Carbene Structure of Stable Acyl (Formyl) Anion Equivalents☆

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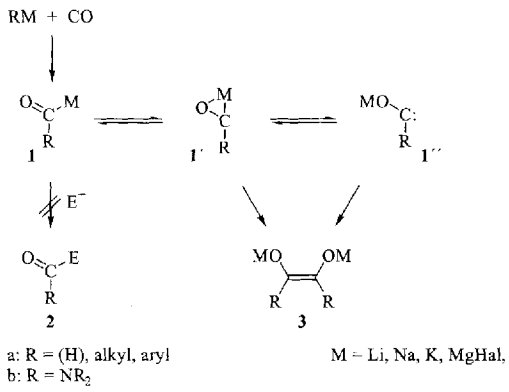
3-Lithiated 4-*tert*-butyl-imidazol-2-ylidene, 3-lithiated 4-*tert*-butyl-thiazol-2-ylidene, and the ZnBr species of the latter, are shown to be stable carbenes by X-ray crystal structure determination. The crystal data are confirmed by ^{13}C-NMR investigations in solution and quantum-chemical calculations. The exceptional stability of these acyl anion equivalents is due to the p(π) stabilization of the carbene carbon atoms by the adjacent amino (thio) substituents, as is also the case in the structurally related stable carbenes, which have recently been isolated for the first time by A. J. Arduengo III et al., and in stable nitrenium ions, as found by our group.

Introduction

Nucleophilic acylation with compounds of type **1** (Scheme 1) have intrigued chemists since the beginning of this century[1-3]. Although at least acyl(formyl)*lithium* species, **1a** (M = Li), are easily accessible by reaction of organolithium reagents, RLi, with carbon monoxide, CO, at low temperatures, and **1b** by carbonylation of lithiated amines, R_2NLi, (or by deprotonation of formamides, $R_2NC(O)H$, with a lithium base), the trapping of **1** with electrophiles E^+ to give the desired products, **2**, was successful only in very rare cases (e.g. with R being sterically hindered)[1] (see Scheme 1).

Scheme 1



In general, dimeric species, **3**, (and derivatives thereof) have been isolated instead, even at temperatures as low as −120°C[1]. This strongly suggested an intermediate, structurally and chemically different from **1**, being either the metal-bridged, **1′**, or even the carbene isomer, **1″**. Both, **1′** and **1″**, would be consistent with the facile formation of **3**.

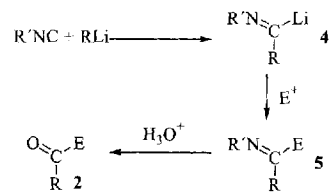
Theoretical investigations have first been concerned with structures and energies of carbonyl anions, ^-CHO[4a,1r]. More relevant are the calculations of MCHO species with M = Li, Na, HBe, HMg and H_2Al[4b]. In LiCHO, which is of foremost interest to this work, a Li atom bridges the elongated carbon−oxygen bond (as in **1′**), and the compound has "strong carbene character"[4b]. Calculations of the C-lithiated carbamoyl species, $LiC(NMe_2)O$, led to a similar result[1r].

The synthetic problems resulting from the undesired carbene-like reactivity of acyl (formyl) metal compounds have been solved by two routes; the concept of *umpolung*[5] is complemented by the use of more stable *acyl (formyl) anion equivalents*. In the following, we will deal with the latter. After a short survey on acyl (formyl) anion equivalents and their candidacy for the elucidation of their structure we will report on the X-ray crystal structures of three stable acyl (formyl) anion equivalents and discuss the question whether they are of the structural type **1**, show strong carbene character like **1′**, or indeed, are carbenes like **1″**. Finally we address the structural relationship between stable acyl (formyl) lithium equivalents and stable carbenes.

Acyl (Formyl) Anion Equivalents

Lithiated aldimines, **4**, which are easily formed from isocyanides R′NC and RLi are much more stable than their oxygen analogues, **1**. They react with electrophiles, E^+, to give **5** which are hydrolised to the envisaged products, **2** (Scheme 2)[6].

Scheme 2



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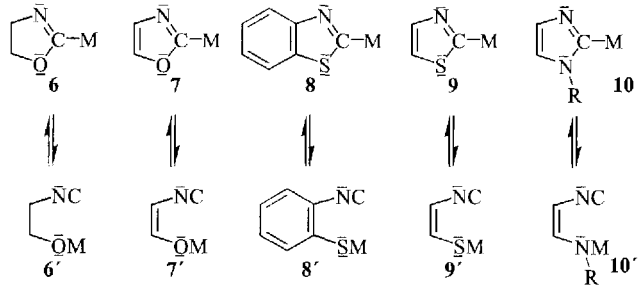
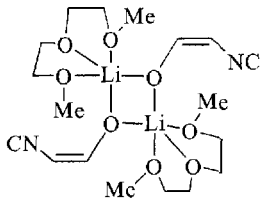
Surprisingly, compounds, **4**, are only rarely used in synthesis[6]. So far, there is also no report of their structure in the literature.

Scheme 3



A more widely studied, as well as synthetically used, group of acyl (formyl) anion equivalents are metalated heterocyclic five-membered ring compounds of the types **6**–**10**, see Scheme 3. C2-lithiated oxazolines, **6** (and substituted derivatives of **6**), react with electrophiles at C2 to give the expected products, which on acidic workup lead to the corresponding carbon acids. In most cases, however, the ring-opened isocyanides **6′**, or a mixture of **6** and **6′**, are trapped[7]. In other cases, facile decomposition of **6** by retro-1,3-dipolar cycloaddition is observed[7h,i].

In the case of lithiated oxazoles, **7**, an even faster ring-opening takes place to give **7′**[8]. We have determined the structure of the diethyleneglycol dimethyl ether (diglyme) complexed dimer [**7′**(M = Li) · diglyme]$_2$ by X-ray crystallography[9].



[7′· diglyme]$_2$

Trapping with electrophiles of either **7** or **7′** from the equilibrium **7** ⇌ **7′** depends strongly on the nature of the electrophile E^+ and the gegenion M^+ (Li^+ or $ZnHal^+$)[8].

2-Lithio-benzothiazole **8** was one of the first acyl(formyl)lithium equivalents used in synthesis[10]. The facile reduction of the C–S bond makes **8** an especially useful formyl anion equivalent. However, elimination to give **8′** again takes place rather easily. Apparently, and understandably, this occurs to a lesser extent with 2-lithio-thiazole **9**[11], which should therefore be a good candidate for the structure elucidation of an acyl anion equivalent. **9**, as well as 2-trimethylsilyl-thiazole[12] have been used with great success by Dondoni et al. as formyl anion equivalents in stereoselective syntheses[13]. The latter, however, is not an appropriate model for our goal.

2-Lithiated imidazoles, **10**, have rarely been used as acyl (formyl) anion equivalents in organic synthesis[14]. Since the ring opening reaction to give **10′** is not reported to be a major problem in that case[14,15], **10** is also of interest for this study.

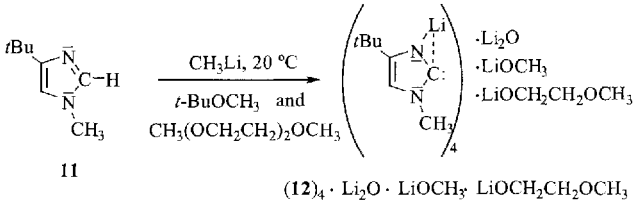
An X-ray crystal structure determination of a compound of the type, **6**–**10**, had not been reported at the outset of our investigations. Here we report on the crystal structures of two metalated thiazoles, **9** with M = Li[16] and ZnBr, respectively, and of a lithiated imidazole, **10**.

Results and Discussion

Crystal Structure of (1-Methyl-3-lithium-4-*tert*-butyl-imidazol-2-ylidene)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$ [(**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$]

(**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$ was prepared from 1-methyl-4-*tert*-butylimidazole (**11**) with methyllithium in *tert*-butyl methyl ether and diethyleneglycol dimethyl ether (diglyme) at 20°C (Scheme 4).

