The Reduction of Oxalic Amidines with Metallic Lithium: Preparation of Lithiated Bisamides $[R''N(RR'N)C{=}C(NRR')NR'']Li_2$ and Their Use as Intermediates in a Novel Synthesis of Tetraaminoethenes

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Reduction of the 1,4-diaza-1,3-butadiene substructure of hexasubstituted oxalic amidines with lithium metal yields the new lithium diamides **3**. Subsequent reaction of **3** with various electrophiles gives the title substances **4**, **5**, and the acylated derivative **6**, respectively. The first SET step in this reaction is the formation of monolithium radical anions **2**, which were detected by EPR spectroscopy. The second electron transfer leads to the deeply colored dianions **3**. – In the case of compound **3a** [*cis*-**3a** · 3 Et_2O], the X-ray crystal structure reveals the *cisoid* arrangement of the bidental ligand and three molecules of diethyl ether which are located in a 2:1 fashion in the first coordination sphere of the lithium cations. The NMR 2D-^1H,^6Li-HOESY investigations of **3a** in [D_{10}]diethyl ether/diethyl ether (8:1) show Li^+ contacts to the hydrogen atoms of the ether molecules and to the *ortho*-hydrogen atoms of the aryl moieties. Results of semiempirical calculations (PM3) are throughout in acceptable agreement with the experimental data and explain the unusual coordination pattern of the lithium cations of compounds **3**.

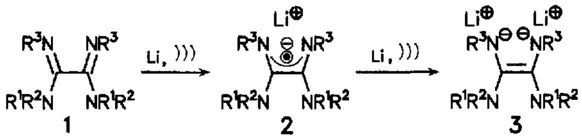
Due the their acceptor properties 1,4-diaza-1,3-dienes such as the bisimines of glyoxal, diacetyl, and benzil may be readily reduced by alkali metals[1,2]. The oxalamidines[3], which we have been studying for some time, contain the structural element of these diazabutadienes. They should thus be reduced to the corresponding dianions by two consecutive SET reactions. To our knowledge these is only a single report on such an experiment: In 1967 Trofimenko[4] described the reduction of a bis-borylated tetraphenyloxalamidine with potassium without studying however the intermediate species or the synthetic potential of this process. This is astonishing because dianions of oxalamidines may be considered to be precursors of the interesting class of tetraaminoethenes (Scheme 1) which are characterized by a wide range of applications in synthetic and physical-organic chemistry[5].

Moreover, the precursors of dianions, i.e. the monometalated radical anions, may play an important role in synthetic chemistry: In 1984 Cohen et al. reported on the related compound class of lithiated dimethylaminoarenes using lithium (1-dimethylamino)naphthalenide as an example which exhibits a variety of application possibilities. These species are for example employed in the transformation of dithioacetals into olefins proceeding according to a Peterson olefination or into isolable precursors of the latter, (α-phenyllthio)trimethylsilanes and β-silylcarbinols[6].

Results and Discussions

We made use of the concept of Trofimenko by treating persubstituted compounds **1**, which cannot be deprotonated at the nitrogen atom, with metallic lithium (Scheme 1). The reductions of **1a** and **1b** in THF proceed straightforwardly via EPR spectroscopically detectable dark-colored radical anions **2a** and **2b** to afford dark red diamides **3a** and **3b**. The reaction was carried out advantageously in an ultrasonic bath. The reaction times could thus be reduced from more than 24 hours to ca. 3 hours.

Scheme 1



1–3	R^1	R^2	R^3
a	Ph	Me	4–Tol
b	Et	Et	2,4,6–$Me_3C_6H_2$

The EPR signals are observed already shortly after the beginning of the reaction. Due to their stability and their secondary reactions these compounds will be the subject of further investigations. In the studied cases the conversion of the radical anions into the dilithium complexes of type **3** required longer reaction times (ca. 3 hours). The electron transfer occurred quantitatively without formation of byproducts and could be followed by EPR and NMR spectroscopy.

