Crystal Structure of [2-ZnCl-benzoxazole · 2THF]$_2$: The Remarkable Difference between 2-ZnHal- and 2-Li-oxazoles

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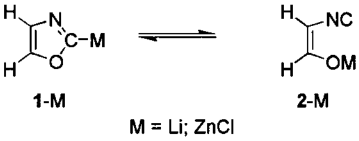
Abstract: Ring opening of 2-lithiated oxazole (**1**-Li) leads to an equilibrium with the corresponding (*Z*)-2-isocyanolithium enolate **2**-Li which lies far towards the **2**-Li side. In contrast, the ZnCl species exists only in the cyclic form, 2-chlorozinc oxazole (**1**-ZnCl). We provide the first crystal structure of a 2-metalated oxazole, 2-chlorozinc benzoxazole, crystallized as a dimer ([**3**-ZnCl · 2THF]$_2$) from THF, and discuss the strong effect of the metal (M) on the equilibrium **1**-M $\rightleftharpoons$ **2**-M.

Keywords: benzoxazoles · carbene complexes · lithium · quantum-chemical calculations · zinc

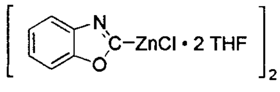
Introduction

All attempts to prepare a 2-lithiated oxazole derivative **1**-Li, or the corresponding benzoxazole, have so far failed because the ring-opening reaction **1**-Li →**2**-Li, even at −78 °C, leads to the corresponding (*Z*)-2-isocyanolithium enolate **2**-Li (> 97 ± 3 %).[1] This reaction can be considered as an intramolecular α-elimination of the Li/OR carbenoid **1**-Li[2] to give the isocyanide **2**-Li, a stabilized carbene.[3]



A totally different situation results if zinc chloride ($ZnCl_2$) is added to the Li compound **2**-Li: immediate ring closure leads to the exclusive formation (> 97 ± 3 %) of a ZnCl-substituted oxazole, **1**-ZnCl. This was first indicated by Pd-catalyzed coupling reactions with aryl and vinyl halides to give 2-substituted oxazoles[4] and further supported by NMR investigations.[1e, 4a, 5]

In this work we report the first solid-state structure elucidation of a 2-metalated oxazole, 2-ZnCl-benzoxazole (**3**-ZnCl), which crystallized from tetrahydrofuran (THF) as a dimer [**3**-ZnCl · 2THF]$_2$). What causes the remarkable difference between 2-lithiated and 2-zincated (benz)oxazoles? For the reasons outlined above, this question cannot be answered on experimental grounds alone, so we performed quantum-chemical calculations with appropriate model compounds. These led to a general understanding of the difference between lithium and zinc-halide oxazoles (and thus between Li and ZnHal carbenoids). Both types of compounds are of eminent importance in synthesis.


[**3**-ZnCl · 2THF]$_2$

Results and Discussion

[**3**-ZnCl · 2THF]$_2$ crystallized from THF at −30 °C. The structure is shown in Figure 1. The two benzoxazole units are connected to each other through Zn 1 and Zn 1A with each zinc bonded to the C2(C2A) atom of one and the N3A(N3) atom of the other molecule. Of special interest are the bonds at C2 of [**3**-ZnCl · 2THF]$_2$. Thus, in comparison with the mean value of the corresponding bonds in 55 other oxazoles, O1–C2 is 2.2 pm longer (137.8 pm),[11] C2–N3 is 1.9 pm longer (129.3 pm),[11] and O1-C2-N3 is 2.9° narrower than the corresponding mean angle in oxazoles (113.7°).[11] Similar differences have been observed between non-metallated thiazoles and 2-ZnBr-thiazole.[12] In 2-Li-thiazole (which is stable towards ring opening!)[12] the C–N and C–S bonds, as determined by X-ray crystal structure analysis, are even longer than in 2-ZnBr-thiazole, and the N-C-S bond angle is narrower.[12]