Scheme 4



(**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$

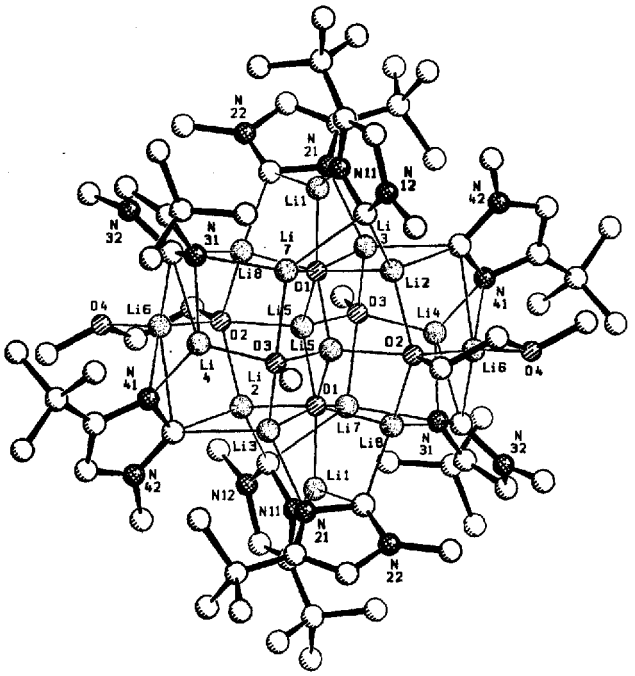
The *tert*-butyl substituted **11** was found to be the only imidazole derivative which upon deprotonation led to crystals suitable for an X-ray crystal structure analysis. Interestingly, the lithiated **12** crystallized only in the presence of lithium oxide Li_2O, lithium methanolate $LiOCH_3$, and lithium (2-methoxy)-ethanolate $LiOCH_2CH_2OCH_3$. Li_2O is part of the CH_3Li solution, $LiOCH_3$ is formed from the two ether solvents by β-and/or α-elimination with CH_3Li[17], and $LiOCH_2CH_2OCH_3$ results similarly from diglyme. We have isolated and structurally characterized two different modifications of (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$, namely monoclinic crystals of the space group $P2_1/c$, $Z = 4$ (Figure 1) and of the space group $P2_1/n$, $Z = 4$ (Figure 2).

Undoubtedly, the massive accumulation of Li and O atoms in the core of these supramolecules plays a significant role for the formation of the two crystal structures. In both cases the lithiated 1-methyl-4-*tert*-butylimidazole molecules, **12**, together with the alkoxide molecules form a hydrophobic shell which surrounds the polar Li and O centers.

As one can see from Figure 3, which shows the four different lithiated imidazoles **12** of the asymmetric unit of the $P2_1/c$ modification (Figure 1) and their next Li^+ neighbors, the imidazole anion N11–C11–N12–C13–C12 has three bonds to three lithium atoms, N21–C21–N22–C23–C22 has four bonds to three lithium atoms, and N31–C31–N32–C33–C32 as well as N41–C41–N42–C43–C42 have five bonds to four lithium atoms.

The N11(21,31,41)–Li bonds are distinctly shorter (mean value 208.7 pm) than the lithium bonds to the carbene C atoms C11(21,31,41) (mean value 230.6 pm). Since the individual, as well as the mean values, of the N(C)–Li bond lengths in the $P2_1/n$ modification (Figure 2) are rather similar (mean values: N–Li 209.0 pm; C–Li 231.7 pm) to

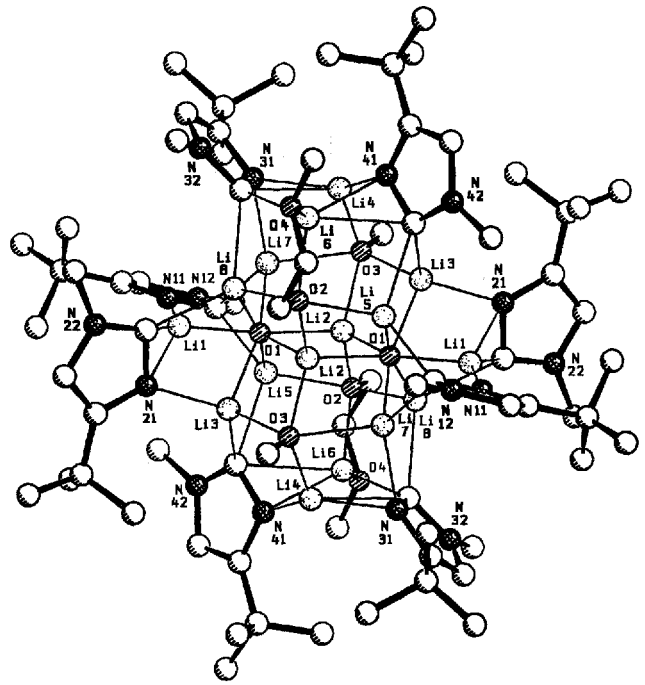
Figure 1. Crystal structure of the monoclinic $(\mathbf{12})_4 \cdot Li_2O \cdot LiOCH_3 \cdot LiOCH_2CH_2OCH_3$, space group $P2_1/c$, $Z = 4$. The carbon labels have been omitted for clarity (see Figure 3)



the ones given above, we have omitted a detailed listing of the numbers and an illustration of these anion–Li^+ interactions here.

Bond distances and angles within the imidazole anion rings of the two modifications of $(\mathbf{12})_4 \cdot Li_2O \cdot LiOCH_3 \cdot LiOCH_2CH_2OCH_3$ which are significant for the evaluation of the carbene nature of **12**, are summarized in Table 1.

Figure 2. Crystal structure of the monoclinic $(\mathbf{12})_4 \cdot Li_2O \cdot LiOCH_3 \cdot LiOCH_2CH_2OCH_3$, space group $P2_1/n$, $Z = 4$. The carbon labels have been omitted for clarity

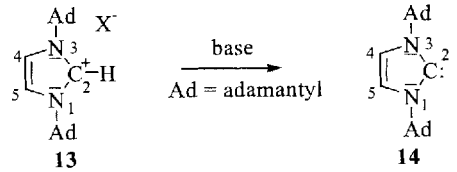


What is the significance of the bond lengths and bond angles within the imidazole anions (Table 1) and the bond lengths of the bonds between the Li cations and these anions (Figure 3)? Are these structural data consistent with **12** being acyl(formyl)lithium equivalents with carbene character? If this is indeed the case, then the *structural changes* on going from the imidazole, **11**, to the lithiated imidazole, **12**, should be comparable to those observed in the transformation of imidazolium cations such as **13** into imidazol-2-ylidenes such as **14**, the first stable carbenes which have been prepared and structurally characterized by A. J. Arduengo III et al.[18] (see Scheme 5[19,20]).

Table 1. Bond lengths [pm] and angles [°] in $[(\mathbf{12})_4 \cdot Li_2O \cdot LiOCH_3 \; LiOCH_2CH_2OCH_3]$, space group $P2_1/c$, $Z = 4$, and $P2_1/n$, $Z = 4$, respectively

	$P2_1/c$	mean value	$P2_1/n$	mean value
N11-C11	136.5	"N1-C1"	136.7	"N1-C1"
N21-C21	136.2	136.8	136.4	137.2
N31-C31	137.2		138.2	
N41-C41	137.5		137.4	
N12-C11	137.9	"N2 - C1"	136.9	"N2 - C1"
N22-C21	137.1	137.5	137.3	137.5
N32-C31	138.2		138.9	
N42-C41	137.0		137.1	
N11-C11-N12	105.5	"N1-C1-N2"	105.1	"N1-C1-N2"
N21-C21-N22	105.9	105.2	105.4	104.9
N31-C31-N32	104.3		104.2	
N41-C41-N42	105.5		105.1	

Scheme 5



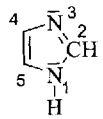
13 **14**

The *absolute values* of the bond lengths to, and the bond angle at, the carbene carbon atoms in **12** and **14** are of special interest. Since the structural data for the *tert*-butyl substituted **11** are unknown, we have had to use those of the unsubstituted imidazole, **15**[21].

In Table 2 the significant bond lengths (pm) and angles (°) of the imidazolium cation, **13**, and the imidazol-2-ylidene, **14**, are listed together with the changes on going from **13** to **14**[18a].