^1H-NMR spectroscopic investigations of **3a** do not allow conclusions to be drawn as to the number of coordinatively

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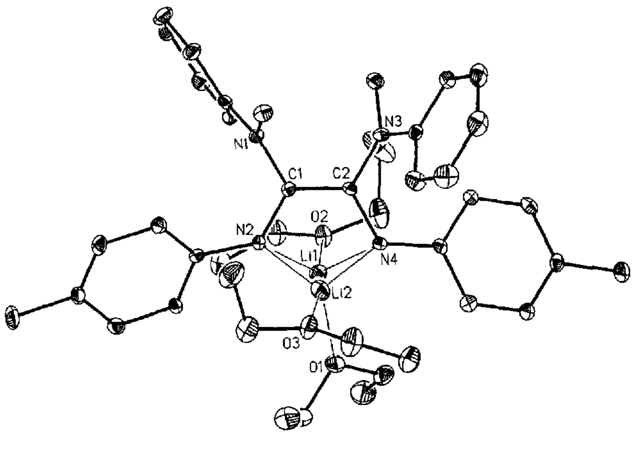
bound ether molecules in solution. Thus, drying under vacuum and subsequent dissolution of the residue in [D$_8$]THF afforded crystalline **3a** containing a different number of ether molecules (e.g. drying at 100 mbar 3 molecules and at 1 mbar 2 molecules).

These results reveal that the coordination of the fourth ether molecule involves only a slight energy gain. Cautious removal of the solvent furnished single crystals of compound **3** which was prepared in diethyl ether. However, an X-ray structural analysis indicated the presence of only three ether molecules.

Thus, the lithium cations of **3a** do not undergo tetracoordination as detected for a large number of complexes[7]. Bridging of the two lithium cations by an ether oxygen atom (O1) can be excluded because of the large distance of 3.241 Å. A structure derived from a bisamine of benzil[2] found recently exhibited an astonishing agreement with the one we obtained. Moreover, the crystal displays the *cisoid* arrangement of the reduced 1,4-diaza-1,3-butadiene moiety although a *transoid* arrangement would a priori be possible: This may be especially inferred from PM3 investigations[8]; this semiempirical method recently proved to be particularly suitable for the calculation of Li–N and Li–O systems[9]. The applicability of PM3 to the substance class discussed in this paper was tested by calculating the crystal structure of *cis*-**3a** · 3 Et$_2$O (Figure 1 and Table 1). Application of the MNDO method[10] does not allow us to reproduce this complex. Starting from different initial geometries, we found as the most stable form of *cis*-**3a** · 3 Et$_2$O a structure in which the lithium cations are exclusively coordinated to the amine nitrogen atom (Figure 2).

Figure 1. Representation of the molecular structure of **3a** · 3 Et$_2$O as ellipsoid (30%)[a]



[a] Selected distances [Å] and angles [°]: Li1–O1 2.017(8), Li1–N2 2.018(8), Li1–N4 2.161(9), Li1···Li2 2.588(11), Li2–N2 2.091(9), Li2–N4 1.948(9), Li2–O3 1.893(9), N2–C1 1.424(6), C1–C2 1.360(6), C2–N4 1.400(6); O1–Li1–O2 105.7(4), O1–Li1–N4 105.1(4), O1–Li1–N2 121.6(4), O2–Li1–N2 121.5(4), O2–Li1–N4 120.3(4), N2–Li1–N4 80.2(3), O3–Li2–N2 129.0(5), O3–Li2–N4 141.2(5), N2–Li2–N4 83.6(3)

Table 1. Comparison of selected bond lengths and angles of the structure of *cis*-**3a** · 3 Et$_2$O in the crystal with PM3 values

Bond lengths [Å]			Bond angles [°]		
	Crystal	PM3		Crystal	PM3
Li1-N2	2.018(8)	2.172	Li1-N2-C1	101.1(3)	101.4
Li1-N4	2.161(9)	2.173	Li2-N2-C1	85.3(3)	90.9
Li1-O1	2.017(8)	2.070	Li1-N4-Li2	77.9(3)	86.0
Li1-O2	1.993(8)	2.072	N2-Li1-O2	121.5(4)	140.8
Li2-N2	2.091(9)	2.142	N2-Li1-O1	121.6(4)	117.5
Li2-N4	1.948(9)	2.016	N2-Li2-O3	129.0(5)	136.2
Li2-O3	1.893(9)	1.939	N2-Li1-N4	80.2(3)	74.1
C1-C2	1.360(6)	1.390	Li2-Li1-O1	88.6(3)	100.5
C1-N1	1.424(6)	1.468	O1-Li1-O2	105.7(4)	94.2
C2-N3	1.435(6)	1.467	N1-C1-C2	120.2(4)	127.2
C1-N2	1.424(6)	1.448	N2-C1-C2	117.1(4)	115.0
C2-N4	1.400(6)	1.447	N3-C2-C1	119.2(4)	126.9

