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Lithio-diazomethane and Lithio-(trimethylsilyl)diazomethane: Theoretical and Experimental Studies of Their Structures, Reactions and Reaction Products

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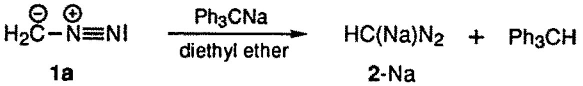
Abstract: The first report of a metalated diazomethane by Eugen Müller and his coworkers appeared in 1933. Then, in a thirty-six years ongoing story,[1-6] this group revealed several highly interesting but also puzzling details about the chemistry of metalated diazomethane and metalated substituted diazomethanes: 1. Metalation of diazomethane **1a** (the parent compound) to give the corresponding Li (or Na) species followed by protonation led to "isodiazomethane" which finally turned out to be *N*-isocyano amine **1c**. Ab initio calculations of the structures and energies of the three non-cyclic CH_2N_2 isomers **1a-c** and of the four non-cyclic lithiated diazomethane isomers **2**-Li(I)-**2**-Li(IV), as well as their dimers, provide an understanding of this reaction sequence. 2. Metalation of mono-substituted diazomethanes $RCHN_2$, R= Ph, Me, Me_3Si, e.g. by methyllithium, followed by protonation, resulted in a completely different observation, namely the formation of 4,5-bis-R-substituted 1,2,3-triazoles (e.g. **10**) and methylamine **11**. In the crystals of lithiated trimethylsilyl-diazomethane **13**-Li, which allowed for the first time to determine the crystal structure of a lithiated (substituted) diazomethane, is also present the corresponding Li-triazole **14**-Li ([6 **13**-Li · 2 **14**-Li · 6 Et_2O · hexane]). Model calculations traced the pathway of the triazole formation via a nitrenoid (e.g. **9**-Li) which is also responsible for the formation of methylamine **11**.

The completely different chemistry of diazomethane **1a** and mono-substituted diazomethanes in the deprotonation-protonation sequence is due to the different structures of the corresponding Li(Na) species and their different reactivities (selectivities).

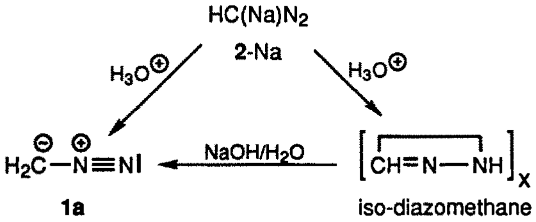
1. Historical Background

In a preliminary communication in 1933, Müller and Disselhoff reported on the reaction of diazomethane **1a** with sodium probably to give the metalated diazomethane $HC(Na)N_2$ **2**-Na.[1] Further details were released in two publications in the following year.[2,3] It was firmly established that the above mentioned reaction as well as the deprotonation of diazomethane **1a** with triphenylmethylsodium led to the metalated diazomethane **2**-Na. Structural investigations have not been performed because **2**-Na is extremely explosive at least in the solid state.[2]

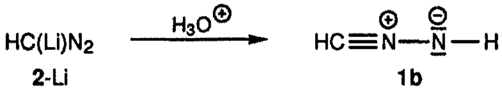


$$\underset{\textbf{1a}}{H_2\overset{\ominus}{C}-\overset{\oplus}{N}\equiv N|} \xrightarrow[\text{diethyl ether}]{Ph_3CNa} \underset{\textbf{2-Na}}{HC(Na)N_2} + Ph_3CH$$

Protonation of **2**-Na led to a remarkable result. First, as anticipated, diazomethane **1a** was formed. In addition, the authors isolated a compound which was an isomer of H_2CN_2 **1a**. They called it "iso-diazomethane" and assumed it to have the cyclic structure $[\overline{CH{=}N{-}NH}]_x$.[3] Treatment of iso-diazomethane with $NaOH/H_2O$ resulted in the formation of the more stable isomer diazomethane **1a**.



Protonation of lithio-diazomethane **2**-Li also gave iso-diazomethane for which in 1954 Müller and Ludsteck proposed an alternative to the cyclic structure, namely that of the nitril imine isomer **1b**.[4]

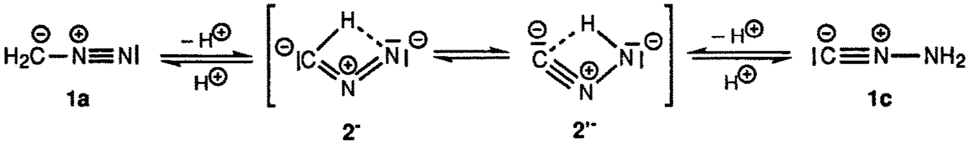


A real break-through was the discovery in 1968 by means of nmr and IR investigations according to which iso-diazomethane has not the structure **1b** but that of the *N*-isocyano amine **1c**.[5]

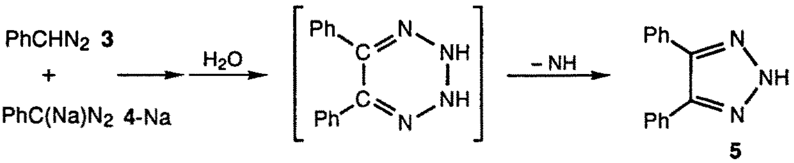
$$\overset{\ominus}{|C}\equiv\overset{\oplus}{N}-NH_2$$

1c

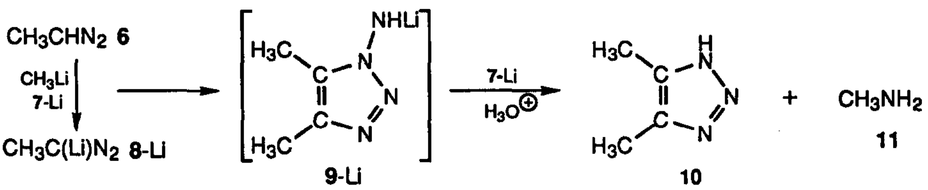
Since the nitrile imine **1b** was never detected it was assumed that it is by far the the most unstable linear CH_2N_2 isomer.[5] Therefore, it was proposed that it is not involved in the "double tautomerisation" of **1a** into **1c**, and vice versa. Rather, this "double tautomerization" should be established via an equilibrium of the anion $\mathbf{2}^-$ with its isomer $\mathbf{2}'^-$.[5]



A result completely different from that of the parent compound **1a** was obtained when *mono-substituted diazomethanes* like phenyldiazomethane **3** were deprotonated, followed by reprotonation of the reaction mixture.[2] The formation of the triazole **5** was thought to occur by the reaction of **3** with its sodium compound **4**-Na, and - very vaguely - loss of NH.