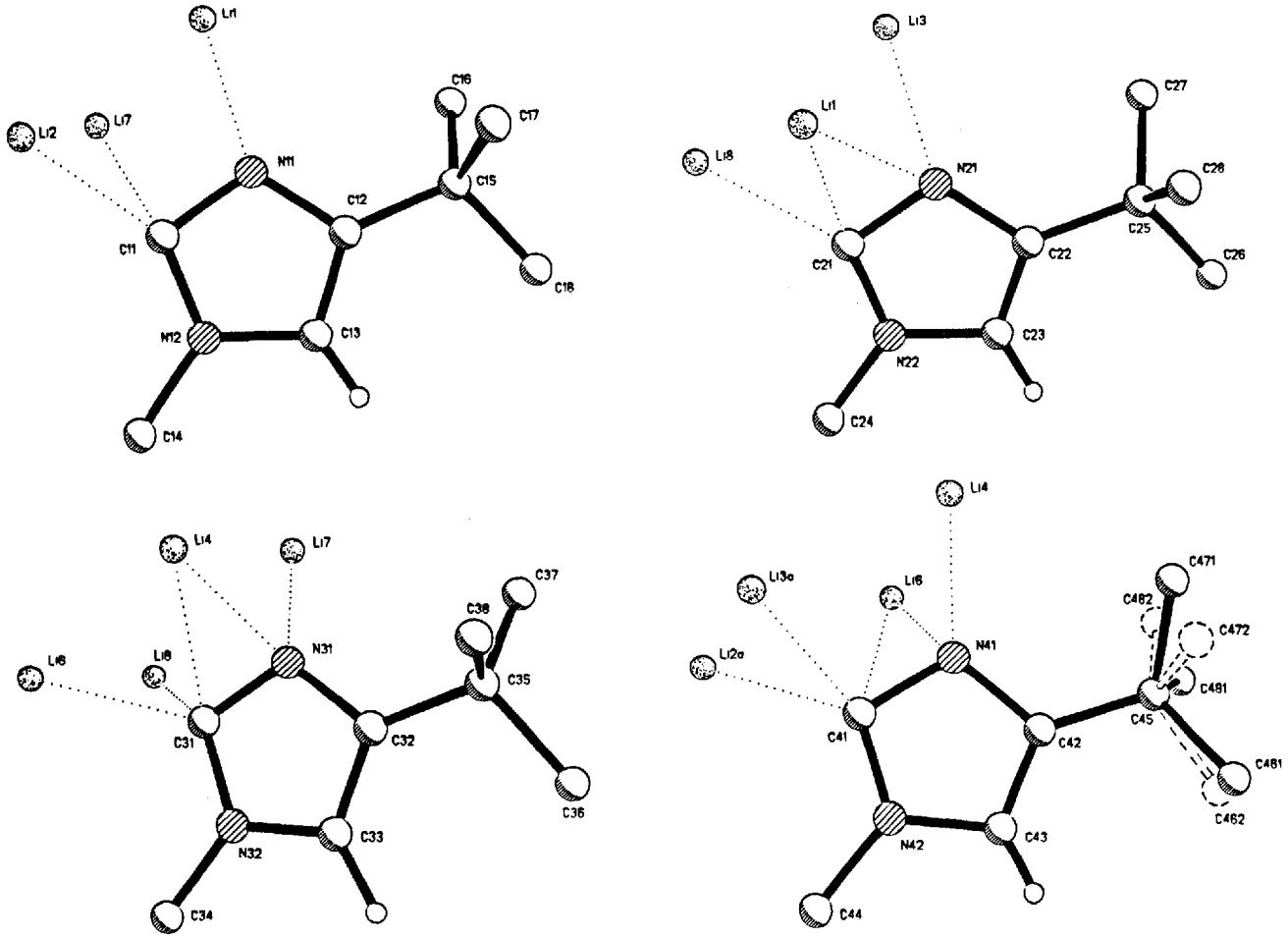
Most significantly, the N1–C2 and C2–N3 bonds in the carbene, **14**, are longer, while the angle at C2 is much more narrow than in the cation **13**. As one can see from Table 3, exactly the same trend is observed if one compares the structures of the imidazole, **15** (the model for **11**), with those of the lithiated imidazoles, **12**.

The N2–C1 and C1–N1 bonds in the four different lithiated imidazole molecules, **12**, are longer and the N2–C1–N1 bond angles narrower, than in **15**. Consequently, the lithiated imidazoles, **12**, should also have at



15 - a structural model for **11**

Figure 3. Bonding of the Li cations to the four different 1-methyl-4-*tert*-butyl-imidazole anions of the asymmetric unit in the crystal structure of $(\mathbf{12})_4 \cdot Li_2O \cdot LiOCH_3 \cdot LiOCH_2CH_2OCH_3$, $P2_1/c$, $Z = 4$ (Figure 1)[a]



[a] The bond lengths [pm] are as follows: N11–C11–N12–C13–C12: N11–Li1 195.5(5), C11–Li2 220.8(5), C11–Li7 235.4(5). N21–C21–N22–C23–C22: N21–Li3 209.3(5), N21–Li1 213.2(5), C21–Li1 221.5(5), C21–Li8 220.2(5). N31–C31–N32–C33–C32: N31–Li7 217.4(5), N31–Li4 203.5(5). C31–Li4 240.9(6), C31–Li8 234.0(6), C31–Li6 225.0(5). N41–C41–N42–C43–C42: N41–Li4 204.3(5), N41–Li6 217.7(5), C41–Li6 246.5(5). C41–Li3a 238.6(5), C41–Li2a 223.7(5).

Table 2. Bond lengths [pm], bond angles [°], and differences thereof, in **13** and **14**[18a]

	13	**14**	**Δ[14-13]**
N1-C2	133.2	137.3	4.1
C2-N3	132.9	136.7	3.8
N1-C2-N3	109.7	102.2	-7.5

Table 3. Bond lengths [pm], bond angles [°], and differences thereof, in **15** and $(\mathbf{12})_4 \cdot Li_2O \cdot LiOCH_3 \cdot LiOCH_2CH_2OCH_3$, $P2_1/c$, $Z = 4$, and $P2_1/n$, $Z = 4$. The bond lengths of the two species in the same line correspond to each other

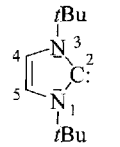
15[21]		$(\mathbf{12})_4 \cdot Li_2O \cdot LiOCH_3 \cdot LiOCH_2CH_2OCH_3$		Δ["(12)$_4$"-15]	
		$P2_1/c$[a]	$P2_1/n$[a]	$P2_1/c$	$P2_1/n$
N1-C2	135.8	"N2-C1"	137.5	137.5	1.7	1.7
C2-N3	133.3	"C1-N1"	136.8	137.2	3.5	3.9
N1-C2-N3	111.8	"N2-C1-N1"	105.2	104.9	-6.6	-6.9

[a] Mean values, see Table 1.

least strong carbene character (such as **1′**), or even be carbenes (such as **1″**).

At this point it is necessary to return to Figure 3, which shows that in the lithiated imidazoles, **12**, it is not only one Li cation which is bonded to one anion, e.g. to N11 (N21, N32, N41), but due to the supramolecular crystal structures of $(\mathbf{12})_4 \cdot Li_2O \cdot LiOCH_3 \cdot LiOCH_2CH_2OCH_3$, $P2_1/c$ ($P2_1/n$), there are also interactions between Li^+ ions and the carbene carbon atoms C11 (C21, C31, C41). The influence of the different (Lewis acidic) lithium cations on the carbene structure of the lithiated imidazole, **12**, must therefore be considered.

Arduengo and Tamm[22] have studied the influence of a Li^+ Lewis acid on the structure of an imidazol-2-ylidene, thus allowing a comparison of the structures of the free species with the Li^+-complexed carbene. If 1,3-di-*tert*-butyl-



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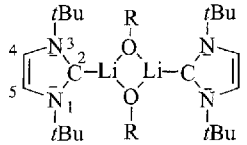


17

R = (2,4,6-trimethyl)-phenyl

imidazol-2-ylidene (**16**) is treated with lithium (2,4,6-trimethyl)phenolate, the complex **17** is formed.