Figure 2. Calculated structure of **3a** · 3 Et$_2$O (PM3)

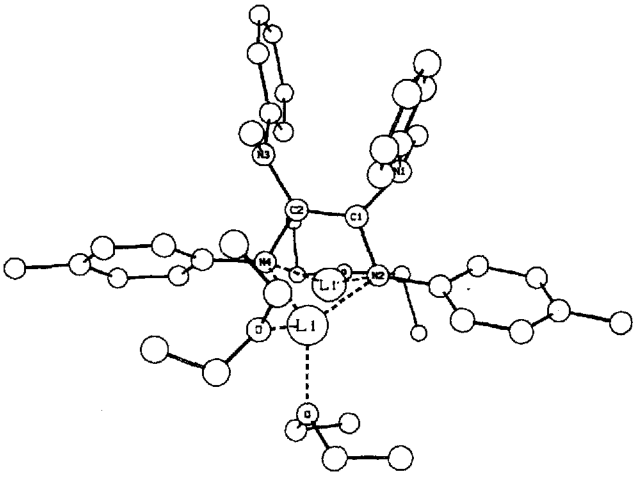
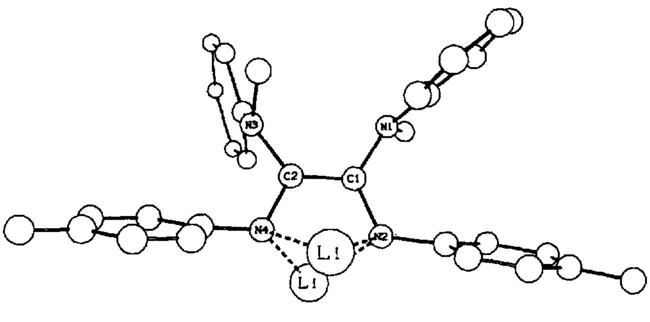


Figure 3. Calculated structure of *cis*-**3a** (PM3)



The PM3 results show that without the effect of ether complexation the energy difference between the *cisoid* form (Figure 3), in which two former imino nitrogen atoms serve as coordination sites for the two lithium cations, and the *transoid* form (Figure 4) with one imino and one amino coordination site is ca. 5.7 kcal/mol in favor of the *trans* form. This distance reduces, as expected, the number of newly entering solvent molecules (Table 2) and reaches after addition of four Et$_2$O molecules a value of 0.8 kcal/mol, so that within the limit of the PM3 accuracy the two species *cis*-**3a** · 3 Et$_2$O and *trans*-**3a** · 3 Et$_2$O are considered to have the same energy content.

Figure 4. Calculated structure of *trans*-**3a** (PM3)

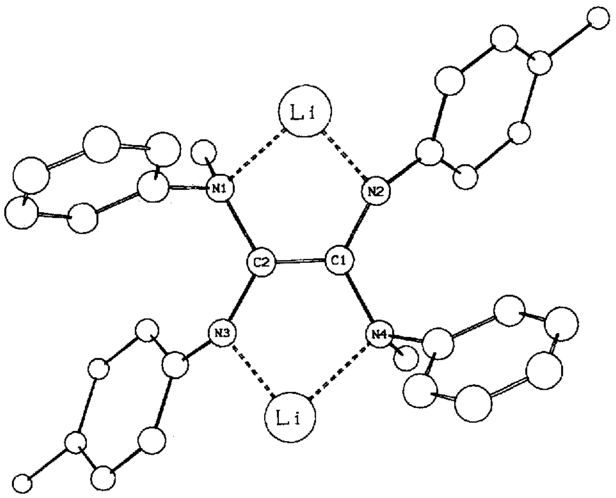


Table 2. Heats of formation ΔH_f and relative energies $E_{rel.}$ of *cis*- and *trans*-**3a** as well as their ether complexes