In order to gain greater insight into the remarkable contrast between the 2-Li-oxazoles such as **2**-Li, which cannot even be observed, and the stable 2-ZnHal-oxazoles such as **1**-ZnCl, we performed quantum-chemical calculations for the oxazole **4**-H, the 2-ZnCl-oxazole dihydrate **4**-ZnCl · 2 H_2O,[13] and

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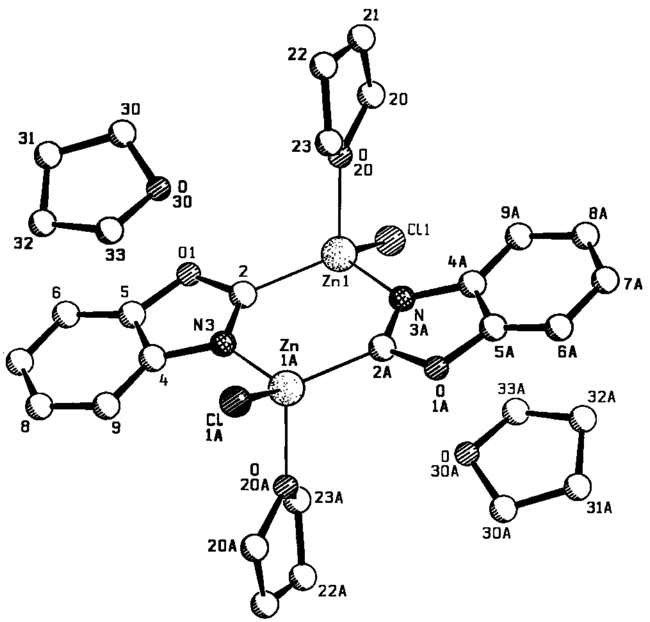


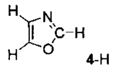
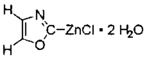
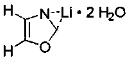
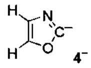
Figure 1. Crystal structure of [**3**-ZnCl · 2THF]$_2$.[6–10] Significant parameters: bond lengths [pm], O1–C2 137.8(3), C2–N3 131.2(3), C2–Zn1 201.0(2), N3–Zn1A 202.3(2), Zn1–Cl1 221.3(1); angle [°], O1-C2-N3 110.8(2).

2-Li-oxazole dihydrate **4**-Li · 2H_2O as model compounds. Additionally, we calculated the structure of the oxazole anion **4**$^-$. The B3LYP/6-31+G(d) results[14, 15] are summarized in Table 1. There is some lengthening of the O–C and C–N bonds and a narrowing of the O-C-N angle in **4**-ZnCl · 2H_2O compared with **4**-H, as observed experimentally in [**3**-ZnCl · 2THF]$_2$. Bond lengthening and angle narrowing are even more pronounced in **4**-Li · 2H_2O than in **4**-ZnCl · 2H_2O. In other words, in 2-metallated oxazoles the α-elimination of Li/OR is more advanced than that of ClZn/OR. Not surprisingly, the strongest bond-lengthening and angle-narrowing effects are observed in the anion **4**$^-$.

A natural bond orbital (NBO) analysis[16] of the bonds involving C2 shows the reasons for the differences in the structures of these compounds (Table 1). In **4**-ZnCl · 2H_2O the hybridization of the carbon orbitals is rather similar to that in the nonmetalated oxazole **4**-H. Especially noteworthy is the carbon orbital of the C–Zn bond in **4**-ZnCl · 2H_2O which is sp$^{1.9}$-hybridized, in contrast to the corresponding lone pair in **4**-Li · 2H_2O, which has a much higher s character (sp$^{1.0}$). The difference is due to the more covalent nature of the C–Zn bond[17] compared with the essentially ionic C–Li bond.[18] Consequently, in **4**-Li · 2H_2O the C–O and C–N bonds have more p character (sp$^{3.6}$ and sp$^{2.3}$, respectively) than in **4**-ZnCl · 2H_2O (sp$^{2.5}$ and sp$^{1.7}$, respectively).[19, 20] Therefore, the carbenoid character of the model compound **4**-Li · 2H_2O is clearly more enhanced than that of the zinc species **4**-ZnCl · 2H_2O. The hybridizations of the carbon orbitals in the anion **4**$^-$ are in agreement with expectations and the structural data: the lone pair has very high s character (sp$^{0.8}$), while the rather long C–O bond shows very high p character (sp$^{5.3}$).