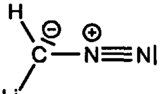
The deprotonation of diazoethane **6** with methyllithium **7** followed by reprotonation led to results similar to those shown above for phenyldiazomethane **3**.[6]

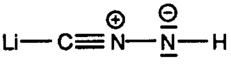


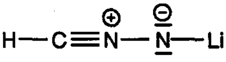
As in the case of **3**, a triazole (**10**) was formed. In addition, methylamine **11** was isolated which had to come from methyllithium **7**-Li, a very perplexing result.The authors assumed that the reaction of **6** with lithiated diazoethane **8**-Li led to the intermediate **9**-Li. It was, however, not at all clear, how **10** and especially **11** had been formed from **9**-Li.

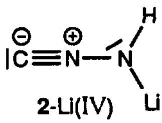
Thus, the very elegant experimental investigations of Eugen Müller and his coworkers performed over thirty-six years[1,5] left some interesting questions open:

1. What are the structures and (relative) energies of the three non-cyclic isomers diazomethane **1a**, nitrile imine **1b** and *N*-isocyano amine **1c**?
2. What are the structures and (relative) energies of lithiated diazomethane **2**-Li, respectively its four possible non-cyclic isomers **2**-Li(I) to **2**-Li(IV)?


2-Li(I)


2-Li(II)

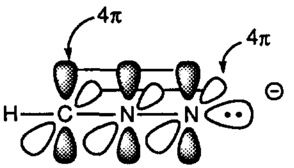

2-Li(III)


2-Li(IV)

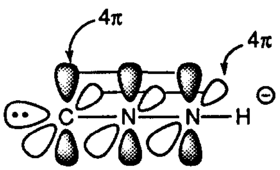
3. What is the mechanism of the "double tautomerisation" **1a** $\rightleftharpoons$ **1c**? Are the lithiated compounds **2**-Li(I) to **2**-Li(IV) involved in this transformation?
4. Why react mono-substituted diazomethanes like phenyldiazomethane **3** or diazoethane **6** completely different from the parent diazomethane **1a** with base, followed by acidification? How are triazoles like **5** and **10** formed? How can one understand the formation of methylamine **11** in such a reaction?

In the following we shed some light on these questions by means of theoretical calculations and an X-ray structure determination, the first of a lithiated (substituted) diazomethane. The crystals were isolated from the reaction of trimethylsilyldiazomethane with butyllithium in diethyl ether/hexane.

Before, we would briefly like to point out that the descriptions of the lithiated compounds **2**-Li(I) - **2**-Li(IV) with only one resonance structure is rather arbitrary. In fact one is dealing with two (orthogonal) 4π electron systems in the anions **2**-Li(I)$^-$-**2**-Li(IV)$^-$ with Li$^+$ being positioned at the nitrogen or carbon ends, respectively.



2-(I)$^-$ and 2-(III)$^-$



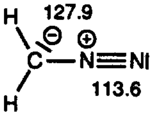
2-(II)$^-$ and 2-(IV)$^-$

Similarly, the CH_2N_2 isomers **1a**, **1b** and **1c** have been written in only one resonance structure which likewise cannot give an adequate description of the real situation.

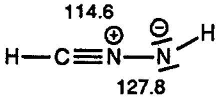
2. Ab initio Calculations of Diazomethane 1a, Nitril Imine 1b and N-Isocyano Amine 1c

Earlier theoretical investigations[7-10] of the CH_2N_2 isomers **1a-c** confirmed the assumption of Müller et al. with regard to the instability of the nitrile imine isomer **1b**, see Table 1.[9]

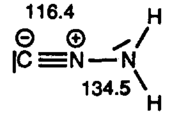
Table 1. HF/6-31G Structures of **1a**, **1b** and **1c**. E_{rel} in [kcal/mol]; Bond Lengths in [pm][9]



1a, 0.0



1b, 35.3



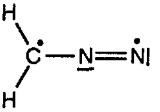
1c, −2.6

Thus, **1b** is 35.3 (37.9) kcal/mol less stable than **1a**(**1c**). These calculations, however, can not be completely reliable: **1c** is calculated to be 2.6 kcal/mol more stable than **1a**, while experimentally **1c** was found to isomerize into **1a**, as pointed out earlier.[1-6] On the HF/3-21G level **1c** is even more stable (8.85 kcal/mol) than **1a**.[10]

In order to clarify this point we performed more elaborate calculations of **1a**, **1b**, and **1c**, see Table 2.

Geometry optimizations were performed at the HF/6-311++G(d,p) and the MP2(FC)/6-311++G(d,p) levels. The fully optimized structures were characterized as minima by frequence analysis. In order to estimate the effects of correlation on the relative energies of the isomers, single point calculations (MP2(full), MP3(full), MP4(full), CISD(FC) and QCISD(T)(FC))[12] were carried out. The energies listed in Table 2 were corrected to zero point vibration (ZPE). HF/6-311++G(d,p) zero point energies were scaled by 0.91, whereas the MP2(FC)/6-311++G(d,p) ZPE's were scaled by 0.94.[13]

Even on the Hartree-Fock level HF/6-311++G(d,p) **1c** is now slightly less stable (0.9 kcal/mol) than **1a** - in agreement with the experiments.[1-6] If the correlation energy is included (MP2/6-311++G(d,p) **1c** becomes remarkably less stable (14.5 kcal/mol) than **1a**. The other methods summarized in Table 2 similarly give higher correlation energies for **1a** than for **1c**. It has already been shown by Goddard[14] that the biradical structure **1a'** contributes to the ground state of diazomethane **1a**. Such biradical type structures are only considered by correlated methods thus making **1a** more stable than, e.g., **1c**.