Compound	ΔH_f [kcal/mol]	$E_{rel.}$ [kcal/mol]
cis-**3a** [a]	136.1	5.7
trans-**3a** [b]	130.4	0.0
cis-**3a**·1Et_2O	64.3	3.8
trans-**3a**·1Et_2O	60.5	0.0
cis-**3a**·3Et_2O [c]	-68.2	1.6
trans-**3a**·3Et_2O	-69.8	0.0
cis-**3a**·4Et_2O	-128.0	0.8
trans-**3a**·4Et_2O	-128.8	0.0

[a] Cf. Figure 3. – [b] Cf. Figure 4. – [c] Such a structure cannot be calculated by means of the MNDO method on account of the underestimation of the Li–N interaction with the amine moiety; MNDO prefers a structure in which the lithium cations are exclusively in contact with the amidine molecular parts ($\Delta H_f = -71.1$ kcal/mol).

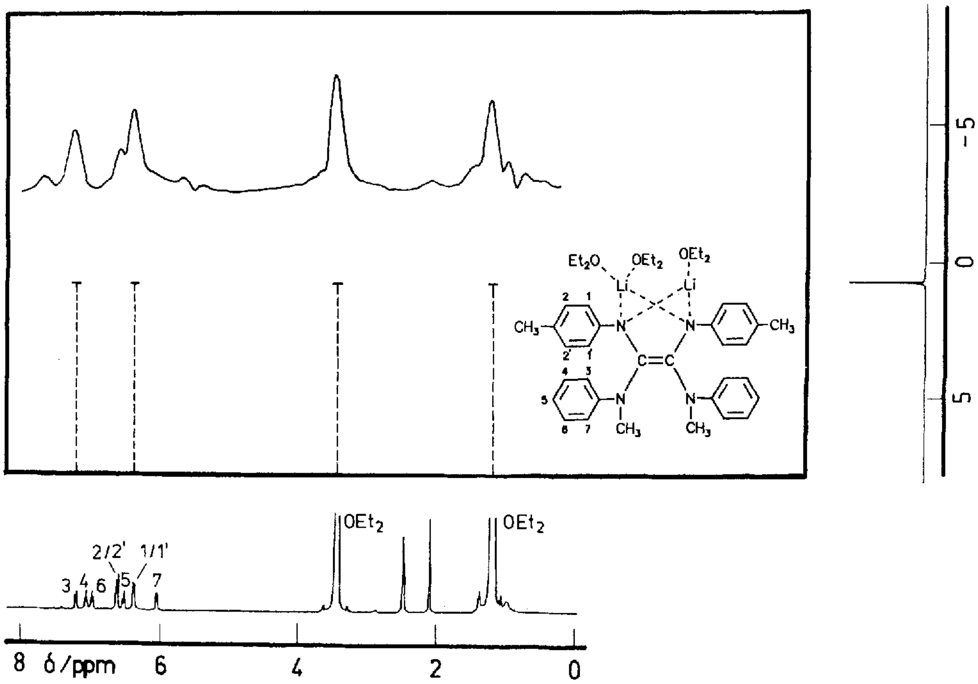
How can we explain the unusual coordination pattern of structure **3a** in the crystal? According to the equation **3a** · 3 Et_2O + Et_2O → **3a** · 4 Et_2O we now calculated for both configurations the complexation energies for the fourth ether molecule. In both cases it was found to vary from –2 kcal/mol (*cis*) to –0.8 kcal/mol (*trans*). For comparison: The coordination of the first ether molecule to the *cis* or *trans* form (Figures 2 and 3) according to the equation **3a** + Et_2O → **3a** · Et_2O is exothermal with ca. 13 kcal/mol (*cis*) and ca. 11 kcal/mol (*trans*), respectively. It is therefore not surprising that during drying of the crystals of **3a** isolated from ethereal solution a different number of complexed solvent molecules was found, depending on the drying process. Three Et_2O molecules in the crystal were detected only accidentally.