In Figure 2 the absolute energies of **4**-H, **4**-ZnCl · 2H_2O, **4**-Li · 2H_2O, and **4**$^-$ are listed together with those of their acyclic isomers **4'**-H, **4'**-ZnCl · 2H_2O, **4'**-Li · 2H_2O, and **4'**$^-$. Furthermore, the relative energies [kcal mol^{-1}] of the cyclic and acyclic isomers are given. Thus, oxazole **4**-H is 28.2 kcal mol^{-1} more stable than the acyclic **4'**-H. In the case of the ZnCl species, it is again the cyclic **4**-ZnCl · 2H_2O which is more stable than the acyclic **4'**-ZnCl · 2H_2O, but the difference is only 8.0 kcal mol^{-1}. Completely reversed stabilities are found in the case of the anions and the Li species: the acyclic **4'**$^-$ is 19.9 kcal mol^{-1} more stable than the cyclic **4**$^-$, and **4'**-Li · 2H_2O is 15.7 kcal mol^{-1} more stable than **4**-Li · 2H_2O. It is interesting to note that $Li^+ \cdot 2H_2O$ has only a marginal effect on the relative energies of the anions **4**$^-$ and **4'**$^-$: the cyclic **4**-Li · 2H_2O is only slightly more stabilized than the acyclic **4'**-

Table 1. B3LYP/6-31G+G(d)-calculated[14] bond lengths [pm] and angles [°] of **4**-H, **4**-ZnCl · 2H_2O, **4**-Li · 2H_2O, and **4**$^-$. The hybridizations of the carbon orbitals in the respective bonds are given (NBO analysis).[16]

		Bonds		Bond angle
	C–H(M)	C–O	C–N	O-C-N
 4-H	108.0 sp$^{1.7}$	135.8 sp$^{2.8}$	129.5 sp$^{1.7}$	114.5
 4-ZnCl • 2H$_2$O	197.5 sp$^{1.9}$	136.9 sp$^{2.5}$	132.0 sp$^{1.7}$	111.1
 4-Li • 2H$_2$O	205.5 sp$^{1.0}$	137.8 sp$^{3.6}$	134.1 sp$^{2.3}$	108.3
 4$^-$	– sp$^{0.8}$	146.2 sp$^{5.3}$	133.0 sp$^{2.3}$	106.4

Abstract in German: *Bei 2-lithiierten Oxazolen **1**-Li liegt das Gleichgewicht mit der acyclischen Verbindung **2**-Li ganz auf der Seite von **2**-Li. Dagegen findet man bei den **2**-ZnCl-Verbindungen nur das cyclische **1**-ZnCl vor. Wir berichten hier über die erste Kristallstrukturbestimmung eines 2-metallierten Oxazols ([**3**-ZnCl · 2THF]$_2$) und diskutieren den enormen Einfluß des Metalls auf das Gleichgewicht **1**-M$\rightleftharpoons$**2**-M.*

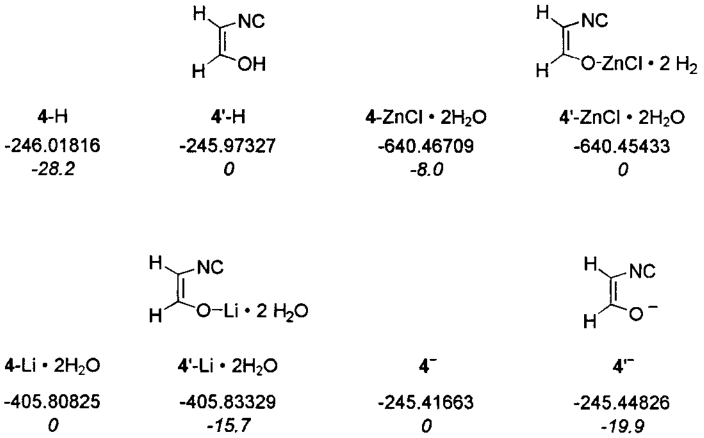
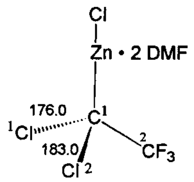


