{6 Lithio(trimethylsilyl)diazomethane · 2 Lithio[4,5-bis(trimethylsilyl)triazene] · 7 Diethyl Ether}: The First X-Ray Structure Analysis of a Lithiated Diazoalkane

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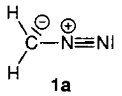
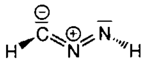
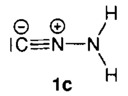
The crystals of {6 lithio(trimethylsilyl)diazomethane · 2 lithio[4,5-bis(trimethylsilyl)triazene] · 7 diethyl ether} provide for the first time insight into the structure of a lithiated diazomethane, namely that of lithiated (trimethylsilyl)diazomethane (**11c**). Furthermore, the crystals contain lithiated 4,5-bis(trimethylsilyl)triazene (**12**), a reaction product of (trimethylsilyl)diazomethane and its Li compound **11c** which is analogously found in deprotonation/protonation reactions of other monosubstituted diazomethanes. This structure, together with quantum chemical calculations, leads to a better understanding of the so far rather complex chemistry of lithiated (monosubstituted) diazoalkanes.

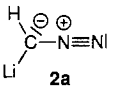
The chemistry of metallated (monosubstituted) diazomethane(s) has been investigated by E. Müller and his group over a long period of time[1]. Two aspects of these studies are especially remarkable.

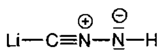
i) Deprotonation of the parent compound diazomethane (**1a**), followed by protonation with acid, leads to "isodiazomethane"[1] which turned out to be *N*-isocyanoamine **1c**[1f]. In the presence of sodium hydroxide in water, however, **1c** is transformed back to **1a**. The other possible noncyclic CH_2N_2 isomer **1b**, a nitrile imine, was never detected.


1a


1b

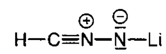

1c


2a



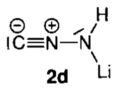
$\mathrm{Li{-}C{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{\underline{N}}{-}H}$

2b



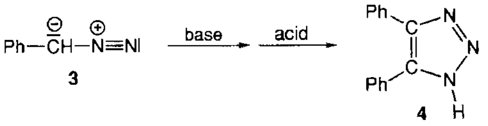
$\mathrm{H{-}C{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{\underline{N}}{-}Li}$

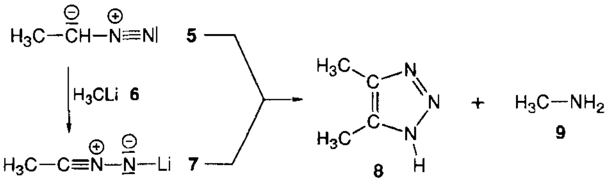
2c


2d

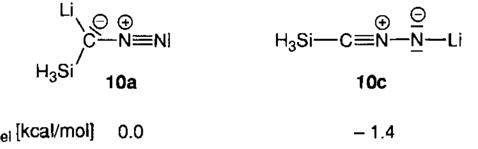
We have recently calculated the structures and energies of the CH_2N_2 isomers **1a–c** as well as their lithiated derivatives **2a–d**[2]. It was found that **2d** is the most stable Li isomer. From these experimental and theoretical results one can conclude, that *N*-protonation of **2d** gives **1c**. Furthermore, the transformation **1c** → **1a** in the presence of $NaOH/H_2O$ should occur because diazomethane (**1a**) is the most stable CH_2N_2 isomer being formed by *C*-protonation of **2a**, the second most stable Li isomer. Under basic conditions ($NaOH/H_2O$) **2d** should be in equilibrium with **2a** [**2d** $\rightleftharpoons$ **2b**(**c**) $\rightleftharpoons$ **2a**].

ii) When monosubstituted diazomethanes $RCHN_2$ like phenyldiazomethane (**3**)[1b] or diazoethane (**5**)[1i] were studied, the deprotonation/reprotonation experiments by Müller et al. led to a completely different result. **3** gave the 4,5-diphenyltriazol (**4**), while in the case of diazoethane (**5**), with methyllithium (**6**) being the base, besides the 4,5-dimethyltriazol (**8**) methylamine (**9**) was isolated.