The strong drilling of the phenyl residues resulting from the crystal structure may be inferred both from the PM3 and the NMR data in solution. The interaction between one *ortho*-hydrogen atom each and the anisotropy cone of the tolyl structure is reflected by the their shift of $\delta = 1.5$ to lower field. Interestingly, as follows from the NMR data, rotation of the tolyl residues on the lithiated aniline unit occurs rapidly and that of the phenyl residues on the methylaniline residue slowly. This may be attributed to shortened *ipso*-C–N bond lengths of the latter (1.398 and 1.403 Å, respectively) compared with those of the tolyl structure (1.434 and 1.423 Å, respectively).

The 2D-^{1}H,^{6}Li-HOESY investigation revealed cross peaks to the methylene and methyl hydrogen atoms of the ether molecules as well as to the *ortho*-hydrogen atoms of the aryl moieties, but not to the N–CH_3 hydrogen atoms (Figure 5). The found contacts of these *ortho*-hydrogen atoms were confirmed by correspondingly short distances in the crystal structure and reproduced by PM3 calculations. Thus, we could demonstrate with high probability that both in the crystal and in solution the *cisoid* form either predominates or even exists exclusively.

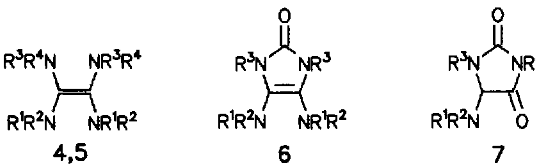
Unfortunately, a detailed ^{1}H-NMR study did not give a definite answer to the still unsolved question whether in solution an equilibrium exists between the *cisoid* and *transoid* form which is possibly strongly shifted to the one or the other side. An interconversion between *cis*-**3a** and *trans*-**3a** can be excluded due to the constant line width (+25 to –100 °C). We suppose that the *cis*/*trans* isomers are separated by a sufficiently high activation barrier. Furthermore, the preferential formation of the *cisoid* species with some probability may be accounted for by a prefixation of the 1,4-diaza-1,3-butadiene moiety on Li(0). Different working groups reported on comparable metal(0) complexations[11]. Such a complexation is assumed to occur in our case: Already before the first electron transfer, an interaction of the later ligand on lithium(0) takes place, an effect which was also observed in reactions proceeding via late transition states of stereoselective, metal-assisted processes. Rotation around the central C–C single bond in the starting molecule **1a** requires, as expected, a low energy. The resulting facile interconversion of different isomers was already previously studied[3]. In addition, the formation of the dilithium compounds **3** strongly depends on the effect of the solvent used. Reduction experiments employing the unpolar solvent *n*-heptane failed as did the use of the sterically more demanding *tert*-butyl methyl ether. The use of dioxane leads selectively to radical anions **2** which presumably form coordination polymers precipitating as amorphous substances. In connection with the above-mentioned studies of Cohen et al. these radicals have attracted considerable interest and will be the subject of further investigations. Besides THF, diethyl ether is especially suited for obtaining crystals of dilithium complexes appropriate for X-ray structural analyses. In addition to their interesting structural properties species of type **3** are useful C_2 building blocks for olefin syntheses. This was exemplified by the reaction of **3a** with methyl iodide, 1,3-dibromopropane, and oxalyl chloride. In all three cases stable alkylated or acylated products could be isolated and characterized spectroscopically. The reaction of a solution of **3a** in THF cooled to –78 °C with methyl iodide afforded within several minutes in nearly quantitative yield compound **4**. Under anaerobic conditions solutions of **4** display chemolumines-

Figure 5. 2D-^{1}H-^{6}Li-NMR HOESY spectrum of **3a** ([D$_{10}$]diethyl ether/diethyl ether 8:1, −100°C)



cence indicating oxidation of the newly formed electron-rich olefin by atmospheric oxygen. Besides the obtained spectral data this clearly indicates the relation to compounds of the tetrakis(dimethylamino)ethene type.

Scheme 2


4,5 **6** **7**

	R^1	R^2	R^3	R^4
4	Ph	Me	4-Tol	Me
5	Ph	Me	4-Tol	-(CH$_2$)$_3$-
6,7	Ph	Me	4-Tol	–

1,4-Diazepine derivative **5** was readily prepared in 65% yield by alkylation of **3a** with 1,3-dibromopropane during 24 hours. Compound **6** was synthesized by acylating cyclization of **3a** with oxalyl chloride. We know already from earlier works that cyclization reactions with oxalyl chloride frequently proceed with liberation of carbon monoxide[12]. Also in our studied example a conceivable six-membered heterocyclic compound with a 1,2-dicarbonyl substructure could be detected mass spectrometrically in traces only on the basis of its molecular mass (*m/z*: 503). However, when the lithium chloride generated during acylation was separated by treatment of the raw product with ethanol, the hydantoine derivative **7** instead of **6** was formed.

