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Carbenoids, Nitrenoids, Oxenoids: Very Electrophilic „Anions“

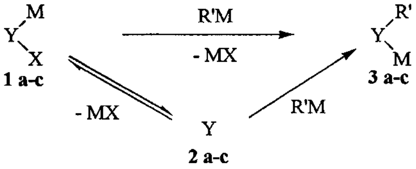
Gernot Boche*

Fachbereich Chemie, Philipps-Universität Marburg,
D-35032 Marburg, Germany

Abstract: The rather interesting question why the "anionic" carbenoids **1a**, nitrenoids **1b** and oxenoids **1c** react so easily with nucleophiles is answered by experimental investigations of their structure and by means of quantumchemical calculations. It turns out that the bond to the leaving group (C(N,O)-X is weakened (elongated), and that the energy of the $\sigma^*_{C(N,O)-X}$ orbital is lowered. This allows for a more facile substitution of X^- by a nucleophile. The substitution of X^- is further supported by the metal cation M^+.

INTRODUCTION

Carbenoids **1a** as well as the related nitrenoids **1b** and oxenoids **1c** have something in common which is not observed in the case of "normal anions": besides the usual reaction with electrophiles they also react with *nucleophiles*, as e.g. organolithium species R'Li, to give the substitution products **3**.



a : Y = R_2C ; **b** : Y = RN ; **c** : Y = O
M = Li, Na, K, MgX, ZnX ; X = Hal, OR

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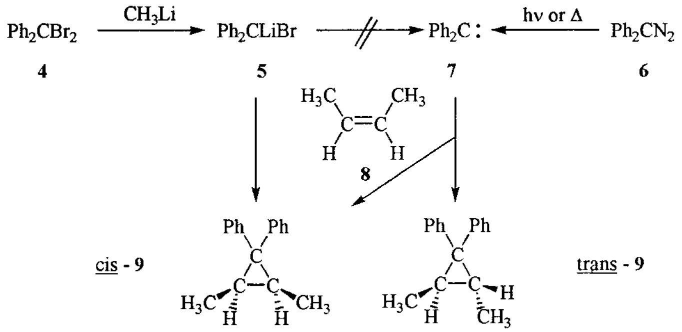
This rather astonishing *electrophilic* behaviour of the "anionic" **1** has intrigued chemists from the very beginning of the discovery of **1**. Concomitantly the question was raised about the reason for this unexpected property. Furthermore, one had to exclude that the reaction actually started with an α-elimination of MX at **1** to give first the six-electron intermediates **2** which are expected to react very fast with nucleophiles like R'Li also to give **3**. Since carbenoids **1a** are the most intensively studied species discussed here, it is first shown that in most cases indeed **1a** reacts with nucleophiles - even with much weaker nucleophiles than organolithium compounds. Then structural investigations of **1** are reported which agree perfectly with the electrophilicity of **1**. Quantumchemical calculations support these experimental findings and lead to a final understanding of the case. Reactions of **1** with electrophiles are not the subject of this article (Ref. 1).

REACTIONS OF **1a-c** WITH NUCLEOPHILES

Compounds of the type **1a** (M = Li, Na, MgX, ZnX; X = Hal, OR) have been prepared for the first time by Wittig et al. in 1941 (Ref. 2a), although their properties were not investigated systematically at that time. The term "carbenoid molecule" was coined in 1962 by Closs and Closs (Ref. 3), and later changed into "carbenoid" by Closs and Moss (Ref. 4). These authors noticed that e.g. diphenyldibromomethane **4** and methyllithium reacted stereospecifically with the olefin (*Z*)-**8** to give only the cyclopropane *cis*-**9**, while Skell et al. (Ref. 5) had found that the photolysis of diphenyldiazomethane **6**, which is known to lead to the diphenylcarbene **7**, resulted in the presence of the olefin (*Z*)-**8** in a mixture of *cis*-**9** and *trans*-**9**.



Thus, **5** is not the desired "carbene precursor" like **6**. Rather it shows an electrophilic reactivity with a CC double bond of its own kind. The S_N2-type transition state for the reaction of **5** with **8** with a backside attack of the π-orbital of **8** at the $\sigma^*_{C\text{-}Br}$-orbital of **5** as proposed by Closs et al. (Ref. 3,4) was supported by theoretical investigations (Ref. 6). A recent study of the intramolecular cyclopropane formation of diastereomeric carbenoids provided the proof for the preferred S_N2-type transition state topology (Ref. 7).