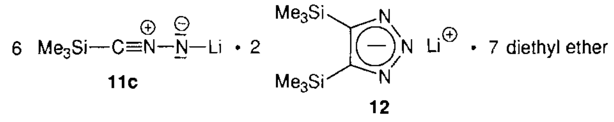
Müller et al. found[1b,i] that **4**, and **8** + **9**, respectively, are only formed if the monosubstituted diazomethanes $RCHN_2$ and the corresponding Li compounds as, e.g., **5** and **7** are simultaneously present which indicates a reaction of **5** with **7**. From model calculations with the monosubstituted Li compounds **10a** and **10c** it was concluded[2a] that – in contrast to the parent **2a** and **2c** – the nitrile imine isomer **10c** is more stable than the *C*-lithiated diazomethane isomer **10a**[3].



What are the structures of lithiated (monosubstituted) diazomethane(s)? Do they agree with the above-mentioned experimental and quantum chemical results which indicate the highest stabilities for the parent **2d** and the structural type **10c** in the case of monosubstituted Li-diazomethanes?

Results and Discussion

So far we have been unable to get monocrystalline material of the parent lithiated (metallated) diazomethane. In the following we report on the structural details of lithiated (trimethylsilyl)diazomethane[4] which crystallizes in the form of {6 lithio(trimethylsilyl)diazomethane · 2 lithio[4,5-bis(trimethylsilyl)triazene] · 7 diethyl ether} (6 **11c** · 2 **12** · 7 diethyl ether), the crystal structure of which is shown in Figure 1.



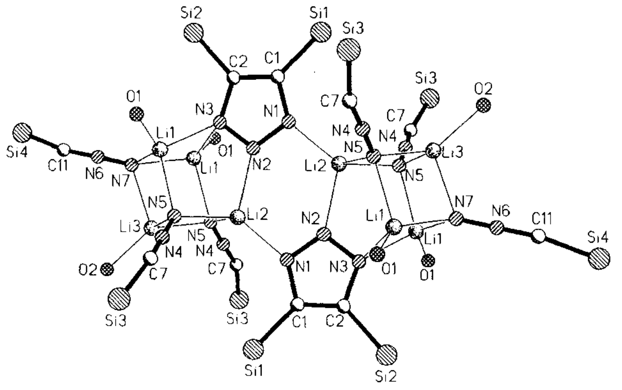
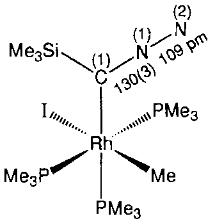


Figure 1. Crystal structure of [6 **11c** · 2 **12** · 7 diethyl ether]. The methyl groups of $SiMe_3$, the ethyl groups of diethyl ether, and the uncoordinated diethyl ether molecule have been omitted for the sake of clarity. Symmetry-equivalent atoms have been given the same label