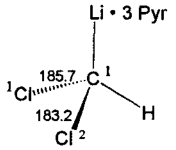
Figure 2. Absolute [au] and relative [kcal mol^{-1}] energies of the cyclic **4**-H, **4**-ZnCl · 2H_2O, **4**-Li · 2H_2O, and **4**$^-$, and their acyclic isomers **4'**-H, **4'**-ZnCl · 2H_2O, **4'**-Li · 2H_2O, and **4'**$^-$.

Li$\cdot$2H_2O. This is in strong contrast to $ZnCl^+\cdot 2H_2O$, relative to which the cyclic **4**-ZnCl$\cdot$2H_2O is much more stabilized (see above). Furthermore, if one considers that the oxophilic Li^+ undoubtedly facilitates the ring-opening reaction of 2-lithiated oxazoles **1**-Li, the results of the calculations are totally in agreement with the experimental ones: it is only the acyclic isomers **2**-Li of 2-lithiated oxazoles, but the cyclic isomers **1**-ZnCl in the case of 2-zincated oxazoles, that are observed.

No other pair of carbenoids differing only in the nature of the metal (Li and ZnHal, respectively) has yet been investigated. However, there are indications that the differences revealed here are of general significance. Thus, in the ZnCl/Cl carbenoid **5**-ZnCl$\cdot$2DMF[21] the C–Cl bonds are 176 and 183 pm long, and the sum of the bond angles Cl1-C1-Cl2, Cl1-C1-C2, and Cl2-C1-C2 amounts to 319.4° (instead of 328° in the case of sp^3-hybridized bonds; normal C–Cl bonds are 174.6 pm long (mean value)).[22]



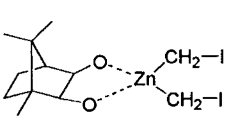
5-ZnCl • 2DMF



6-Li • 3Pyr

In the related Li/Cl carbenoid **6**-Li$\cdot$3Pyr[22] (Pyr = pyridine) the C–Cl bonds are clearly more elongated (185.7 and 183.2 pm); this agrees with the smaller sum of the bond angles Cl1-C1-Cl2, Cl1-C1-H1, and Cl2-C1-H1 of 308°. Unfortunately, there is no information yet about the comparative influences of CF_3 in **5**-ZnCl$\cdot$2DMF and of H in **6**-Li$\cdot$3Pyr on the structural details discussed above.

Experimentally determined structures of Zn/I carbenoids of the Wittig type $Zn(CH_2I)_2$, or of the Simmons–Smith type $IZnCH_2I$, cannot be compared with an Li/I carbenoid, because structural details of Zn/I species are the only ones available. In the $Zn(CH_2I)_2$ compound **7**[23] and in the $IZnCH_2I$ species **8**[24] the C–I bonds are not even elongated in comparison with normal C–I bonds.



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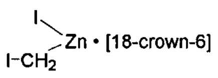

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Quantum-chemical calculations (MP2 6-311++G(d,p)) also shed more light on this case: in $IZnCH_2I$ the C–I bond (217.8 pm) is only 1.4% longer than the C–I bond in CH_3I (214.7 pm), in agreement with the results of the solid-state structure elucidations mentioned above. This contrasts strongly with the case of $LiCH_2I$, in which the calculated C–I bond length (226.6 pm) is 5% longer than in CH_3I. It is therefore not surprising that Simmons–Smith reagents normally react with olefins to give cyclopropanes in boiling diethyl ether (35 °C),[25] whereas Li carbenoids form cyclopropanes even at very low temperatures (below −100 °C).[26,27]