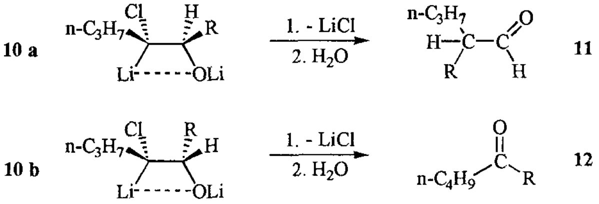
At this point the question arises whether it is always the carbenoid which reacts with the CC double bond (in general: a nucleophile). As it turned out this is generally the case except for those examples in which the carbenes are strongly stabilized by appropriate substituents and thus more easily formed, as for example in metalated haloform type pairs like $LiCCl_3/CCl_2$ (Ref. 8,9), and in the case of $LiC(SPh)_3/C(SPh)_2$ (Ref. 10). Hine, in his classical work (Ref. 8), was the first to demonstrate that in aqueous dioxane haloforms are hydrolysed by alkali through dihalocarbenes CX_2 formed from the corresponding MCX_3 species, while Köbrich showed that it is not the carbenoid $LiCCl_3$ but rather the carbene CCl_2 which reacted with olefins (Ref. 9). Furthermore, in a kinetic investigation, it was demonstrated by Seebach (Ref. 10), that $LiC(SPh)_3$ "decomposes" to give finally $(PhS)_2C{=}C(SPh)_2$ via $(PhS)_2C$ as an intermediate. The behaviour of $LiCCl_3/CCl_2$ is in stark contrast to that of, e.g., $LiCHCl_2$ in which case formation of the monochloro-carbene CHCl was never observed (Ref. 11). The significance of the stabilization of the carbene is nicely supported by the $\Delta H^\circ_{f,\,298^\circ}$ values of various carbenes, see Table 1.

Table 1. Heats of formation ($\Delta H^\circ_{f,\,298^\circ}$) [kcal/mol] of carbenes (Ref. 12,13)

$\tilde{a}\,1\,A_1$ CH_2, g (Ref. 12)	$\tilde{x}\,^1A_1$ CCl_2 (Ref. 13)	$\tilde{x}\,^1A_1$ CF_2 (Ref. 13)
101.9 ± 0.5	52.1 ± 3.4	-39.4 ± 3.4

Thus, dichlorocarbene is 49.8 kcal/mol and difluorocarbene even 141.3 kcal/mol more stable than the CH_2 singlet (Ref. 14). The isolation of stable carbenes by Arduengo (Ref. 15), stabilized by two R_2N-, or R_2N- and RS-substituents, highlights the tendency as indicated above.

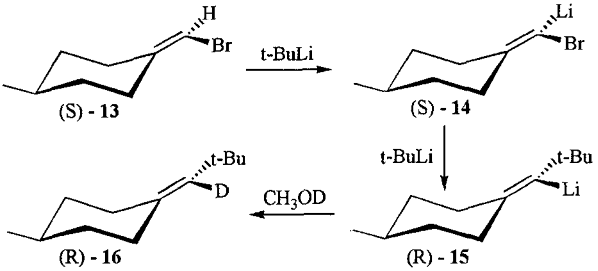
Examples of a carbenoid reacting with a C-C bond were also reported (Ref. 16-19). In a recently published case (Ref. 20) either the neighboring C-C or the C-H bond acts as a nucleophile. In the diastereoisomer **10a**, the C-R bond adopts the prefered conformation for the backside substitution of Cl at the carbenoid carbon atom to give **11**, while in **10b** it is the C-H bond, which leads to the migration of hydrogen to the carbenoid atom finally giving **12**. In both cases the selectivity is 99:1.



It is obvious that only carbenoids with a stereogenic carbon atom like in **10a** and **10b** can undergo such chemoselective rearrangements. If a carbene would be the product determining intermediate, **10a** and **10b** should lead to the same product ratio of **11** and **12**.