The supramolecular structure is composed of two halves which are connected by the two N1−Li2 bonds [201.3(9) pm]. A similar connectivity has recently been found in [Li-benzotriazene · 2 DMSO]$_\infty$[5]. N1−N3 belong to the 4,5-bis(trimethylsilyl)triazenyl anions which are excellent ligands for lithium cations as one can judge from the interactions with four lithium cations: in addition to the N1−Li2 bond one observes a Li2−N2 bond [208.4(8) pm] and two N3−Li1 bonds [214.7(7) pm] for each anion. The incorporation of the two 4,5-bis(trimethylsilyl)triazenyl anion units into the crystal shows also their facile formation even under the low temperature conditions of the preparation of **11c** (deprotonation with *n*-BuLi in diethyl ether/hexane at −78°C and crystallization at −28°C). This situation corresponds nicely to the results described above for the two other monosubstituted diazomethanes, namely phenyldiazomethane (**3**) and diazoethane (**5**) and their reactions with base. The bond lengths in the five-membered rings are as follows: N1−N2 134.6(6), N2−N3 133.2(5), N1−C1 136.9(6), N3−C2 137.8(6), C1−C2 140.1(7). Most significantly, the Me_3SiCNN units are end-on bonded to three lithium cations: N7 to two Li1 [204.6(7) pm] and to Li3 [204.7(9) pm], and N5 to Li1 [204.2(7) pm], Li2 [209.4(6) pm], and Li3 [205.0(7) pm]. The atoms Li1, N3, Li1, N7, N5, Li2, N5 and Li3 form a distorted cube in which N2 is placed between Li2 and N3. The structures of the lithiated trimethylsilyl diazomethane units **11c** thus agree with the results of the model calculations: the nitril imine type model $H_3SiCNNLi$ **10c** was found to be more stable than the C-lithiated model **10a**. The following bond distances and angles have been determined for the two slightly different types of $(Me)_3SiCNN$ anions (two Si4−C11−N6−N7 and four Si3−C7−N4−N5 anions) in the crystal: Si4−C11 176.7(8) pm, C11−N6 120.6(9) pm, N6−N7 119.4(6) pm; Si4−C11−N6 166.2(5)°, C11−N6−N7 178.8(6)°, and Si3−C7 176.0(5) pm, C7−N4 120.0(6) pm, N4−N5 121.5(4) pm; Si3−C7−N4 162.4(5)°, C7−N4−N5 178.9(4)°. The experimentally determined C−N bond lengths [120.6(9) and 120.0(6) pm, respectively] and the calculated one (**10c**: 122.1 pm) as well as the N−N bonds (exp. 119.4 and 121.5 pm; calcd. 121.8 pm) are in agreement. The same holds for the calculated linearity of **10c** and the bond angles of **11c**: the C−N−N bond angles (178.8 and 178.9°, respectively) amount almost to the calculated one (180°). The experimentally determined Si−C−N angles deviate more strongly from 180° (166.2 and 162.4°, respectively). The mean value of the C−N bonds in five stable nitril imines amounts to 116.9 pm[2d] which is ≈2.5 pm shorter than the C−N bonds in the *N*-lithiated nitril imines **11c**, while the mean N−N bond length (126.3 pm[2d]) is ≈6 pm longer than the N−N bonds in **11c**. Compared with diazomethane **1a** (exp. values[6] C−N 132 pm, N−N 112 pm) the C−N bonds in **11c** are strongly shortened to 120.6 (119.4) pm, while the N−N bonds elongate to 119.4 (121.5) pm. The shorter C−N bonds in the "anions" **11c** might explain the rather high stability of the lithiated (trimethylsilyl)diazomethane **11c** against loss of N_2 which makes it a very useful reagent in organic synthesis[7]. For that purpose the deprotonation of (trimethylsilyl)diazomethane has to give "instantaneously" the Li compound **11c** in order to avoid the formation of the triazene "anion" **12**. This is achieved by deprotonation in tetrahydrofuran instead of ether/hexane[7].

The rather small energy preference calculated for the *N*-lithiated model compound **10c** as compared to the *C*-lithiated (trimethylsilyl)diazomethane isomer **10a** (1.4 kcal/mol) suggests an equilibrium between the Li compounds **10a** and **10c** (and a similar situation in other Li compounds of that structural type). Furthermore, in the case of other metals than lithium a preferred binding of the metal to the carbon instead to the nitrogen atom seems likely. It is therefore not surprising that iodomethyltris(trimethylphosphane)rhodium(III) (trimethylsilyl)diazomethane $[Rh(ICH_3)(PMe_3)_3\text{-}Me_3SiCN_2]$ (**13**) corresponds exactly to the structural type **10a**[8].



13

13 is sp²-hybridized at C1 while the diazomethane carbon atoms in **11c**, C7 and C11, respectively, are sp-hybridized.