The X-ray crystal structure determinations of **16** and **17** reveal that the N1–C2 and C2–N3 bond lengths in **17** (136.9 and 136.6 pm respectively) are essentially the same as in **16** (136.7 and 137.3 pm, respectively). This is also true for the N1–C2–N3 bond angles: 102.8° in **17** and 102.2° in **16**. Thus, a Li^+ Lewis acid has only a marginal influence on the structure of "uncharged" imidazol-2-ylidenes such as **16**. If this is similarly the case for the lithiated imidazol-2-ylidenes, **12**, and their interactions wih lithium cations, then the structural changes observed in the transformation of **11** to **12**, and thus the carbene structure **12**, must clearly not result from the additional Li–cation interactions with the carbon atoms of the Li-imidazol-2-ylidenes, **12**. Rather, it is the inherent carbene nature of the acyl(formyl)lithium equivalents, **12**, which is essentially unaffected by the additional interaction with the Li^+ Lewis acids.

A comparison of the *absolute bond lengths* in the carbene, **14**, with those in the "lithiated carbenes", **12**, confirms the carbene nature of **12**: N1–C2 (**14**) is 137.3 pm long (Table 2); the corresponding bonds N2–C1 in **12** amount to 137.5 (137.5) pm (Table 3). C2–N3 (**14**) is 136.7 pm long (Table 2); the corresponding bonds C1–N1 in **12** amount to 136.8 (137.2) pm (Table 3). Thus, the N–C bonds to the carbene C atoms in **14** and in the lithiated **12** are practically identical. The bond angles at the carbene carbon atoms are slightly different: **14**: 102.2° (Table 2); **12**: 105.2 (104.9)° (Table 3). The widening in the lithiated **12** might be caused by some σ/π polarization at the lithiated nitrogen atom in **12** (N1), which leads to a stronger shift of π-density from N1 to the carbene carbon atom C1. Imidazol **15**, which has an NC double bond between the corresonding atoms (C2–N3, 133.3 pm), has an angle N1–C2–N3 of 111.8° (Table 3).

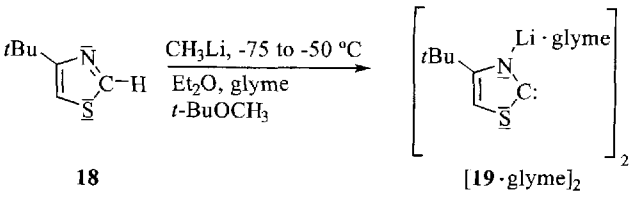
In this context it is also interesting to mention the influence of transition metals (metal fragments) in carbene complexes with imidazol-2-ylidenes such as **14** or **16** on the structure of the carbene part. It has been found that the N–C–N bond angles are slightly widened from 101–102° to 103–105°[18–20]. Furthermore, the X-ray data suggest a trend towards a shortening of the $C_{carbene}$–N bonds in the carbene complexes, although the suggested trent cannot be regarded as proven[19a]. The other bond lenghts and angles are essentually unaffected. Thus, complexation with transition metals also has no dramatic influence on the structure of imidazol-2-ylidenes.

Crystal Structure of [3-Lithium-4-*tert*-butyl-thiazol-2-ylidene–Glycoldimethyl Ether]$_2$ ([**19** · glyme]$_2$)

[**19** · glyme]$_2$ was formed from 4-*tert*-butylthiazole (**18**) by deprotonation with methyllithium in diethyl ether, glycoldimethyl ether (glyme) and *tert*-butyl methyl ether.

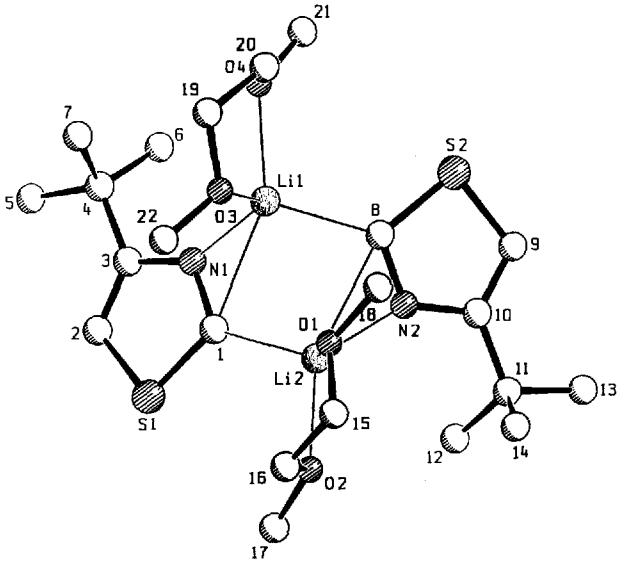
The dimer structure of [**19** · glyme]$_2$ is shown in Figure 4.

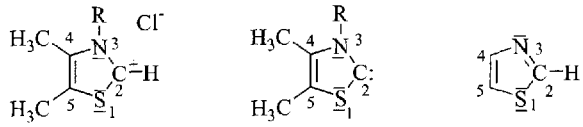
Since the recent publication of our short communication on [**19** · glyme]$_2$[16] Arduengo et al. have been able to determine both the X-ray crystal structure of the thiazolium cation **20**, as well as the thiazol-2-ylidene **21**[23].



18 [**19**·glyme]$_2$

Figure 4. Crystal structure of [**19** · glyme]$_2$





20 **21** **22**

R = 1-(2,6-diisopropylphenyl)

It is of interest to compare the structural differences between the pairs **20/21** and **22/19** by analogy with the lithiated imidazole **12**; the unsubstituted **22**[24] serves as a model for the *tert*-butyl-substituted **18**, whose structure is not known. The significant bond lengths and angles of **20** and **21** are listed in Table 4, and those of **22** and [**19** · glyme]$_2$ in Table 5.

Table 4. Bond lengths [pm], bond angles [°], and differences thereof, in **20** and **21**[23]

	20	**21**	**Δ[21-20]**
S1-C2	166.6	171.5	4.9
C2-N3	131.8	134.5	2.7
S1-C2-N3	112.0	104.2	-7.8

As one can see from Table 5, a similar picture emerges in the case of the lithiated thiazole [**19** · glyme]$_2$ to that of the lithiated imidazoles (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$ (Table 3); the bonds S1(2)–C1(8) and C1(8)–N1(2) are distinctly longer than in thiazole **22**, while the angle S1(2)–C1(8)–N1(2) is much smaller than the corresponding angle in **22**. Exactly the same is true for the thiazol-2-

Table 5. Bond lengths [pm], bond angles [°], and differences thereof, in **22** and [**19** · glyme]$_2$. The bond lengths in the same line correspond to each other

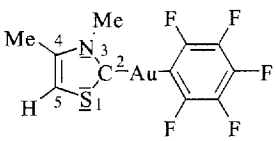
22		[19·glyme]$_2$[a]		Δ["19"-22]
S1-C2	172.4	S1(2)-C1(8)	176.2	3.8
C2-N3	130.4	C1(8)-N1(2)	132.9	2.5
S1-C2-N3	115.1	S1(2)-C1(8)-N1(2)	108.0	-7.1
		Li1(2)-N1(2)	200.0	
		Li1(2)-C1(8)	253.5	
		Li2(1)-C1(8)	217.6	
		N1(2)-C1(8)-Li1(2)	51.5	

[a] Mean values of the two different molecules **19**.

ylidene, **21**, if compared with the thiazolium cation, **20** (see Table 4). Since the changes of bond lengths and angles, given in Table 4, are important criteria for the carbene nature of **21** (and for **14**, see Table 2), the lithiated thiazole **19** is, corresponding to the lithiated imidazole **12**, an acyl(formyl)lithium equivalent with strong carbene character.

The contacts between the Li cations and the thiazole anions are also of interest. As shown in Table 5, Li1(2) has a short bond to N1(2) (200.0 pm). The bridging character of Li1(2) is, however, rather weak since the bond Li1(2)–C1(8) is very long (253.5 pm). This corresponds to a small angle N1(2)–C1(8)–Li1(2) (51.5°). In the model calculations of the bridged LiCHO[4b] (**1′**, M = Li, R = H) the Li–C bond length amounts to 189.1 pm, while Li–O is 183.5 pm long; this leads to a Li–C–O angle of 67.6°. It thus seems that the interaction of Li^+ with the thiazole anion in **19** corresponds more to the non-bridged structural type of an acyl(formyl)lithium compound (type **1″**).