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Experimental

General: CHN Analyses: Leco CHN automat CHNS-932. The elementary analyses of the compounds described in this paper all provided correct analytical data. Mass spectra: TRIO 2000 FISONS. – Melting points: Cambridge Instruments micro hot stage Galen III according to Boetius. – Chemical yields are not optimized. All used solvents ketyl-dried. – ^{1}H, ^{13}C, and ^{6}Li NMR: Bruker AC 250 and DRX 400. 2D NMR: DRX-400 spectrometer (9.4 Tesla; ^{1}H: 400.13 MHz). 5-mm multinuclear probe head. ^{1}H-NMR shifts: relative to ^{1}H signals of the solvent. ^{6}Li spectra (58.9 MHz): standard LiBr (1 M solution in THF). Spectral data for 2D-NMR measurements: temperature −100°C, spectral width 1260 Hz (^{6}Li, f_2) and 3307 Hz (^{1}H, f_1), 90°. Pulse length 7.8 µs (^{6}Li) and 8.7 µs (^{1}H), mixing time 2 s, relaxation delay 5 s. 1024 complex data points in t_2 and 64 in t_1; each t_1 increment was recorded with 16 scans; FID in t_1: 128 points (linear prediction, software package UXNMR Bruker) and zero-filled to 512 points; spectra were recorded in the phase-sensitive (TPPI) mode; prior to the double Fourier transformation a $\sin^2 x$ was applied as window function in both cases.

Structure Determination of **3a**: An amber-colored crystal (0.36 × 0.27 × 0.22 mm) was measured with a P4 Siemens four-circle diffractometer (Mo-K_α radiation, graphite monochromator) at 120 K. Monoclinic crystal system, cell dimensions (refined by using diffractometer angles of 30 centered reflections in the 2Θ range 15–25°): a = 12.884(4), b = 15.690(5), c = 20.238(7) Å, β = 94.85(3)°, V = 4075(2) Å^3; space group $P2_1/c$ (No. 14), Z = 4, $\rho_{\text{calcd.}}$ = 1.125 gcm^{-3}, μ = 0.07 mm^{-1}. Data collection of 6683 intensities up to $2\Theta_{\text{max}}$ = 45°, 5306 independent intensities (R_{merg} = 0.0338) out of which 3595 were considered observed [$(F_o \geq 4\sigma(F)$]. The structure was solved by direct methods and refined to F by using the SHELXTL-Plus program package (version 4.11/V). For the refinement of 429 parameters anisotropic displacement factors were used for all atoms except for hydrogen atoms, and the phenyl rings including the hydrogen atoms were treated as idealized groups. $R = 0.0704$, $R_w = 0.0662$, $w^{-1} = [\sigma^2(F_o) + 0.00029 \cdot F_o^2]$, maximal residual electron density 0.49 eÅ^{-3}. Further details of the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404317, the names of the authors, and the journal citation.

Calculations: Calculations were carried out on the RHF level by means of the PM3 and MNDO method using the program MOPAC 6/PC[13]. Geometries were completely optimized without symmetry restrictions.

General Procedure for the Synthesis of Dilithium Complexes of Type **3**: In a 250-ml Schlenk vessel 4.5 mmol of the corresponding amidine was dissolved under argon in ca. 30 ml of THF. To the obtained solution was added 4.3 mmol (0.3 g) of lithium. The mixture was brought to reaction in an ultrasonic bath. After 3 h, a clear red solution was obtained from which excess lithium was removed by filtration.