Correspondingly C1−N1 in **13** is longer [130(3) pm] than the analogous bonds in **11c** [120.6(9), (120.0(6) pm]. The calculated value for the model **10a** is 128.7 pm which corresponds nicely to the findings in **13**. N1−N2 in **13** amounts to 109 pm which is "remarkably short"[8]: the model calculations (**10a**) led to 117.2 pm. In the case of **11c** the lengths of the N−N bonds [119.4(6) and 121.5(4) pm] agree much better with the model **10c** (121.8 pm).

In conclusion, the completely different chemistry of the parent diazomethane **1a** and monosubstituted diazomethanes like phenyldiazomethane (**3**), diazoethane (**5**), and (trimethylsilyl)diazomethane in deprotonation/reprotonation reactions can be traced back to the different structures of the corresponding Li compounds. While in the case of **1a** calculations indicate the *N*-lithiated *N*-isocyano amine type **2d** to be the most stable isomer, it is the *N*-lithiated nitrile imine type **10c** in the case of the monosubstituted diazomethanes. The proof for the latter case is given in this work: **11c** which corresponds to the structural type **10c** crystallizes together with its Li-triazene reaction product **12** to give [6 **11c** · 2 **12** · 7 diethyl ether].

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Experimental

Preparation of (Trimethylsilyl)diazomethane: This compound was prepared according to Aoyama et al.[7]. On the basis of IR- and NMR-spectroscopic data it corresponds to the substance described in ref.[7].

Preparation of Single Crystal of [6 **11c** · 2 **12** · 7 diethyl ether]: 0.25 ml (0.50 mmol) of a 2 M solution of (trimethylsilyl)diazomethane in hexane was treated at −78°C in the presence of 0.3 ml diethyl ether with 0.34 ml (0.54 mmol) of a 1.6 M solution of *n*-butyllithium in *n*-hexane. After 1 h at −78°C the solution was cooled down for a few seconds to −196°C. Afterwards crystals suitable for X-ray structural analysis had formed on standing for 3 d at −28°C.

Crystal Structure Investigation of [6 **11c** · 2 **12** · 7 diethyl ether]: $C_{68}H_{160}Li_8N_{18}O_7Si_{10}$ (1678.56); monoclinic space group $C2/m$, a = 2335.6(5), b = 1607.8(3), c = 1540.2(3) pm, β = 101.92(3)°, V = 5659(2) pm^3 · 10^6, Z = 2, D_c = 0.985 g · cm^{-3}, $\mu(MoK_\alpha)$ = 1.62 cm^{-1}. Diffractometer: Enraf-Nonius CAD4, MoK_α radiation, graphite monochromator, T = 293(5) K, ω scans. 3817 reflections measured (Θ_{max} = 22.2°), 3707 independent (R_{int} = 0.0859). The structure was solved by direct methods[9] and refined[10] on F^2 with all independent reflections, all non hydrogen atoms anisotropic, hydrogen atoms with fixed isotropic temperature factors on calculated positions. Three of the four independent trimethylsilyl groups [with Si(1), Si(2) and Si(4)] and the two independent diethyl ether molecules (with O1 and O2) connected to Li were disordered and have been refined with restraints for geometry and temperature factors. Remaining peaks in the difference Fourier synthesis have been refined in that way that the formula sum of diethyl ether has been fitted. Due to the poor crystal quality and the disorder of a big part of the structure the full-matrix least squares refinement (on F^2) converged two wR^2 = 0.2531 (all data, calculated on F^2, goodness-of-fit = 1.057), and to the conventional $R1$ = 0.0853 [calculated for 3350 reflections with $I > 2\sigma(I)$] for 372 parameters and 156 restraints. Weighting scheme: $w^{-1} = \sigma^2(F_o)^2 + (0.1498p)^2 + 12.1724p$ where $p = (F_o^2 + 2F_c^2)/3$. The extinction parameter x was 0.0030(8). All calculations have been performed on a Micro Vax II and a DEC AXP 3000−300. − Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, under specification of the deposition no. CSD 400714, the names of the authors, and the journal reference.

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