In addition to Li1(2), Li2(1) is bonded to the lithiated thiazole [Li2(1)–C1(8) 217.6 pm]. This bond distance corresponds almost exactly to the $C_{carbene}$–Li bond distance in the imidazol-2-ylidene · LiOR complex, **17** (215.2 pm), in which Li^+ acts as a Lewis acid at the carbene C atom. It was shown there that this interaction has essentially no effect on the structure of the imidazol-2-ylidene part of the complex **17**. One can therefore conclude that the Lewis acid Li2(1)$^+$ binding to C1(2) should similarly be of little influence on the structure of [**19** · glyme]$_2$. A similar conclusion is reached from the structure of a complex of a thiazol-2-ylidene in which the carbene C atom is bonded to gold (**23**)[25].



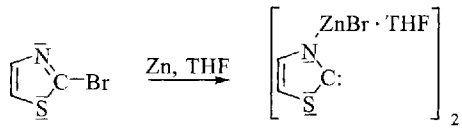
23

The C2–N3 distance in **23** (133.3 pm) corresponds closely to C1(8)–N1(2) in [**19** · glyme]$_2$ (132.9 pm). The S1–C2–N3 angle in **23** (105.7°) is somewhat smaller than S1(2)–C1(8)–N1(2) in [**19** · glyme]$_2$ (108.0°). The S–$C_{carbene}$ bonds show a larger difference; in **23**, S1–C2 is 172.1 pm long, while the corresponding bond in the lithiated [**19** · glyme]$_2$ [S1(2)–C1(8)] amounts to the comparatively large value of 176.2 pm.

The S1(2)–C1(8) bond in [**19** · glyme]$_2$ (176.2 pm) is also rather long if compared to the S1–C2 bond in the carbene, **21** (171.5 pm), while the C1(8)–N1(2) bond length in [**19** · glyme]$_2$ (132.9 pm) essentially corresponds to the C2–N3 bond length in **21** (134.5 pm). The angle in the Li compound [**19** · glyme]$_2$ (108.0°) is larger than in the carbene **21** (104.2°), which was similarly observed in the case of the Li-imidazolylidene, **12**, if compared with the imidazolylidene, **14**. We will comment on the long S1(2)–C1(8) bond and the wider angle in the lithiated [**19** · glyme]$_2$ in the following Section dealing with the *ZnBr*-thiazol-2-ylidene [**25** · THF]$_2$.

Crystal Structure of [3-(Zinc bromide)thiazol-2-ylidene–Tetrahydrofuran]$_2$ ([25 · THF]$_2$)

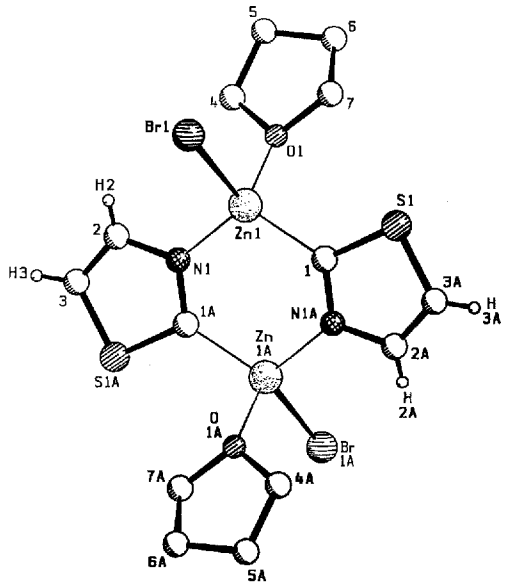
Since it is interesting to see how the structure of the lithiated thiazole anion is influenced by a different counterion to Li^+, the ZnBr-species [**25** · THF]$_2$ was studied next. [**25** · THF]$_2$ was prepared from the thiazole bromide **24** by reaction with zinc.



24 [**25** · THF]$_2$

The crystal structure of [**25** · THF]$_2$ is shown in Figure 5, and Table 6 summarizes significant bond lengths and angles of [**25** · THF]$_2$ together with those of the lithium compound [**19** · glyme]$_2$.

Figure 5. Crystal structure of [**25** · THF]$_2$



As shown in Table 6, the bond length from sulphur to the carbene carbon atom is distinctly shorter in the zinc compound [**25** · THF]$_2$ (S1A–C1A 173.3 pm) than in the lithiated [**19** · glyme]$_2$ [S1(2)–C1(8) 176.2 pm]. This difference of the C–S bond lengths should indicate different

Table 6. Bond lengths [pm], bond angles [°] in [**25** · THF]$_2$ and [**19** · glyme]$_2$

	[25·THF]$_2$		[19·glyme]$_2$[a]
S1A-C1A	173.3	S1(2)-C1(8)	176.2
C1A-N1	132.7	C1(8)-N1(2)	132.9
S1A-C1A-N1	109.2	S1(2)-C1(8)-N1(2)	108.0
Zn1-N1	202.1	Li1(2)-N1(2)	200.0
Zn1-C1A	293.9	Li1(2)-C1(8)	253.5
Zn1A-C1A	200.0	Li2(1)-C1(8)	217.6
N1-C1A-Zn1	36.0	N1(2)-C1(8)-Li1(2)	51.5

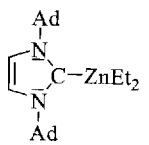
[a] Mean values of the two different molecules **19**.

tendencies of the two compounds for ring opening (**9** → **9′**, s. Scheme 3), i.e., the cyclic Zn species, **25**, should be more stable than the cyclic Li species, **19**. To the best of our knowledge there is no report in the literature comparing the stabilities of a C-2 lithiated with a "zincated" *thiazole*. Two recent publications, however, deal with Li- and ZnX-*oxazoles*, respectively (**7**, see Scheme 3)[26,27]. They confirm nicely the conclusions drawn from the longer S−C$_{carbene}$ bond in the Li compound [**19** · glyme]$_2$ in comparison to the shorter one in the ZnBr-species, [**25** · THF]$_2$, first by synthetic investigations. NMR investigations of the metalated oxazoles also show that the ring-opened isomer, **7′** is preferred if the gegenion is Li^+, while the cyclic **7** is favoured with ZnX^+ as the gegenion[26,28].

The N−C$_{carbene}$ bond distances are essentially the same in [**25** · THF]$_2$ and [**19** · glyme]$_2$ (132.7 and 132.9 pm, respectively). While there is at least a weak bridging bond between Li1(2) and carbene C1(8) (253.5 pm) in the lithiated [**19** · glyme]$_2$, there is no tendency for such bridging of Zn1 to C1A in [**25** · THF]$_2$; the Zn1−C1A distance amounts to 293.9 pm. Correspondingly, the angle N1−C1A−Zn1 in [**25** · THF]$_2$ is much smaller (36.0°) than the comparable angle [N1(2)−C1(8)−Li1(2) 51.5°] in [**19** · glyme]$_2$. The bond angle at the carbene C atom S1A−C1A−N1 in [**25** · THF]$_2$ (109.2°) is even wider than the corresponding one in the lithiated [**19** · glyme]$_2$, S1(2)−C1(8)−N1(2) = 108.0°.

A comparison of significant bond lengths and angles of the ZnBr species [**25** · THF]$_2$ (Table 6) with those of the parent thiazole **22** (Table 5) shows that in [**25** · THF]$_2$, S1A−C1A is 0.9 pm and C1A−N1 2.3 pm longer than the corresponding bonds in **22**, while the angle S1A−C1A−N1 is 5.9° smaller than S1−C2−N3 in **22**.

As in the cases of (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$ and [**19** · glyme]$_2$, aggregation to give the dimer [**25** · THF]$_2$ leads to a bond between the carbene atom and a "Lewis acid"; the C1A−Zn1A bond length amounts to 200.0 pm. A longer C$_{carbene}$−Zn bond was found in the complex of carbene **14** with diethyl zinc, **14** · $ZnEt_2$[29].