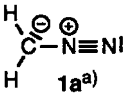
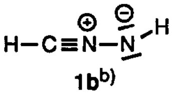
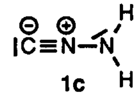


1a'

The calculated bond lengths on the MP2 level for diazomethane **1a** agree nicely with the experimentally determined ones:[15] C-N exp. 132 pm, calcd. 131.6 pm; N-N exp. 112 pm, calcd. 114.2 pm. In the nitrile imine **1b** C-N is calculated to be much shorter (118.8 pm) than in **1a** (131.6 pm). The N-N bond in **1b** (126.3 pm) is much longer than in **1a** (114.2 pm). The *N*-isocyano amine **1c** has - similar to **1b** - a short C-N bond (118.7 pm) and a very long N-N bond (135.8 pm), essentially a single bond.

It is quite clear from the results of Table 2 that the nitril imine isomer **1b** is much higher in energy at all calculational levels than **1c**, and especially **1a**. Again, this is in agreement with the experiments of Müller et al.[1-6] who could never detect this isomer. The high energy of **1b** raises the question whether it is an intermediate in the isomerization **1a** $\rightleftharpoons$ **1c**. We will discuss this point in more detail in the following sections.

Table 2. Structures and Energies of **1a**, **1b**, and **1c**; Energies in [a.u.]; Relative Energies in [kcal/mol]; Bond Lengths in [pm]. Cartesian Coordinates of **1a-c** are available on request.

	 **1a**[a)]	 **1b**[b)]	 **1c**
HF/6-311++G(d,p)	-147.88488	-147.83284	-147.88595
ZPE	0.03384	0.03294	0.03663
E_{rel} (+ZPE)	0.0	32.1	0.9
C-N	128.5	113.4	114.8
N-N	110.7	125.8	135.2
MP2(FC)/6-311++G(d,p)	-148.37598	-148.33685	-148.35552
ZPE	0.03121	0.03203	0.03401
E_{rel} (+ZPE)	0.0	25.0	14.5
C-N	131.6	118.8	118.7
N-N	114.2	126.3	135.8
MP2(full)/6-311++G(d,p)	-148.43279	-148.39368	-148.41207
E_{rel} (+ZPE)	0.0	25.0	14.7
MP3(full)/6-311++G(d,p)	-148.43225	-148.38761	-148.42005
E_{rel} (+ZPE)	0.0	28.5	9.3
MP4(full)/6-311++G(d,p)	-148.47361	-148.43393	-148.45513
E_{rel} (+ZPE)	0.0	25.4	13.2
CISD(FC)/6-311++G(d,p)	-148.32684	-148.28040	-148.31742
E_{rel} (+ZPE)	0.0	29.6	7.6
QCISD(T)(FC)/6-311++G(d,p)	-148.41000	-148.36897	-148.39371
E_{rel} (+ZPE)	0.0	26.2	11.9

[a)] Geometry optimization on the MP2(FC = frozen core) level leads to a diazomethane **1a** with a non-planar carbon atom ((C_s)-**1a**) as also found by P.v.R. Schleyer et al.[11a] Since the energy difference between (C_s)-**1a** and (C_{2v})-**1a** amounts only to 0.1 kcal/mol (taking zero point vibration into account (C_s)-**1a** is 0.3 kcal/mol *less* stable than (C_{2v})-**1a**), and since on the QCISD/6-31G(d) level the (C_{2v})-**1a** isomer is more stable than (C_s)-**1a**[11] we performed all single point calculations with the (C_{2v})-**1a**) geometry.

[b)] On the MP2 level the C_s symmetry of **1b** is reduced to C_1 due to out-of-plane bending of the C and N bound hydrogens. The C-N-N angle amounts roughly to 170°. The same has been reported recently by Wong and Wentrup[11b].

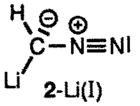
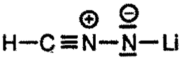
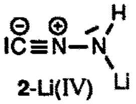
3. Ab initio Calculations of the Monomeric LiCHN$_2$ Isomers 2-Li(I) - 2-Li(IV)

The experiments of Müller et al.[1-6] and the results of the calculations in Table 2 convincingly agree on the fact that *N*-isocyano amine **1c** is clearly less stable than diazomethane **1a**. Thus the question arises why **1c** is formed at all in the protonation reactions of lithiated (metalated) diazomethane. Furthermore, when and how gets the second hydrogen atom from the carbon atom in **1a** to the nitrogen atom in **1c**?

In order to get more information on this point we calculated the structures and energies of the four monomeric isomers **2**-Li(I), **2**-Li(II), **2**-Li(III) and **2**-Li(IV) on the same calculational levels as those of the CH_2N_2 isomers **1a-c**. The results are listed in Table 3.

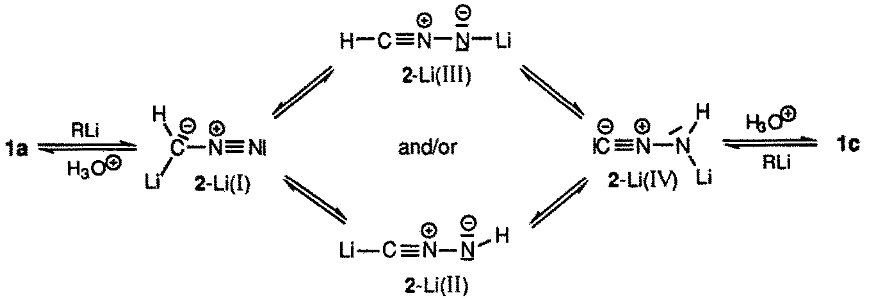
It is immediately clear from Table 3 that it is not the lithiated diazomethane **2**-Li(I) which is the global minimum at all levels of the calculations but rather the lithiated *N*-isocyano amine **2**-Li(IV). The QCISD(T)/6-311++G(d,p) method predicts **2**-Li(IV) to be 6.0 kcal/mol more stable than **2**-Li(I). The two isomers **2**-Li(II) and **2**-Li(III) are generally higher in energy than **2**-Li(I) and **2**-Li(IV).

Table 3. Structures and Energies of 2-Li(I), 2-Li(II), 2-Li(III) and 2-Li(IV); Energies in [a.u.]; Relative Energies in [kcal/mol]; Bond Lengths in [pm]. Cartesian Coordinates of 2-Li(I)-2Li(IV) are available on request.