Dilithium Complex **3a**: When diethyl ether was used as the solvent instead of THF an amber-colored solution was obtained after reaction timers of 4–5 h from which single crystals were isolated at −18 °C for X-ray crystal structure analysis. – ^{1}H NMR ([D$_{10}$]diethyl ether, 400.13 MHz, −100 °C): δ = 2.08 (s, 6H, tolyl-CH$_3$), 2.46 (s, 6H, N-CH$_3$), 6.02 [d, ^3J(H,H) = 8.3 Hz, 2H], 6.36 [d, ^3J(H,H) = 7.6 Hz, 4H], 6.50 [t, ^3J(H,H) = 7.0 Hz, 2H], 6.59 [d, ^3J(H,H) = 7.6 Hz, 4H], 6.95 [t, ^3J(H,H) = 7.6 Hz, 2H], 7.03 [t, ^3J(H,H) = 7.6 Hz, 2H], 7.18 [d, ^3J(H,H) = 7.2 Hz, 2H]. – ^{13}C NMR ([D$_{10}$]diethyl ether, 100.62 MHz, −100 °C): δ = 20.63, 34.32, 111.36, 114.87, 116.09, 118.96, 119.45, 126.64, 127.02, 128.65, 129.31, 150.71, 152.83. – ^{6}Li NMR ([D$_{10}$]diethyl ether, 58.9 MHz, −100 °C): δ = 0.67 (s, ^{6}Li).

Dilithium Complex **3b**: ^{1}H NMR ([D$_8$]THF, 250 MHz, 25 °C): δ = 0.84 [t, ^3J(H,H) = 6.8 Hz, 12H, CH$_2$C*H*$_3$], 2.12 (s, 6H, *p*-CH$_3$), 2.29 (s, 12H, *o*-CH$_3$), 2.92 [q, ^3J(H,H) = 6.8 Hz, 8H, NC*H*$_2$CH$_3$], 6.57 (s, 4H). – ^{13}C NMR ([D$_8$]THF, 62.9 MHz, 25 °C): δ = 15.00, 20.28, 46.89, 121.66, 128.08, 129.93, 132.55, 154.17.

N^1,N$^{1'}$,N^2,N$^{2'}$-Tetramethyl-N^1,N^2-diphenyl-N$^{1'}$,N$^{2'}$-di-p-tolyl-1,1,2,2-ethenetetramine (**4**): To a solution of ca. 4.5 mmol of **3a** was added with stirring at −78 °C 9 mmol of methyl iodide. After completion of the addition the reaction mixture was allowed to warm to room temp. and stirring was continued for ca. 20 min until the solution was nearly colorless. The solvent was then evaporated under vacuum, the residue was taken up in toluene and lithium iodide was filtered off. The filtrate was concentrated and the obtained **4** was purified by gel filtration (silica gel, Merck KG 60, grain size 0.2–0.5 mm, eluent: toluene/acetone, 9.5:1). – Yield: 90%, yellow crystals, m.p. 83 °C. – ^{1}H NMR ([D$_8$]THF, 250 MHz, 25 °C): δ = 2.15 (s, 6H), 2.60 (s, 6H), 3.06 (s, 6H), 6.60–6.69 (m, 10H), 6.86 [d, ^3J(H,H) = 7.50, 4H], 7.02 [d, ^3J(H,H) = 7.32, 4H]. – ^{13}C NMR ([D$_8$]THF, 62.9 MHz, 25 °C): δ = 20.50, 40.37, 41.46, 115.75, 118.65, 127.64, 129.04, 129.68, 144.95. – MS, *m/z* (%): 478 (24) [M$^+$ + 2], 476 (100) [M$^+$], 250 (38), 238 (49), 223 (86), 207 (22), 120 (26), 91 (54), 77 (38). – $C_{32}H_{36}N_4$ (476.7): calcd. C 80.55, H 7.55, N 11.74; found C 80.30, H 7.69, N 11.20.

