 , under the solvent's signal), 55.1 (C_βH), 67.3 (NCH_2 , under the solvent's signal), 78.2 (C_α , q, $J_{\text{C-Li}} = 31$ Hz), 115.9 (C_p), 123.0, 123.2, 125.4, 126.5, 126.7, 127.4, 146.9 (C_i), 160.5 (C_i). ^7Li NMR (233 MHz, THF- d_8 , 195 K) δ 0.24.

Spectroscopic Data of *trans-N-Propyl-2,3-diphenylaziridine 1* in Toluene- d_8 . Two slowly equilibrating invertomers, dr: 50/50. ^1H NMR (600 MHz, toluene- d_8 , 195 K) δ 0.89 (t, $J = 6.9$ Hz, 3 H), 1.47–1.63 (m, 2 H), 1.94–2.05 (m, 1 H), 2.28–2.38 (m, 1 H), 2.74 (d, $J = 3.1$ Hz, 1 H), 3.14 (d, $J = 3.1$ Hz, 1 H), 7.00–7.06 (m, 2 H), 7.07–7.13 (m, 3 H), 7.15–7.21 (m, 1 H), 7.27–7.32 (t, $J = 7.1$ Hz, 2 H), 7.52 (d, $J = 7.3$ Hz, 2 H). ^{13}C NMR (150 MHz, THF- d_8 , 195 K, assignment on the basis of HSQC-DEPT experiment) δ 12.5 (CH_3), 23.7 (CH_2), 45.0 (CH), 51.6 (CH), 54.1 (NCH_2), 126.5, 127.7, 127.9, 130.2, 134.5 (C'_i), 141.3 (C_i).

Spectroscopic Data of Aziridine *trans-1-Li-TMEDA* Complex in Toluene- d_8 . ^1H NMR (600 MHz, toluene- d_8 , 195 K) δ 0.75 (m, 2 H, CH_2 bonded TMEDA), 0.93 (t, $J = 6.7$ Hz, 3 H), 0.94 (s, 3 H, CH_3 bonded TMEDA), 1.53 (s, 3 H, CH_3 bonded TMEDA), 1.60 (m, 2 H, CH_2 bonded TMEDA), 1.66–1.76 (m, 1 H), 1.79–1.89 (m, 1 H), 2.04–2.09 (m, 1 H, under free TMEDA's signal),

2.12 (CH_3 free TMEDA), 2.36 (CH_2 free TMEDA), 2.85 (s, 1 H), 3.03–3.11 (m, 1 H), 6.95 (t, $J = 7.3$ Hz, 1 H), 7.12–7.16 (m, 1 H), 7.17–7.27 (m, 4 H), 7.42–7.50 (m, 4 H). ^{13}C NMR (150 MHz, THF- d_8 , 195 K, assignment on the basis of HSQC-DEPT experiment) δ 12.8 (CH_3), 25.0 (CH_2), 43.7 (CH_3 bonded TMEDA), 46.9 (CH_3 bonded TMEDA), 56.2 (CH_2 bonded TMEDA), 56.9 (CH_2 bonded TMEDA), 57.5 (NCH_2), 59.8 (C_βH), 73.6 (C_α , septet-like, $J_{\text{C-Li}} = 19$ Hz), 120.3 (C_p), 126.2, 126.3, 126.8, 127.2, 127.4, 147.7 (C'_i), 154.3 (C_i). ^7Li NMR (233 MHz, THF- d_8 , 195 K) δ 1.30.

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Supporting Information Available: Experimental procedures, spectra for *trans-1*, *trans-1-Li*, and *cis-1-Li*, and copy of 1D and 2D NMR experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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