	 **2-Li(I)**	 **2-Li(II)**	 $H{-}C{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{\underline{N}}{-}Li$ **2-Li(III)**[a)]	 **2-Li(IV)**
HF/6-311++G(d,p)	-154.74512	-154.74560	-154.72520	-154.77397
ZPE	0.02391	0.02430	0.02304	0.02469
E_{rel} (+ZPE)	0.0	-0.1	12.0	-17.6
C-N	129.4	115.0	115.1	114.9
N-N	111.2	127.9	120.0	135.3
MP2(FC)/6-311++G(d,p)	-155.25254	-155.24625	-155.24982	-155.25764
ZPE	0.02257	0.02284	0.02249	0.02253
E_{rel} (+ZPE)	0.0	4.1	1.7	-3.2
C-N	131.3	120.1	121.7	120.2
N-N	115.5	128.0	121.7	134.8
MP2(full)/6-311++G(d,p)	-155.32279	-155.31665	-155.32068	-155.32798
E_{rel} (+ZPE)	0.0	4.0	1.3	-3.3
MP3(full)/6-311++G(d,p)	-155.31287	-155.30832	-155.29737	-155.32785
E_{rel} (+ZPE)	0.0	3.0	9.7	-9.4
MP4(full)/6-311++G(d,p)	-155.36298	-155.35602	-155.35808	-155.36955
E_{rel} (+ZPE)	0.0	4.5	3.0	-4.1
CISD(FC)/6-311++G(d,p)	-155.18983	-155.18620	-155.17428	-155.20664
E_{rel} (+ZPE)	0.0	2.4	9.7	-10.6
QCISD(T)(FC)/6-311++G(d,p)	-155.28010	-155.27318	-155.26852	-155.28970
E_{rel} (+ZPE)	0.0	4.5	7.2	-6.0

a) On the MP2 level the C_{∞} symmetry of 2-Li(III) is reduced to C_s due to out-of-plane bending of the C bound hydrogen.

The transformation of diazomethane **1a** first with RLi and then with acid into *N*-isocyano amine **1c** thus could proceed in the following manner (Eq. 1).



(1)

Deprotonation of diazomethane **1a** first leads to lithiated diazomethane 2-Li(I) which rearranges to a large degree either via the *C*-lithiated nitrile imine 2-Li(II) (migration of H) and/or the *N*-lithiated nitrile imine 2-Li(III) (migration of Li) to the most stable Li-isomer, the lithiated *N*-isocyano amine 2-Li(IV). Finally, protonation of 2-Li(IV) at the lithiated N atom under kinetically controlled conditions, directed by the lithium cation, leads preferentially to *N*-isocyano amine **1c**. C-Protonation of 2-Li(IV) is less likely because it leads to the more unstable nitril imine isomer **1b**.

If **1c** is treated with NaOH/H_2O (reversible protonation/deprotonation), which leads back to diazomethane **1a**,[1-6] the reaction is controlled by the most stable CH_2N_2 isomer **1a**. **1a** results from protonation of 2-Li(I) at the lithiated C atom. N-Protonation of **2**-Li(I) is less likely because it forms the higher energy isomer nitril imine **1b**.

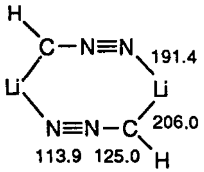
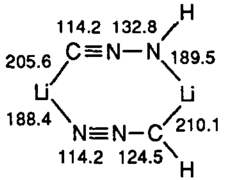
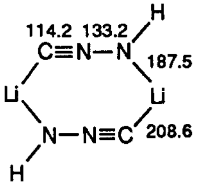
As indicated before Müller et al. had suggested a H-migration between the anions **2**$^-$ and **2'**$^-$ to be responsible for the formation of *N*-isocyano amine **1c** from **1a**, and vice versa.[5] We will return to the details of the tautomerization **2**-Li(I) $\rightleftharpoons$ **2**-Li(IV) in the next section which is dealing with the favorable dimer formation of the lithium species **2**-Li.

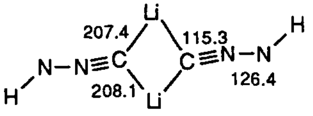
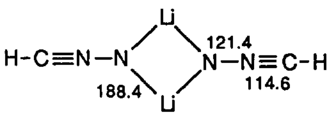
Before, we would like to comment on some of the calculated bond lengths in the **2**-Li isomers (MP2/6-311++G(d,p) level). In the lithiated diazomethane **2**-Li(I) the C-N bond (131.3 pm) is almost as long as in diazomethane **1a** (131.6 pm); the same is true for the N-N bond: **2**-Li(I) 115.5 pm; **1a** 114.2 pm. Small differences in the bond lengths are also observed between **2**-Li(IV) (C-N 120.2 pm; N-N 134.8 pm) and **1c** (C-N 118.7 pm; N-N 135.8 pm). The bent *C*-lithiated **2**-Li(II) (C-N 120.1 pm; N-N 128.0 pm) corresponds to the bent nitrile imine **1b** , while larger differences are observed between the *N*-lithiated **2**-Li(III) (C-N 121.7 pm; N-N 121.7 pm) and **1b** (C-N 118.8 pm; N-N 126.3 pm). It is especially the N-N bond which becomes shorter in **2**-Li(III).

4. Ab initio Calculations of 2-Li Dimers

Since organolithium compounds like **2**-Li have high energies of dimerization (in general: aggregation) we originally wanted to know about the energy gain on their dimerization. A closer look at the dimer structures then revealed that the H-migration between the **2**-Li isomers as discussed in section 3 actually might occur within the dimers (a similar situation might be expected in higher aggregates as, e.g. **2**-Li tetramers which however have not been calculated because of computer time). Table 4 summarizes the results.

Table 4. MP2/6-311++G(d,p)//HF/611++G(d,p) Structures and Energies of the Dimers [2-Li(I)]$_2$, [2-Li(I)·2-Li(IV)], [2-Li(IV)]$_2$, [2-Li(II)]$_2$ and[2-Li(III)]$_2$; E_{Dim} [kcal/mol] is Related to the Energy of the two Monomers; E_{rel} [kcal/mol]; Bond Lengths [pm]. Cartesian Coordinates of the Dimers are available on request.