Conclusions

ZnHal carbenoids differ from Li carbenoids mainly because of the differences in the properties of the carbon–metal bonds: according to B3LYP/6-31+G(d) calculations for the model compounds **4**-ZnCl$\cdot$2H_2O and **4**-Li$\cdot$2H_2O, the carbon orbital of the C–M bond is $sp^{1.9}$-hybridized in the former and $sp^{1.0}$-hybridized in the latter. Correspondingly, the hybridizations of the carbon orbitals in the C–O bonds are $sp^{2.5}$ and $sp^{3.6}$, respectively, leading to a longer C–O bond in the lithium (137.8 pm) than in the ZnCl species (136.9 pm). Furthermore, since the cyclic **4**-ZnCl$\cdot$2H_2O is 8.0 kcal mol^{-1} more stable than its acyclic isomer **4′**-ZnCl$\cdot$2H_2O, whereas in the case of the Li species the cyclic **4**-Li$\cdot$2H_2O is 15.7 kcal mol^{-1} less stable than the acyclic **4′**-Li$\cdot$2H_2O, the quantum-chemical calculations are in perfect agreement with the existence of 2-lithiated oxazoles only as the acyclic isomers such as **2**-Li, whereas the cyclic isomers such as **1**-ZnCl predominate in the case of the 2-zincated species, as demonstrated by the solid-state structure of [**3**-ZnCl$\cdot$2THF]$_2$. When other experimental results and quantum-chemical calculations are taken into account, it is also evident that the carbenoid character and thus the electrophilicity of ZnHal carbenoids is less pronounced than those of Li carbenoids. It is interesting that the same differences in the nature of the C–M bonds which eventually determine the lower electrophilicity of ZnCl carbenoids compared with Li carbenoids also determine the lower nucleophilicity of the organometallic compounds of zinc compared with those of lithium.

Experimental Section

Preparation of [3-ZnCl·2THF]$_2$: After reaction for 1 h of benzoxazole (420 mg, 3.5 mmol) in THF (18 mL) at −78 °C with a 1.6 M solution of *n*BuLi (2.2 mL, 3.5 mmol) in *n*-hexane, a 1 M solution of $ZnCl_2$ (7 mL, 7 mmol) in diethyl ether was added dropwise, kept for 1 h at 0 °C, and then cooled to −50 °C. After 24 h a crystalline solid had formed, which after separation from the solvent was dissolved in THF (12 mL) and then cooled to −30 °C for 24 h. Under these conditions crystals appropriate for an X-ray crystal structure determination had formed. Yield: 820 mg (2.2 mmol; 63 %).

Crystal structure analysis of [3-ZnCl·2THF]$_2$: $C_{15}H_{20}ClNO_3Zn$, triclinic space group $P\bar{1}$; $a = 860.2(2)$, $b = 1016.4(2)$, $c = 1022.5(1)$ pm, $\alpha = 86.61(1)$, $\beta = 79.60(1)$, $\gamma = 69.70(1)°$, $V = 824.8(2) \times 10^{-30}$ m^3, $Z = 2$, data collection on a Siemens *P*4 diffractometer using $Mo_{K\alpha}$ radiation, $T = 213(2)$ K, 3281 reflections, 2745 unique ($R_{int} = 0.0175$); semiempirical absorption correction from ψ scans. Solution with direct methods (SHELXTL-PLUS), full-matrix least-squares refinement on F^2(SHELXL-93), non-hydrogen atoms anisotropic, hydrogen atoms on calculated positions with fixed isotropic temperature factors, aromatically bonded hydrogen atoms located and isotropically refined; $wR_2 = 0.0753$ (2745 reflections, on F^2, parameters for the weighting scheme calculated by the program: 0.0378, 0.4864), conventional $R = 0.0281$ for 2640 reflections with $I > 2\sigma(I)$, goodness of fit (F^2) = 0.880, 207 parameters. All calculations were performed on a DEC-AXP 3000/300X.[6–10]

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Patt, C. J. Connolly, *J. Org. Chem.* **1991**, *56*, 449–452; d) S. E. Whitney, B. Rickborn, *ibid.* **1991**, *56*, 3058–3063; e) C. Hilf, F. Bosold, K. Harms, M. Marsch, G. Boche, *Chem. Ber./Recueil* **1997**, *130*, 1213–1221. The crystal structure of [(*Z*)-2-isocyanolithium enolate · diglyme]$_2$ is also reported in this work.