14 · $ZnEt_2$, Ad = adamantyl

In **14** · $ZnEt_2$, the C$_{carbene}$−Zn bond is 209.6 pm long. As usual in such carbene complexes[19a], the N−C$_{carbene}$ bonds in **14** · $ZnEt_2$ are slightly shorter (136.0 and 135.6 pm) than in the uncomplexed **14** (136.7 and 137.3 pm), while the angle at the carben carbon C2, N1−C2−N3, in **14** · $ZnEt_2$ is wider (104.1°) than in **14** (102.2°). The mutual Lewis acid complexations at the carbene atoms of the two molecules, **25**, in the dimer, [**25** · THF]$_2$, should therefore also contribute to some shortening of the S1A−C1A and C1A−N1 bonds, and to some widening of the S1A−C1A−N1 angle.

Altogether it thus seems that in the "zincated" [**25** · THF]$_2$ the carbene nature is less pronounced than in the lithiated [**19** · glyme]$_2$, as indicated by the shorter C−S bond and wider S−C−N angle in [**25** · THF]$_2$ than in [**19** · glyme]$_2$, and the short C$_{(carbene)}$−Zn bond in [**25** · THF]$_2$. The following NMR investigations fully support this interpretation.

^{13}C-NMR Investigations of Acyl (Formyl) Lithium Equivalents

NMR investigations revealed that the carbene carbon atoms, ^{13}C2, of stable imidazol-2-ylidenes and thiazol-2-ylidenes show a strong downfield shift. The mean value in the case of five imidazol-2-ylidenes amounts to δ_{C2} = 216.1[18−20], while two thiazol-2-ylidenes give a mean value of δ_{C2} = 252.0[23]. From the information given in the previous sections, it is not surprising that 3-lithiated imidazol-2-ylidenes and 3-lithiated thiazol-2-ylidenes show very similar behaviour. Table 7 gives the results for several examples.

Table 7. ^{13}C-NMR chemical shifts [ppm] of the carbene carbon atoms of 3-Li-imidazol-2-ylidenes (**1** to **4**), 3-Li-thiazol-2-ylidenes (**5** to **10**), and a ZnBr-thiazol-2-ylidene (**11**)

Entry	Compound	δ^{13}C [ppm]
1	1-methyl-3-Li-imidazol-2-ylidene	201.6
2	1-methyl-3-Li-4-*tert*-butyl-imidazol-2-ylidene **12**	195.0
3	1-methyl-3-Li-4-phenyl-imidazol-2-ylidene	200.9
4	1-methyl-3-Li-benzoimidazol-2-ylidene	216.1
5	3-Li-thiazol-2-ylidene	231.8
6	3-Li-4,5-dimethyl-thiazol-2-ylidene	229.6
7	3-Li-4-*tert*-butyl-thiazol-2-ylidene **19**	231.9
8	3-Li-4-(N,N-dimethylaminomethyl)thiazol-2-ylidene	234.8
9	3-Li-5-phenyl-thiazol-2-ylidene	231.9
10	3-Li-benzothiazol-2-ylidene	234.6
11	3-ZnBr-thiazol-2-ylidene **25**	198.5

The mean value of the 3-lithiated imidazol-2-ylidenes (entries 1 to 4) amounts to δ = 203.6, which compares well with the value of the non-lithiated carbenes (216.1). The ^{13}C signal of C2 in 1-methyl-imidazole is observed at δ = 137.7. The ^{13}C-NMR investigations thus nicely support the results of the crystal structures of (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$ and their interpretation.

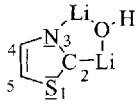
In the case of the 3-lithiated thiazol-2-ylidenes, a mean value of 232.4 is determined, (entries 5 to 10). The ^{13}C signal of C2 in thiazol is found at δ = 152.6 pm. Thus, in 3-lithiated thiazoles, the ^{13}C signal of the carbene carbon atom is also characterized by a significant downfield shift which almost equals that in thiazol-2-ylidenes (252.0). A remarkable difference is observed in the case of 3-*ZnBr*-thiazol-2-ylidene **25** (entry 11), in which case the ^{13}C signal is found at δ = 198.5; the mean value of the *lithiated* thia-

zol-2-ylidenes is 232.4. If this indicates a distinctly less pronounced carbene character of the 3-*ZnBr*-thiazol-2-ylidene **25**, then this result again nicely agrees well with the result of the X-ray crystal structure of [**25** · THF]$_2$.

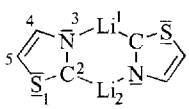
In spite of the corroboration of the crystal structures by the ^{13}C-NMR investigations one should still express a caveat: transformation of vinylic or aromatic compounds in their lithiated species leads *generally* to a strong downfield shift of the respective ^{13}C atom, as detailed in the following paper[9]. The interpretation of ^{13}C-NMR data without a knowledge of structural details therefore can be misleading.

Model Calculations of Lithiated Thiazole and its Dimer

Are the structural changes observed on going from *tert*-butyl-thiazole (**18**) to the lithiated *tert*-butyl thiazole dimer, [**19** · glyme]$_2$, reproduced by calculations? What are the significant differences between a neutral carbene such as the thiazol-2-ylidene, **21**, and a lithiated derivative thereof, such as **19**? In order to investigate this problem we calculated the structures of two model compounds, the Li-thiazole-LiOH complex, **26** · LiOH, and the Li-thiazole dimer, [**26**]$_2$, both unsolvated at Li.



26 · LiOH



[**26**]$_2$

Table 8 gives the MP2/6-31G(d) data of **26** · LiOH and [**26**]$_2$ and the experimentally determined values of [**19** · glyme]$_2$.

Table 8. Calculated [MP2/6-31G(d)] bond lengths [pm] and bond angles [°] of **26** · LiOH and [**26**]$_2$ compared with the experimental ones of [**19** · glyme]$_2$

	26·LiOH	[**26**]$_2$	[**19**·glyme]$_2$[a]	
S1-C2	174.2	174.3	S1(2)-C1(8)	176.2
C2-N3	135.4	135.4	C1(8)-N1(2)	132.9
S1-C2-N3	108.6	108.6	S1(2)-C1(8)-N1(2)	108.0
Li1-N3	196.6	192.5	Li1(2)-N1(2)	200.0
Li1-C2	251.1	236.0	Li1(2)-C1(8)	253.5
Li2-C2	209.7	209.6	Li2(1)-C1(8)	217.6

[a] Mean values of the two different molecules **19**.

The experimental data of the lithiated thiazole [**19** · glyme]$_2$ are in good agreement even with these simple models; S1–C2 in **26** · LiOH and [**26**]$_2$ (174.2 and 174.3 pm) are clearly longer than the S–C bonds in thiazol **22** (172.4 pm, Table 5), although they do not reach the experimental value of [**19** · glyme]$_2$ (176.2 pm). The C2–N3 bond in **26** · LiOH and [**26**]$_2$ is also elongated if compared to that in **22** (135.4 versus 130.4 pm) (Table 5); in [**19** · glyme]$_2$, 132.9 pm is found. The calculated bond angles, S1–C2–N3, in **26** · LiOH and [**26**]$_2$ amount to 108.6°, which is almost exactly the value found in [**19** · glyme]$_2$ (108.0°). In thiazole **22** this angle amounts to 115.1° (Table 5). In addition, the bond distances calculated for the two cations Li1 and Li2 to the thiazole anions in **26** · LiOH and [**26**]$_2$ are also in line with the experimental ones in [**19** · glyme]$_2$ (see Table 8). In summary, the changes observed on lithiation of thiazole are nicely reproduced even by calculations of simple model compounds.

Why are the Acyl (Formyl) Lithium Equivalents, (12)$_4$ · Li$_2$O · LiOCH$_3$ · LiOCH$_2$CH$_2$OCH$_3$, [19 · glyme]$_2$ and [25 · THF]$_2$ so stable?

It is the purpose of this work to show, by means of appropriate model compounds, that the inherent instability of "normal" acyl(formyl)lithium compounds, **1**, is indeed due to their *strong carbene character* (bridged structure **1′**) or even to their existence as *carbene isomers*, **1″**.