			
	[2-Li(I)]2	[2-Li(I)·2-Li(IV)]	[2-Li(IV)]2
E_{rel}	0.0	–6.3	–14.3
$E_{Aggr.}$	–55.7	–59.7	–65.5

		
	[2-Li(II)]2	[2-Li(III)]2
E_{rel}	+20.2	+9.9
$E_{Aggr.}$	–43.5	–56.7

As one can see from Table 4 all dimers are very favorably formed. The dimerization energies $E_{Dim.}$ extend from -43.5 kcal (four-membered ring dimer [**2**-Li(II)]$_2$) to -65.5 kcal/mol (eight-membered ring dimer [**2**-Li(IV)]$_2$). One can therefore assume that the dimers exist also in solution even if the Li atoms are solvated (e.g. with THF).

The most stable dimer is the Li-*N*-isocyano amine dimer [**2**-Li(IV)]$_2$. It is 14.3 kcal/mol more stable than the Li-diazomethane dimer [**2**-Li(I)]$_2$. This result indicates that the Li-*N*-isocyano amine isomer should be even more stable due to aggregation than concluded from the calculations of the monomers **2**-Li(I) - **2**-Li(IV), see Table 3.

In the three eight-membered ring dimers of Table 4 the sequences of atoms in the rings are the same. The differences come from the positions of the hydrogen atoms: at C in [**2**-Li(I)]$_2$, at N in [**2**-Li(IV)]$_2$, and at C and N in the mixed dimer [**2**-Li(I)·**2**-Li(IV)]. The atom topology of this mixed dimer suggests it to be composed either of **2**-Li(I) and **2**-Li(II), or **2**-Li(IV) and **2**-Li(III). However, as one can see from the bond lengths of the C-N-N units, it contains the two most stable C-N-N fragments as found in the dimers [**2**-Li(I)]$_2$ and [**2**-Li(IV)]$_2$. The most significant geometry changes on going from the monomers **2**-Li(I) - **2**-Li(IV) to the dimers of Table 4 is the shortening (ca. 6 pm) of the C-N bonds.

How do these dimers relate to the tautomerization **2**-Li(I) $\rightleftharpoons$ **2**-Li(IV) which seems to play a crucial part in the "double tautomerization" **1a** $\rightleftharpoons$ **1c**? The reaction scheme is outlined in Scheme 1.

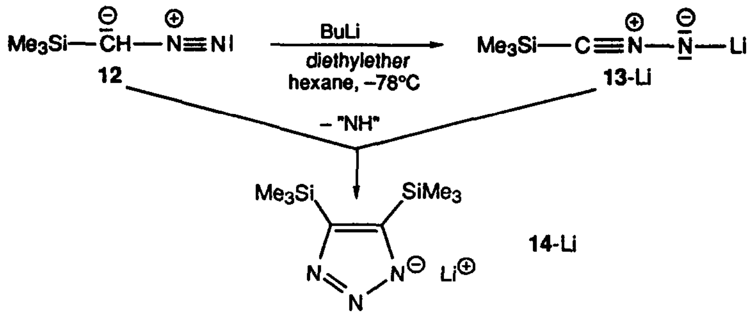
Starting from diazomethane **1a** the reaction with base first leads to the monomeric lithiated diazomethane **2**-Li(I) which forms very favorably (-55.7 kcal/mol) the dimer [**2**-Li(I)]$_2$. Cleavage of [**2**-Li(I)]$_2$ into the two monomers **2**-Li(III) is even more unlikely (66.6 kcal/mol) than cleavage into two **2**-Li(I). Instead, migration of one hydrogen atom in [**2**-Li(I)]$_2$ from carbon to nitrogen gives the slightly more stable (-6.3 kcal/mol) mixed dimer [**2**-Li(I)·**2**-Li(IV)]. A second hydrogen migration in [**2**-Li(I) ·**2**-Li(IV)] from C to N gives the most stable Li-dimer [**2**-Li(IV)]$_2$. Again, the formation of either the two monomers **2**-Li(II) (78.0 kcal/mol) or the two monomers **2**-Li(IV) (65.5 kcal/mol) is highly unlikely. Protonation of the dimer [**2**-Li(IV)]$_2$ at the lithiated N atoms under kinetic control then leads mainly to *N*-isocyano amine **1c**.

In summary, the calculations especially with correlated wave functions of diazomethane **1a** and its isomers **1b** and **1c**, as well as the lithiated "diazomethanes" **2**-Li(I), **2**-Li(II), **2**-Li(III) and **2**-Li(IV), and their dimers, have shed some light on the complex mechanisms involved in the transformations of **1a** into **1c**, and vice versa, as experimentally investigated by Eugen Müller and his coworkers. The result is determined 1. by the kinetically controlled *N*-protonation of the most stable Li-dimer [**2**-Li(IV)]$_2$, and 2. by the thermodynamically most stable H_2CN_2 isomer diazomethane **1a** under reversible deprotoanion/protonation conditions.

In the next section we will care about the entirely different chemistry of monosubstituted diazomethanes and their metalated species.