N,N'-Dimethyl-N,N'-diphenyl-1,4-di-p-tolyl-4,5,6,7-tetrahydro-1H-1,4-diazepine-2,3-diamine (**5**): To a solution of ca. 4.5 mmol of **3a** cooled to −78 °C was added with stirring 4.5 mmol of 1,3-dibromopropane. Work-up of the reaction mixture was performed in the same manner as described for **4**, but in this case stirring had to be continued for ca. 24 h. – Yield: 65%, pale yellow crystals, m.p. 215 °C. – ^{1}H NMR ([D$_8$]THF, 250.1 MHz, 25 °C): δ = 1.55 (m$_c$, 2H), 2.14 (s, 6H, tolyl-CH$_3$), 2.81 (s, 6H, NCH$_3$), 3.78 (m$_c$, 4H), 6.53–6.99 (m, 18H). – ^{13}C NMR ([D$_8$]THF, 62.9 MHz, 25 °C): δ = 20.69, 23.57, 39.89, 49.10, 114.90, 117.83, 121.61, 128.85, 129.99, 144.64, 146.99. – MS; *m/z* (%): 491 (7) [M$^+$ + 2], 490 (38) [M$^+$ + 1], 489 (100) [M$^+$], 474 (27), 244 (57), 223 (68), 208 (14), 120 (25), 91 (22), 28 (18). – $C_{33}H_{36}N_4$ (488.9): calcd. C 81.00, H 7.77, N 11.45; found C 80.77, H 7.60, N 11.20.

4,5-Bis[methyl(phenyl)amino]-1,3-di-p-tolyl-1,3-dihydro-2H-imidazol-2-one (**6**): To a solution of 4.5 mmol of **3a** was added at −78 °C with stirring 4.5 mmol of oxalyl chloride. The mixture was then allowed to warm to room temp. and stirring was continued for 1 h. The solvent was evaporated under vacuum, the residue was taken up in toluene and lithium chloride was filtered off. The raw product was subsequently purified by column chromatography (aluminum oxide, Riedel de Hean AG, standardized for chromatography, eluent: toluene/acetone, 9.5:1) and recrystallized from *n*-heptane. – Yield: 60%, white crystals, m.p. 172 °C. – ^{1}H NMR (CDCl$_3$, 250.1 MHz, 25 °C): δ = 2.27 (s, 6H, tolyl-CH$_3$), 2.72 (s, 6H, NCH$_3$), 6.64–6.85 (m, 6H), 7.07–7.17 (m, 8H), 7.23 (m, 4H). – ^{13}C NMR (CDCl$_3$, 62.9 MHz, 25 °C): δ = 21.02, 37.30, 113.34, 118.70, 122.34, 126.28, 128.83, 129.12, 131.32, 137.12, 147.62, 148.90 [C=O]. – MS; *m/z* (%): 477 (6) [M$^+$ + 2], 476 (33) [M$^+$ + 1], 475 (93) [M$^+$], 459 (11), 366 (16), 237 (27), 223 (100), 208 (37), 118 (11), 106 (30), 91 (14), 28 (20). – $C_{31}H_{30}N_4O$ (474.6): calcd. C 78.38, H 6.32, N 11.80; found C 77.88, H 6.23, N 11.36.

5-[Methyl(phenyl)amino]-1,3-di-p-tolylimidazoline-2,4-dione (**7**): To a solution of ca. 4.5 mmol of **3a** was added at room temp. on excess of oxalyl chloride. After the reaction, proceeding with vigorous evolution of heat, had ceased the solvent was evaporated under vacuum. The residue was taken up in ethanol and the solution was stored at −18 °C for 2 d while **7** crystallized. The crystals were sucked of and washed with a small amount of cold ethanol. Yield: 50%, brownish needles, m.p. 176 °C. – ^{1}H NMR (CDCl$_3$, 250.1 MHz, 25 °C): δ = 2.29 (s, 3H, tolyl-CH$_3$), 2.36 (s, 3H, tolyl-CH$_3$), 2.86 (s, 3H, NCH$_3$), 6.04 (s, 1H), 6.86–6.92 (m, 3H), 7.10 [d, ^3J(H,H) = 8.36 Hz, 2H], 7.19–7.31 (m, 8H). – ^{13}C NMR (CDCl$_3$, 62.9 MHz, 25 °C): δ = 20.89, 21.17, 32.75, 75.12, 116.57, 120.84, 122.83, 126.00, 128.50, 129.27, 129.73, 132.85, 135.89, 138.46, 148.12, 152.95 (C=O), 168.19 (C=O). – MS, *m/z* (%): 387 (2) [M$^+$ + 2], 385 (9) [M$^+$], 280 (4), 279 (18), 118 (100), 91 (3). – $C_{24}H_{23}N_3O_2$ (385.5): calcd. C 74.70, H 5.97, N 10.89; found C 74.25, H 5.82, N 10.57.

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