Reactions of C-H bonds with α-chlorocyclopropyllithium compounds as electrophiles were reported by Traylor et al. (Ref. 21). They are in agreement with the S_N2-type backside attack of the nucelphile at the carbenoid carbon atom as in **10b**. Inversion of configuration at the carbenoid C atom is also reported from investigations by Oku et al. (Ref. 22). In this case the carbenoid abstracts a hydride H^- from an alkoxide in a bimolecular reaction (Ref. 23,24).

Stereoselective reactions of carbenoids with organometallic compounds RLi have first been reported by Walborsky et al. (Ref. 25). In the reaction of (*S*)-**13** with *t*-butyllithium to give first (*S*)-**14** and then (*R*)-**15**, followed by deuteration with CH_3OD, (*R*)-**16** is formed with 39 (ether) and 53 (THF) % ee.



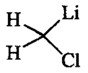
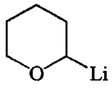
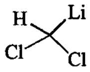
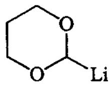
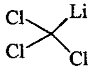
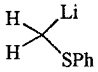
Most importantly, in the reaction of the vinylic carbenoid (*S*)-**14** with t-BuLi inversion of configuration occurs to give (*R*)-**15** as shown by its deuteration to give (*R*)-**16**. Cyclopropyl carbenoids react with "anionic" nucleophiles in a similar S_N2-type fashion with inversion of configuration at the carbenoid C atom (Ref. 25d, 26, 27). It is worth mentioning that "normal" vinylic and cyclopropyl halides are inaccessible to nucleophilic substitution!

All of the examples discussed in this chapter illustrate the high electrophilicity of the "anionic" carbenoids, which is similarly found in reactions of nitrenoids (Ref. 28) and oxenoids with nucleophiles like organolithium compounds RLi (Ref. 29). What is the reason for the strong electrophilic nature of **1a-c**?

STRUCTURAL INVESTIGATIONS AND QUANTUM CHEMICAL CALCULATIONS OF **1a-c**

The first informations about the structure of carbenoids came from ^{1}H-, ^{13}C- and ^{6}Li-nmr investigations by Seebach et al. (Ref. 30). The important discovery was the downfield shift of the carbenoid carbon atom if compared to the nonlithiated species. Normally, organolithium compounds derived from aliphatic hydrocarbons are found to have a highfield shift. The examples in Table 2 illustrate the situation.

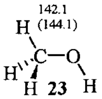
Table 2. Chemical shifts Δδ [ppm] of carbenoid and normal RLi compounds

		CH_3—Li **16**		- 13.0			
17		32.0	[31]	**20**		26.2	[31]
18		50.0	[30]	**21**		40.0	[31]
19		65.9	[30]	**22**		- 10.8	[30]

In methyllithium **16**, the ^{13}C signal is 13.0 ppm at higher field than in methane, while in the carbenoids **17-19** the ^{13}C signal is increasingly shifted towards lower field. A similar observation was made by Boche et al. (Ref. 31) in the Li/OR carbenoid series (see **20** and **21**), while the sulfur-substituted **22** (Ref. 30) obviously has no carbenoid character. Investigation of the ^{13}C-^{6}Li (^{1}H, ^{13}C) coupling contants in carbenoids led to the conclusion that the carbon orbital of the C-Li bond should have higher s-character which leads to more p-character in the other three orbitals (Ref. 30). IGLO-calculation of the chemical shifts in carbenoids (Ref. 32)

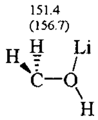
indicate a strong interaction of the electrons in the C-Li bond with the σ^*_{C-X} orbital as the main reason for the strong paramagnetic contribution to the ^{13}C downfield shift.
In a series of publications, Schleyer et al. investigated the properties of carbenoids by means of quantumchemical methods (Ref. 33). As an example , Table 3 gives the results of methanol **23** and the four $LiCH_2OH$ isomers **24a-d** as models for Li/OR carbenoids.

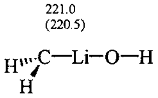
Table 3. MP2/6-311++G(d,p) (Ref. 31a) and (in parenthesis) earlier calculated (Ref. 33d) MP2/6-31G(d) structures of methanol **23** and the $LiCH_2OH$ isomers **24a-d**; bond lengths in [pm]; rel. energies in [kcal/mol].