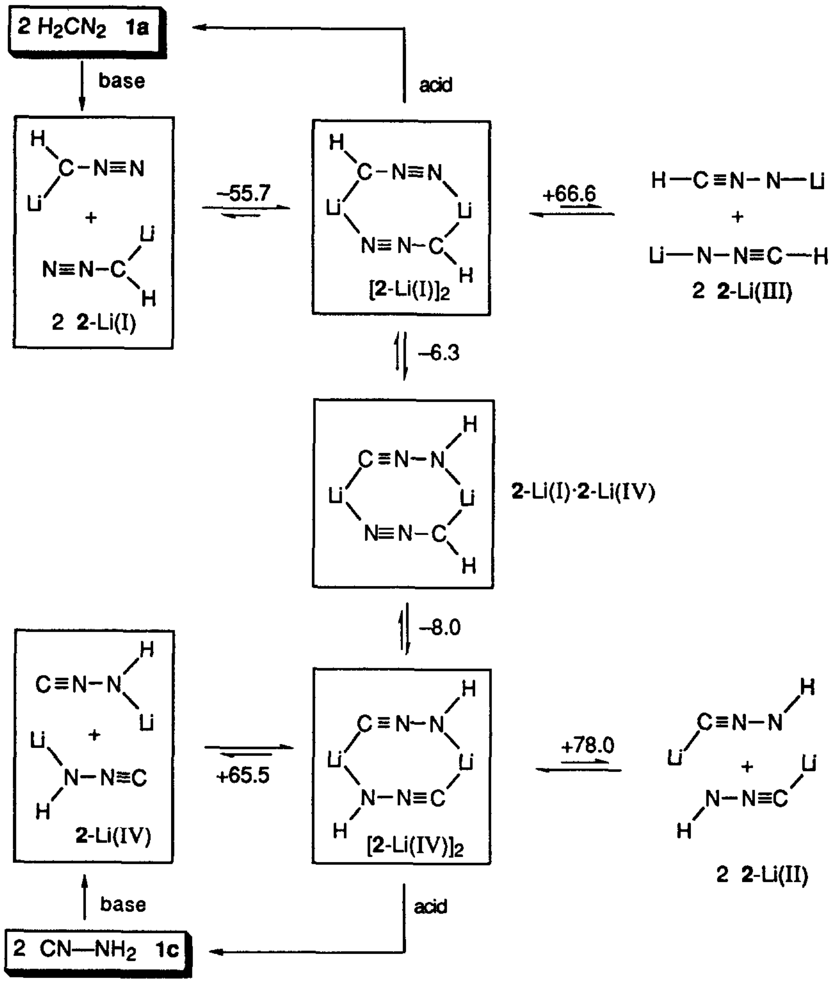
5. The First Crystal Structure of a Lithiated (Substituted) Diazomethane: [6 Lithio-Trimethylsilyl-Diazomethane·2 Lithio-4,5-Bis(trimethylsilyl)-1,2,3-Triazole · 6 Diethyl Ether · Hexane]

The results of the calculations as outlined in section 3 and 4 raise the question whether it is possible to examine the structure of a metalated "diazomethane" by means of an X-ray crystal structure determination. Since so far we have been unable to get crystals of a metalated parent diazomethane ($HC(Li)N_2$ and $HC(Na)N_2$ are rather insoluble and explosive) we turned to lithiated trimethylsilyl-diazomethane **13**-Li which is easily prepared from trimethylsilyl-diazomethane **12** and butyllithium in diethyl ether/hexane[16] (Eq. 2).



(2)

Scheme 1. Transformation of Diazomethane **1a** into *N*-Isocyano Amine **1c** Via Various Monomeric (**2**-Li) and Dimeric ([**2**-Li]$_2$) Lithiated Species; E_{rel} in kcal/mol.



13-Li, which is of importance in the synthesis of heterocycles,[17] is stable even at room temperature. The X-ray structure determination of crystals from the reaction mixture (Eq. 2) nicely corroborate the special behaviour of mono-substituted diazomethanes as observed by Müller et al. and outlined in section 1: **13-Li** crystallizes together with the lithiated 4,5-bis(trimethylsilyl)-1,2,3-triazole **14-Li** to give crystals of the composition [6 **13-Li** · 2 **14-Li** · 6 Et_2O · hexane], see Figure 1.[18]

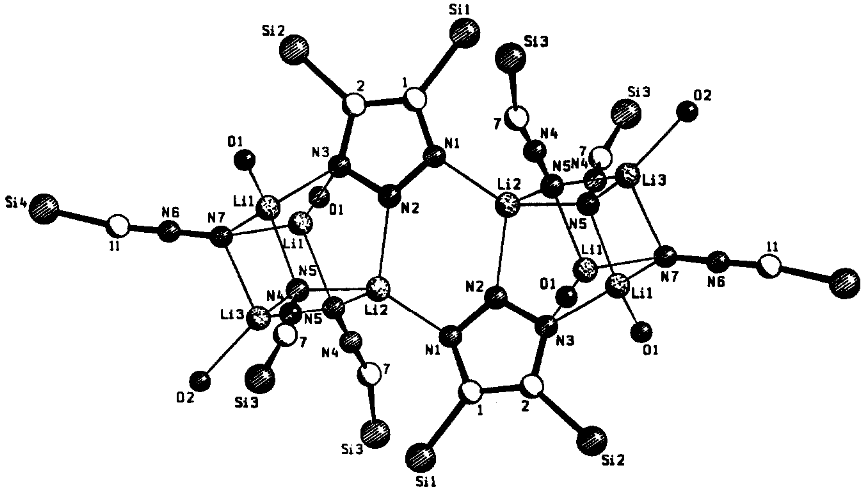
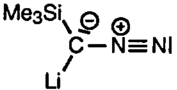


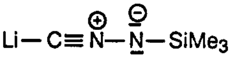
Figure 1. Crystal structure of [6 **13-Li** · 2 **14-Li** · 6 Et_2O · hexane]. The hexane molecule, the methyl groups of the Me_3Si-substituents and the ethyl groups of the six diethyl ether molecules have been omitted for clarity.

In the almost linear **13-Li** units (Si4-C11-N6 172.4(9)°; C11-N6-N7 179.6(9)°) Li is only bonded to the terminal N atom N5 (N7) (three bonds to three Li). Tetra-coordination of Li results from contacts with the nitrogen atoms of the triazole units **14-Li**, which are apparently excellent ligands, and diethyl ether molecules. A Li-C bond is not observed in **13-Li**. This structure of **13-Li** (**13-Li(III)**) thus corresponds to that of the *N*-lithiated nitrile imine **2-Li(III)**, see section 3, Table 3, a rather unstable **2-Li** isomer!



$Me_3Si(Li)\overset{\ominus}{C}-\overset{\oplus}{N}{\equiv}N|$

13-Li(I)

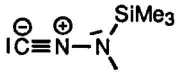


$Li-C{\equiv}\overset{\oplus}{N}-\overset{\ominus}{\underline{N}}-SiMe_3$

13-Li(II)

$Me_3Si-C{\equiv}\overset{\oplus}{N}-\overset{\ominus}{\underline{N}}-Li$

13-Li(III)



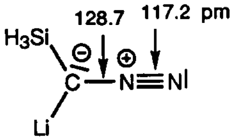
$|\overset{\ominus}{C}{\equiv}\overset{\oplus}{N}-\overline{N}(SiMe_3)Li$

13-Li(IV)

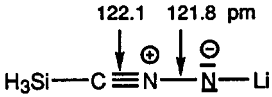
Thus, at least in the crystal the lithiated diazomethane type structure **13-Li(I)** with Li at carbon is less favorable than **13-Li(III)**. It is also interesting to note that the trimethylsilyl group does not migrate to the terminal N atom (as hydrogen does, see sections 4 and 5), otherwise one might find an *N*-isocyano amine type structure (**13-Li(IV)**), the most favorable one of the $HC(Li)N_2$ isomers **2-Li**. Likewise the *C*-lithiated nitrile imine **13-Li(II)** is not observed.