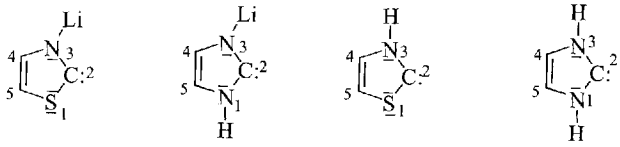
1′

1″

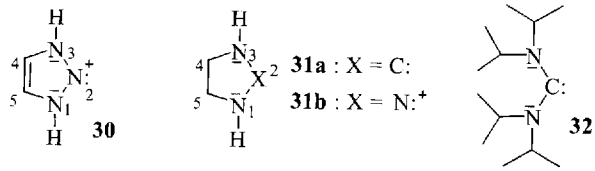
This is demonstrated, not only by means of derivatives of the lithiated thiazole **26** ([**19** · glyme]$_2$), but also the "zincated" [**25** · THF]$_2$), and the lithiated imidazole **27** [(**12**)$_4$ · Li$_2$O · LiOCH$_3$ · LiOCH$_2$CH$_2$OCH$_3$], see Scheme 6.

Why are exactly these acyl(formyl)lithium *equivalents* much more stable than "normal" acyllithium species? Why do they not dimerize to give "olefins" like "normal" acyllithium species [**1′** (**1″**) → **3** (Scheme 1)], a reaction which is also typical for "normal" carbenes?

Scheme 6. Stable acyllithium equivalents (**26**, **27**), carbenes (**28**, **29**, **31a**, **32**), and nitrenium ions (**30**, **31b**)



26 **27** **28** **29**



30 **31a** : X = C: **31b** : X = N:$^+$ **32**

The much greater stability of these acyl(formyl)lithium *equivalents* when compared with "normal" acyllithium species undoubtedly must be due to the same reason which also allowed the first isolation of stable carbenes of the imidazol-2-ylidene type (**29**)[18–20], and more recently, of the thiazol-2-ylidene type (**28**)[23] (Scheme 6). The isoelectronic nitrenium ions, **30** (Scheme 6), which are normally as unstable as carbenes, are also strongly stabilized by such a structural pattern; they, too, can be isolated and characterized by X-ray crystallography[30].

The reasons for the thermodynamic stabilization of carbenes of the type **29** has been of great interest[30–39]. From recent theoretical studies[30,38,39] it is quite clear that the carbenes, **28** and **29**, as well as nitrenium ions such as **30**, profit strongly from cyclic delocalization in the 6π aromatic systems. Aromaticity, however, is not a prerequisite for carbene (nitrenium ion) stability; saturated systems such as **31a**

and **b** (and even the non-cyclic **32**[20b]) (Scheme 6) profit strongly enough from the electronic stabilization of the formally empty p(π) orbital at C(2) [N^+(2)] by the two donor substituents to be isolated[20b,30,38,39] (a structurally related acyllithium equivalent has not yet been studied). It is thus not surprising that the calculated p(π) populations, especially at the atoms 1, 2, and 3 of **28**, **29**, **30**, and **31**, correlate well with other calculated properties which are indicative of the stabilization of these compounds[30,38,39]. In Table 9, the p(π) populations at the ring atoms of the lithiated thiazole, **26**, and the lithiated imidazole, **27**, as models for the stable acyl(formyl)lithium equivalents [**19** · glyme]$_2$ and (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$, are listed together with those of the models for stable carbenes (**28** and **29**).

Table 9. p(π) Populations [MP2-NBO/6-31G(d)//MP2/6-31G(d)] at the ring atoms of the lithiated thiazole **26** and the lithiated imidazole **27** in comparison with the data of the corresponding carbenes **28** and **29**

	atoms				
	1	2	3	4	5
	S or N	C or N	N	C	C
26	1.56	0.91	1.29	1.04	1.11
28	1.56	0.71	1.50	1.05	1.10
27	1.54	0.87	1.34	1.07	1.09
29	1.54	0.67	1.54	1.08	1.08

Table 9 shows that the p(π) populations at the carbon atoms C2 of the carbenes **28** (0.71) and **29** (0.67), which are already rather high, are increased in the corresponding lithiated species **26** (0.91) and **27** (0.87). Correspondingly, the p(π) densities at the lithiated nitrogen atoms N3 are decreased in the lithiated species from 1.50 in **28** to 1.29 in **26**, and from 1.54 in **29** to 1.34 in **27**. These changes in p(π) population are due to σ/π polarization at the lithiated N3 atoms in **26** and **27**, a phenomenon which has already been discussed in the section on the structure of the lithiated imidazoles (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$ to explain structural differences to the corresponding non-lithiated carbenes. The rather long C–S bond in [**19** · glyme]$_2$ has the same origin.

This leads to the following final conclusions. Acyl (formyl) lithium equivalents of the general type **26** and **27** can be isolated and structurally characterized which reveals the carbene nature of these compounds. They are well stabilized by π-donation from the donor atoms next to the carbene carbon atoms, as is the case for the stable carbenes of the same structural type (**28** and **29**). A similar situation is responsible for the extraordinary stability of the structurally related nitrenium ions, **30**. One can further conclude that "normal" acyl(formyl)lithium compounds should also be carbenes; however, it will be difficult to isolate and characterize a non-stabilized species under comparable conditions, as is also the case for nonstabilized carbenes and nitrenium ions.

We are grateful to the *Fonds der Chemischen Industrie*, and the *Deutsche Forschungsgemeinschaft* (SFB 260 and Graduiertenkolleg "Metallorganische Chemie") for support of this work.

Experimental Section

1-Methyl-4-tert-butylimidazole (**11**): **11** was prepared in two steps.

a) *4-tert-Butylimidazole:* This compound was prepared according to a modified version of Jönsson's procedure[40]: 345 g (1.93 mol) of 1-bromo-3,3-dimethyl-butane-2-on were heated with 770 ml (870 g, 18 mol) of formamide for 6 h to 150°C. After cooling to 20°C, the reaction mixture was added to 2 N HCl and briefly heated to reflux. The acidic solution (30°C) was then heated with a conc. NH_3 solution from which the organic layer was separated with *tert*-butyl methyl ether. After drying with $MgSO_4$, the solvent was removed and the remaining 74.8 g (31%) of 4-*tert*-butylimidazole was further used without purification. – ^{1}H NMR ($CDCl_3$) δ = 7.40 (s, 1H, H2), 6.50 (s, 1H, H5), 1.15 [s, 9H, $-C(CH_3)_3$], the NH proton was not detectable. – ^{13}C NMR ($CDCl_3$) δ = 146.8 (C4), 134.9 (C2), 115.7 (C5), 31.4 (C6), 30.7 (C7).

b) *1-Methyl-4-tert-butylimidazole* (**11**): This procedure is analogous to the one described in ref.[41]. 74.8 g (0.60 mol) of 4-*tert*-butylimidazole were treated with 430 ml of a KOH solution (10%; 0.75 mol of KOH). To this solution were added 62 ml (82.0 g, 0.65 mol) of dimethylsulphate at a rate which kept the temperature below 40°C. The reaction was finished by heating the solution to 80°C for 30 min. The cold (20°C) solution was extracted with diethyl ether, and the organic layer was washed with NaOH and H_2O. Drying with $MgSO_4$, removing of the solvent and destillation of the product (60°C, 1 Torr) led to 25.8 g (32%) **11**; m.p.: 11°C. – ^{1}H NMR ($CDCl_3$) δ = 7.27 (s, 1H, H2), 6.51 (s, 1H, H5), 3.55 (s, 3H, $N-CH_3$), 1.21 [s, 9H, $-C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$) δ = 153.2 (C4), 136.9 (C2), 113.7 (C5), 33.1 (C8), 31.7 (C6), 30.2 (C7).

11 prepared by this route is cleaner than otherwise synthesized[42].

4-tert-Butylthiazole (**18**): The procedure described is analogous to the one in ref.[43], although different from that in ref.[44], which was less successful. To 173 g (0.97 mol) of bromopinacolone in 650 ml of acetone was added 67.2 g (1.10 mol) of thioformamide in 400 ml of acetone. The HBr adduct of **18** crystallized on standing overnight at 5°C. The basic solution (after treatment with NaOH) was extracted with *tert*-butyl methyl ether, dried with $MgSO_4$, and the ether removed in vacuo. Destillation of **18** (55°C, 14 Torr) led to 56.1 g (41%) **18**. – ^{1}H NMR ($CDCl_3$ δ = 8.75 (s, 1H, H2), 6.93 (s, 1H, H5), 1.35 [s, 9H, $-C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$) δ = 167.5 (C4), 152.0 (C2), 110.1 (C5), 34.7 (C6), 30.2 (C7).