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[3] In the case of normal Li/OR carbenoids (α-lithiated ethers) the α-elimination of LiOR is unknown. The situation for $LiCH_2Hal$ carbenoids is analogous: in both cases it would be necessary for rather unstable carbenes, such as CH_2, to be formed. Only stabilized carbenes, such as CCl_2 or $C(SPh)_2$, are formed by α-elimination (of LiCl or LiSPh, respectively). It is also interesting that addition of lithium (2,4,6-trimethyl)phenolate to 1,3-di-(*tert*-butyl)imidazol-2-ylidene does not lead to LiOR addition to the carbene C atom of this stable compound. Instead, a Li^+–carbene complex is formed (A. J. Arduengo III, M. Tamm, personal communication, as discussed in ref. [12]).

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[8] A. L. Spek, Platon92, Utrecht, **1992**.

[9] E. Keller, SCHAKAL-88B, A FORTRAN Program, Freiburg, **1988**.

[10] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100713. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] Cambridge Structural Data Base, update April 1997. The structure of benzoxazole is not reported in the literature.

[12] C. Hilf, F. Bosold, K. Harms, J. C. W. Lohrenz, M. Marsch, M. Schimeczek, G. Boche, *Chem. Ber./Recueil* **1997**, *130*, 1201–1212. Quantum-chemical calculations as described later in this paper are in agreement with 2-lithiated thiazole (as well as 2-lithiated imidazole) being more stable (4.2 $kcal\,mol^{-1}$ and 6.9 $kcal\,mol^{-1}$, respectively) than their acyclic isomers.

[13] The calculation of **4**-Li · 3 H_2O led to protonation of **4**-Li · 3 H_2O at C2.

[14] The ab initio calculations were performed with the Gaussian 94 program package. All structures (ref. [15]) were optimized with the hybrid density functional B3LYP and identified as energy minima by the fact that the eigenvalues in the Hessian matrices were only positive. Calculations on the MP2 level did not give structurally or energetically significant differences. A standard 6-31+G(d) basis set was used for the atoms H, C, N, O, and Li. The Zn and Cl atoms were calculated with the following ECPs and valence basis sets: Zn, 311111/22111/411/1; Cl, 31/211. See: A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431; M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* **1987**, *86,* 866.

[15] For **4**-ZnCl · 2 H_2O one imaginary frequency has been found describing a rotation around the C–Zn bond. Because the frequency was so low (76.8 cm^{-1}) and the rotation was barrierless, no further geometry optimization was attempted in this case.

[16] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[17] A direct comparison between C–ZnHal and C–Li bonds could not be found in the quantum-chemical literature. M. Kaupp, H. Stoll, H. Preuss, *J. Comput. Chem.* **1990**, *11*, 1029–1037, reported on the comparison of Me_2Zn with Me_2Mg; they detected higher charge separation in the Mg case. For further theoretical investigations on C–Zn bonds, see: I. Antes, G. Frenking, *Organometallics* **1995**, *14*, 4263–4268, and references therein.

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[19] This has been concluded qualitatively from NMR investigations on the hybridization in Li carbenoids, as quantified in **4**-Li · 2 H_2O (see: D. Seebach, R. Hässig, J. Gabriel, *Helv. Chem. Acta* **1983**, *66*, 308–337, and references therein), and, together with the quantum-chemical results for **4**-ZnCl · 2 H_2O, it is another corroboration of Bent's rule (ref. [20]).

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[27] The different effects of leaving groups X, for example, RO^-, F^-, Cl^-, Br^-, and I^- on the structure and reactivity of Li and ZnHal carbenoids will be reported elsewhere.