In order to find out whether the lithiated diazomethane type structure **13-Li(I)** indeed is not preferred to **13-Li(III)** - one should remember that in the unsubstituted case **2-Li(I)** is calculated to be between 1.3 and 9.7 (12.0) kcal/mol more stable than **2-Li(III)**, see Table 3 - we performed MP2/6-31G(d) calculations of the model

Li species **15**-Li(I) and **15**-Li(III) in which the trimethylsilyl group is replaced by a SiH_3 group. The relative energies [kcal/mol] and the bond lengths [pm] of the two species are given below.



15-Li(I); 0.0 kcal/mol



15-Li(III); −1.4 kcal/mol

Once more the calculations are in agreement with the experimental results:

1. The relative energies in the case of the silylated **15**-Li are in favor of the *N*-lithiated nitril imine isomer **15**-Li(III) although only slightly: **15**-Li(III) is 1.4 kcal/mol more stable than **15**-Li(I); correspondingly, in the X-ray structure of lithiated trimethylsilyl-diazomethane the **13**-Li(III) structural type was found, see Fig. 1.
2. The experimentally determined bond lengths in **13**-Li(III) (C11-N6 118.5(12); N6-N7 122.3(10) pm) are in decent agreement with the calculated ones of the model compound **15**-Li(III) (see above).
3. **15**-Li(III) is calculated to be linear which is essentially the case for **13**-Li(III) in the crystal (see above).

Finally, we would like to hint to the changes in the bond lengths on going from diazomethane **1a**[15] to the *C*-silylated Li-compound **13**-Li(III): the C-N bond shortens from 132 pm (**1a**) to 118.5(12) pm (**13**-Li(III)), while the N-N bond is elongated from 112 pm (**1a**) to 122.3(10) pm. It is probably the shortened C-N bond in **13**-Li(III) which makes this compound rather stable (e.g. against loss of N_2).

Judging from the chemistry of metalated phenyldiazomethane (e.g. **4**-Na) and diazoethane (e.g. **8**-Li) - see section 1 - it seems that these compounds have structures which correspond to that of the silylated **13**-Li(III).

6. How are the Reaction Products Triazole and Base-Derived Amine Formed in the Case of the Mono-substituted Diazomethanes?

As outlined in more detail in section 1 Müller et al.[6] found the triazole **10** and methylamine **11** when they reacted diazoethane **6** first with methyllithium **7**-Li to give the lithiated diazoethane **8**-Li, followed by protonation of the reaction mixture. It is important to note that the triazole **10** was only formed in the presence of both **8**-Li *and* diazoethane **6**. The formation of a corresponding triazole (**5**) has earlier been found in the reaction of phenyldiazomethane **3** with base[2]. The lithiated triazole **14**-Li as discovered in the crystals of [6 **13**-Li · 2 **14**-Li · 6 Et_2O · hexane] is another proof for this reaction pathway , see section 6. Taking the reaction of diazoethane **6** with methyllithium **7**-Li as a typical example the following questions arise: How is the suggested intermediate **9**-Li formed? How does **9**-Li give the triazole **10**? Which reactions lead to methylamine **11**?

We will first study the cyclization reaction to give the triazole topology and then care about the consecutive chemistry.

In order to get more informations on the cyclization reaction we performed a theoretical investigation by means of the MNDO method. From the crystal structure of [6 **13**-Li · 2 **14**-Li · 6 Et_2O · hexane] and the calculations of $H_3Si\text{-}C{\equiv}N^+\text{-}N^-\text{-}Li$ **15**-Li(III) it was concluded that the lithiated nitril imine $H\text{-}C{\equiv}N^+\text{-}N^-\text{-}Li$ **2**-Li(III) is a good model for the lithiated substituted diazomethanes involved in this reaction. The reaction coordinate of the reaction of **2**-Li(III) with diazomethane **1a**, which serves as a model for the substituted diazomethanes, is shown in Figure 2. As mentioned above, it is the reaction of the metalated with the non-metalated substituted diazomethane which leads to the triazole ring.

As one can see from Figure 2 the first product from the reaction of **2**-Li(III) with **1a** is the complex **2**-Li(III)·**1a** in which diazomethane **1a** is end-on bonded to **2**-Li(III). The favorable formation of complexes of lithium compounds with electrophiles (here: -11.7 kcal/mol) is also documented in other cases.[19] In the complex **2**-Li(III)·**1a** one already finds the connectivity of atoms which is significant for the following events. The potential surface around **2**-Li(III)·**1a** is rather shallow which allows easily a bending of the linear structure to lead via the transition state **16**$^{\neq}$ to the C-C connected intermediate **17**. **16**$^{\neq}$ is only 10.5 kcal/mol higher in energy than the reactands **2**-Li(III) and **1a**.[20] Due to its intramolecular character the reaction **2**-Li(III)·**1a** → **17** is also favorable entropy-wise.[22] The energy set free on formation of **17** (-57.2 kcal/mol) is more than enough to overcome the transition state **18**$^{\neq}$ (21.7 kcal/mol) which leads via formation of an N-N bond to the five-membered ring species **19** (-64.0 kcal/mol). Although we could not localize a transition state of the isomerization (H-migration) **19** → **20**, the latter should be formed in a facile manner because it is another 18.0 kcal/mol more stable than **19**. The MNDO model calculations thus reveal that the *N*-lithiated *N*-amino triazole **20** as similarly formulated by Eugen Müller in the reactions of phenyldiazomethane or diazoethane with base indeed is a rather stable species formed in a cascade of reactions.