23

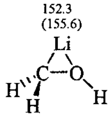
24 c ; 18.0 (19.6)

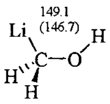




24 d ; 45.7 (50.0)

24 a ; 0.0



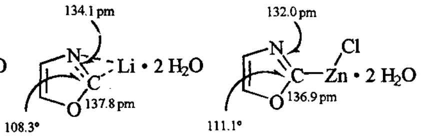


24 b ; 14.0 (13.8)

In the most stable **24a** (rel. energy 0.0 kcal/mol) Li bridges C and O, and the C-O bond (152.3 pm) is lengthened as compared to the one in methanol **23** (142.1 pm). A similar bond lengthening is observed in the C-Li isomer **24b** and in the O-Li isomer **24c**. In **24d** the C-O bond is even broken. **24c** and **24d** are carbene complexes of LiOH. Most importantly, the predictions of the calculations were nicely verified by means of X-ray crystal structure determinations of all four structural types of the model **24** (Ref. 31a, 34): in the cases corresponding to **24a-c** the C-O bonds are significantly longer than in the corresponding non-lithiated species, which indeed turned out to be mostly due to the higher p-character of these bonds.

An illustrating example for the significance of the nature of the carbon centered orbitals of the C-M and the C-X bonds, respectively, in carbenoids is provided by calculations of the structure of a C-lithiated (**25**-$Li\cdot2H_2O$) and a C-zincated oxazole **25**-$ZnCl\cdot2H_2O$ (Ref. 35).

25-Li • 2 H_2O



25-ZnCl • 2 H_2O

NBO - analysis:

lone pair C : $sp^{1.0}$	$\sigma_{C\text{-}Zn}$, C : $sp^{1.9}$
$\sigma_{C\text{-}O}$, C : $sp^{3.6}$	$\sigma_{C\text{-}O}$, C : $sp^{2.5}$
$\sigma_{C\text{-}N}$, C : $sp^{2.3}$	$\sigma_{C\text{-}N}$, C : $sp^{1.7}$

In **25-Li**·$2H_2O$, the "lone pair" orbital on C has $sp^{1.0}$ character. Correspondingly, the carbon orbitals in the C-O and C-N bonds are of comparatively high p-character ($sp^{3.6}$ and $sp^{2.3}$). In the more covalent **25-ZnCl**·$2H_2O$ one finds higher p-character in the C-Zn bond ($sp^{1.9}$) and therefore lower p-character in the C-O ($sp^{2.5}$) and C-N bonds ($sp^{1.7}$), which is reflected in the C-O and C-N bond lengths as well as in the N-C-O angles of these compounds (Ref. 35a). The calculated results agree again nicely with the experiment: lithiathed oxazoles have never been observed because of a very facile ring-opening reaction (LiOR α-elimination) (Ref. 35b). In contrast, the solid state structure of a zincated oxazole was recently determined (Ref. 35a).

Solid state structures of Li/Cl carbenoids (Ref. 36a,b) and a MgBr/Br carbenoid (Ref. 36c) confirmed the above findings: in all cases the C-X bonds are strongly elongated.

Quantum chemical calculations of nitrenoids **1b** and oxenoids **1c** provided similar results as in the case of carbenoids **1a**: the N-X and O-X bonds are elongated in the lithiated as compared to the non-lithiated compounds, which was again proven by solid state structure investigations (Ref. 28d, 29). From the calculations it became furthermore clear why the "anionic" carbenoids **1a**, nitrenoids **1b** and oxenoids **1c** are such strong electrophiles: besides an elongated and thus weakened $\sigma_{C(N,O)\text{-}X}$ bond to the leaving group X, the $\sigma^*_{C(N,O)\text{-}X}$ orbital is energetically lowered which allows for a more efficient back-side interaction of the incoming nucleophile with this orbital. In addition , the Lewis acid character of the metal M in these species facilites both the approach of the nucleophile to the carbenoid (nitrenoid, oxenoid) atom as well as the removal of the anionic leaving group X thereof.

In conclusion, investigations of the structures of carbenoids **1a**, nitrenoids **1b** and oxenoids **1c**, together with quantumchemical studies of their structures, energies and electronic natures, provided a deeper insight into these "anions", and thus an understanding of their electrophilicity.

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