Preparation of the Crystals of (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$: 138 mg (1.00 mmol) of 1-methyl-4-*tert*-butyl-imidazole (**11**) dissolved in 3.00 ml of *tert*-butyl methyl ether and 0.14 ml of diglyme were deprotonated with 0.70 ml (1.12 mmol) of a 1.6 M solution of methyllithium in diethyl ether at 20°C (30 min). After 24 h at 20°C, an amorphous precipitate was removed by passing the solution through a filter (0.2 μm). After another 24 h, crystals of (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$ had formed (14 mg, 8%) which were suitable for an X-ray crystal structure determination. Both modifications, $P2_1/c$, $Z = 4$ as well as $P2_1/n$, $Z = 4$, were formed simultaneously.

Preparation of the Crystals of [**19** · *glyme*]$_2$: This procedure was described in ref.[16].

Preparation of the Crystals of [**25** · *THF*]$_2$: 1.5 g of Zn dust in 2 ml of THF was activated with 65 mg (0.35 mmol) of 1,2-dibromomethane and 21 mg (0.19 mmol) of chlorotrimethylsilane. Another 5 ml of THF and then 1.64 g (0.01 mol) of 2-bromothiazole (**23**) were added, the latter, slowly, and the reaction mixture stirred for 2 h at 35°C. After filtration and dilution with 6 ml of

THF, the solution was kept for 24 h at −78°C. The THF solution was removed from the crystalline [**25** · THF]$_2$ with a syringe, and the crystals dissolved in 12 ml of glyme at 20°C. After 24 h at −25°C, crystals of [**25** · THF]$_2$, suitable for an X-ray crystal structure determination, were formed (2.1 g, 73%).

*Crystal Data for (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$, $P2_1/n$, (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$, $P2_1/c$ and [**25** · THF]$_2$:* (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$, $P2_1/n$: $C_{36}H_{62}Li_8N_8O_4$; monoclinic space group $P2_1/n$; a = 1510.7(1), b = 2041.9(2), c = 1583.5(1) pm, β = 115.70(1)°, V = 4401.4(6) · 10^{-30} m^3, Z = 4; data collection on an Enraf-Nonius CAD4 diffractometer using Cu-K_α-radiation, T = 208(2) K, 7014 reflections, 5504 unique (R_{int} = 0.0591). Solution with direct methods (SHELXTL-PLUS), full matrix least-squares refinement on F^2 (SHELXL-93), nonhydrogen atoms anisotropic, C-bonded hydrogens on calculated positions wit fixed isotropic temperature factors, N-bonded hydrogens located and isotropically refined; wR_2 = 0.2270 (all data, on F^2, parameters for the weighting sheme calculated by the program: 0.0813, 6.8384), conventional R = 0.0641 for 3335 reflections with $I > 2\sigma(I)$, Goodness-of-fit (F^2) = 1.042, 540 parameters.

*(**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$, $P2_1/c$:* Due to the slightly high R value of (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$, $P2_1/n$, a second crystal was measured, but there was another modification: monoclinic space group $P2_1/c$, a = 1223.2(1), b = 2633.0(2), c = 1415.7(1) pm, β = 102.12(1)°, V = 4457.9(6) · 10^{-30} m^3, T = 193(2) K, 6852 reflections, 5511 unique (R_{int} = 0.0289). Solution and refinement as for (**12**)$_4$ · Li_2O · $LiOCH_3$ · $LiOCH_2CH_2OCH_3$, $P2_1/n$, wR_2 = 0.1522 (parameters for the weighting sheme: 0.0822, 1.9736), R = 0.0496 (4070 reflections with $I > 2\sigma(I)$), Goodness-of-Fit: 1.057, 570 parameters (some methyl groups were disordered).

*[**25** · THF]$_2$:* $C_7H_{10}BrNOSZn$: monoclinic space group $P2_1/c$; a = 948.5(1), b = 1415.9(3), c = 807.8(1) pm, β = 108.50(1)°, V = 1028.8(3) · 10^{-30} m^3, Z = 4; data collection on a Siemens P4 diffractometer using Mo-K_α-radiation, T = 208(2) K, 3051 reflections, 2342 unique (R_{int} = 0.0442); semiempirical absorption correction from Ψ-scans. Solution with direct methods (SHELXTL-PLUS), full matrix least-squares refinement on F^2 (SHELXL-93), nonhydrogen atoms anisotropic, hydrogens isotropic; wR_2 = 0.1016 (2341 reflections, on F^2, parameters for the weighting sheme calculated by the program: 0.0541, 0.0), conventional R = 0.0368 for 1550 reflections with $I > 2\sigma(I)$, Goodness-of-fit (F^2) = 0.880, 115 parameters.

All calculations have been performed on a DEC AXP 3000/300X[45-49].

1-Methyl-4-phenylimidazole: The compound was synthesized according to a modified version of the procedure of Hazeldine, Pyman, and Winchester[50]. 31.1 g (0.24 mol) of 4-phenylimidazole were treated with 171 ml of a solution containing 10% KOH (0.30 mol). 23 ml (30.7 g, 0.24 mol) of dimethylsulphate were then added under cooling, and finally heated to 80°C for 30 min. The product was extracted 3 times with chloroform and dried over $CaCl_2$. Distillation at 147−148°C/0.1 Torr led to 8.15 g (22%) of 1-methyl-4-phenyl-imidazole. − ^{1}H NMR ($CDCl_3$) δ = 7.71−7.69 (d, J = 7.27 Hz, 2H, H_{ortho}), 7.40 (s, 1H, H2), 7.33−7.28 (t, J = 7.84 Hz, 1H, H_{para}), 7.19−7.14 (t, J = 7.27 Hz, 2H, H_{meta}), 7.10 (s, 1H, H5), 3.64 (s, 3H, N−CH_3). − ^{13}C NMR ($CDCl_3$) δ = 142.3 (C4), 137.9 (C2), 134.2 (phenyl-C), 128.5 (phenyl-C), 126.6 (phenyl-C), 124.7 (phenyl-C), 115.8 (C5), 33.3 (C10).

1-Methylbenzimidazole: The preparation was performed by methylation of benzimidazole according to the procedure outlined in detail for 1-methyl-4-phenylimidazole. Yield: 15%, m.p. 59°C (lit.[51] 60−61°C). − ^{13}C NMR ($CDCl_3$) δ = 143.8, 143.6, 134.6, 122.9, 122.0, 120.2, 109.4 (ring C's); 30.9 (CH_3).

4-[(N,N-Dimethylamino)methyl]thiazole: The compound was prepared by analogy to a procedure of Sprague, Land, and Ziegler[52]. To a solution of 20.3 g (0.45 mol) of dimethylamine in ethanol was added 25.5 g (0.15 mol) of 4-(chloromethyl)thiazole hydrochloride and then stirred overnight. After 1 h of heating to 80°C, the compound was extracted 3 times with dichloromethane and dried over Na_2SO_4. Distillation at 39°C/0.1 Torr gave 5.79 g (27%) of the pure product. − ^{1}H NMR ($CDCl_3$) δ = 8.71 (s, 1H, H2), 7.12 (s, 1H, H5), 3.67 (s, 2H, −CH_2−), 2.22 [s, 6H, N(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$) δ = 155.3 (C4), 152.3 (C2), 115.3 (C5), 59.1 (C6), 45.3 (C7, 8). − $C_6H_{10}N_2S$ (142.22): calcd. C 50.67, H 7.09, N 19.70; found C 50.52, H 7.22, N 19.72.

5-Phenylthiazole: 5-Phenylthiazole was prepared according to a patent of the Merck company[53]. Yield 21.6 g (18%), m.p. 40°C (lit.[54] 40−41°C). − ^{13}C NMR ($CDCl_3$) δ = 152.0 (C2), 139.5 (C5), 139.0 (C4), 131.1, 129.1, 128.4, 127.0 (phenyl C's).

1-Methylimidazole (Merck), *thiazole* (Aldrich), *4,5-dimethylthiazole* (Lancaster), and *benzothiazole* (Janssen) were commercially available.

Computational Methods: All calculations on geometries, energies, and electronic properties were carried out at the MP2/6-31G(d) level of theory using the program packages TURBOMOLE[55] and GAUSSIAN92[56].

☆ Dedicated to Professor Dr. *Peter Welzel* on the occasion of his 60th birthday.

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