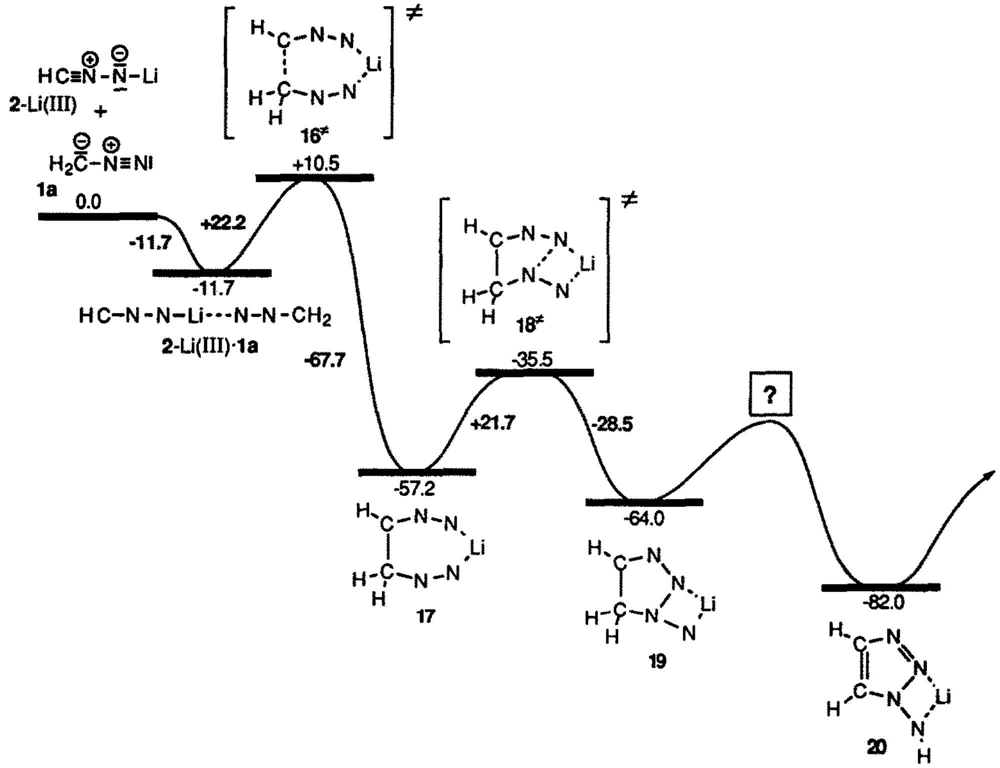
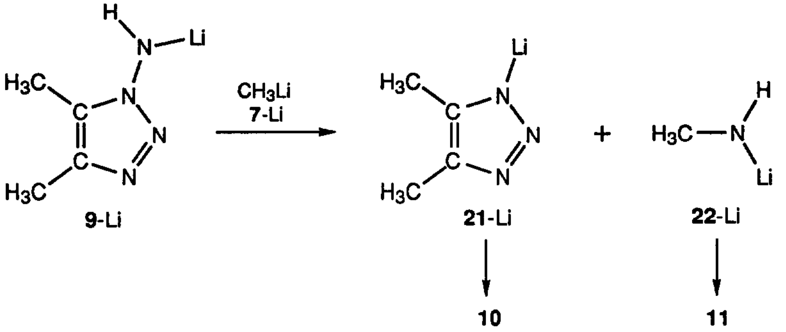


Figure 2. MNDO Reaction Coordinate of the Model Reaction Lithiated Nitril Imine **2**-Li(III) with Diazomethane **1a**; E_{rel} in [kcal/mol]

The formation of the final products triazole **10** and methylamine **11** from the intermediate **9**-Li (Eq. 3) is easily understood.



(3)

A closer look on **9**-Li reveals its nitrenoid character: it has a metal (Li^+) and an excellent leaving group (the corresponding triazole anion) at the same nitrogen atom. Similar nitrenoids have been shown to react as electrophiles with nucleophiles like methyllithium **7**-Li[23,24] to give - in the above case - the lithiated triazole **21**-Li and the lithiated methylamine **22**-Li which on protonation lead to **10** and **11**.

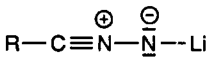
Müller's puzzle - "wie diese an sich bekannte Abspaltung im einzelnen erfolgt, ist nicht geklärt" ("it is not at all clear how this cleavage reaction occurs in detail") - thus is solved.

7. The Different Structures and Reactions of Lithiated (Metalated) Diazomethane and Mono-Substituted Diazomethanes, Respectively

What are the reasons for the completely different behaviour in the reactions of 1. diazomethane **1a** and 2. mono-substituted diazomethanes like phenyldiazomethane **3**, diazoethane **6** or trimethylsilyldiazomethane **12** with base followed by protonation?

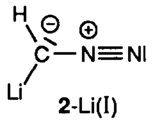
The results of the investigations outlined in this work point to the *different structures of the corresponding metalated species and their different reactivities (selectivities).*

If an *N*-lithiated (metalated) nitril imine type structure like the silylated **13**-Li(III) is formed it evidently reacts very fast with not yet deprotonated mono-substituted diazomethane - in this case **12** - finally to give the corresponding triazole and the base-derived amine. Phenyldiazomethane **3** (with **4**-Li(III)) and diazoethane **6** (with **8**-Li(III)) react in a similar manner.

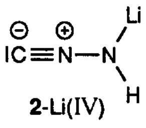


$R-C\equiv\overset{\oplus}{N}-\overset{\ominus}{\underline{\overline{N}}}-Li$

R :	Ph	Me	Me3Si
	4-Li(III)	8-Li(III)	13-Li(III)



2-Li(I)



2-Li(IV)

In contrast, the predominantly formed Li compounds **2**-Li(IV) and (some) **2**-Li(I) in the case of the parent diazomethane **1a** seem not to react with not yet deprotonated diazomethane **1a**.

Rather these Li compounds await the further reaction with protons: **2**-Li(IV) (respectively its dimer $[2\text{-Li(IV)}]_2$) is predominantly *N*-protonated to give *N*-isocyano amine **1c**, and **2**-Li(I) (respectively its dimer $[2\text{-Li(I)}]_2$) is predominantly *C*-protonated to give diazomethane **1a**.

The chemistry of lithiated (metalated) "diazomethanes" thus provides a lucid example about isomeric organometallic compounds, their different structures, and different reactivities (selectivities). Once more the agreement between model calculations and experimental results is encouraging.

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