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The Influence of the Leaving Group X (X=F, Cl, Br, I, OH) on the Carbenoid Nature of the Carbenoids $LiCH_2X$ and $XZnCH_2X$—A Theoretical Study

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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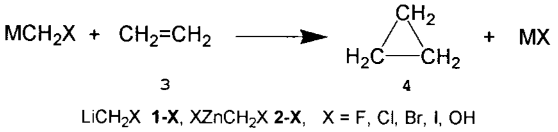
Abstract—A quantum-chemical investigation shows that the reactions of the carbenoids $LiCH_2X$ **1-X**, X=F, Cl, Br, I and OH, with ethene **3** to cyclopropane **4**+LiX profit from a weakening of the C–X bonds by the C–Li bonds in the carbenoids **1-X** and in the complexes [**1-X·3**]. The C–F bond is more affected than the C–I bond. Since in the transition states $[\mathbf{1\text{-}X\cdot 3}]^{\ddagger}$ LiHal is strongly decomplexed, the cleavage of the C–Hal bonds is essentially compensated by the formation of the Li–Hal bonds, which leads to almost equal transition state energies for the reactions of **1-Hal** with **3**. The higher energy for the reaction of **1-OH** with **3** results from the high C–OH bond energy. In the reactions of $XZnCH_2X$ **2-X** with **3** to **4**, the C–ZnX bonds cause almost no elongation of the C–X bonds. This leads to higher activation energies, which is in agreement with experimental results. Furthermore, **2-F** is calculated to have a much higher transition state energy than **2-I**, the normally used Simmons–Smith reagents, again in excellent agreement with the experiment. The latter result is due to the much higher C–F (110.9 kcal/mol) than C–I bond energy (58.2 kcal/mol). © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

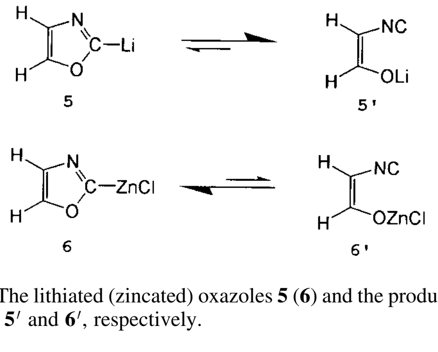
Carbenoids $LiCH_2X$ **1-X**, X=Hal, OR,[1–10] and $XZnCH_2X$ **2-X,** in general X=I ('Simmons–Smith reagents'),[11–14] belong to the synthetically most useful reactive intermediates. As expected for 'carbanions', $LiCH_2X$ **1-X** react as *nucleophiles*. Most interestingly, however, is the *electrophilic* behavior of these species: $LiCH_2X$ **1-X** insert into C–H and C–C bonds; they react with RLi to give $RCH_2Li+LiX$, and with $LiCH_2X$ **1-X** to form $H_2C{=}CH_2$ **3**+2 LiX ('eliminative dimerization'). Furthermore, $LiCH_2X$ **1-X** and $XZnCH_2X$ **2-X** add to olefinic double bonds as, e.g. of ethene **3** to cyclopropanes **4**, see Scheme 1.[15]

From experimental experience it is evident that $LiCH_2X$ **1-X** are by far 'stronger carbenoids' than $XZnCH_2X$ **2-X**: the reaction of **1-X** with olefins like **3** to **4** is fast even at −78°C,[1–10] while **2-X** undergo the same reaction only at room temperature or above.[11–14] What is the reason for the different reactivity of Li/X and XZn/X carbenoids **1-X** and **2-X**?

Li/X carbenoids **1-X**, especially with X=F, Cl and OH (OH as a model for OR), have been analyzed thoroughly by various quantumchemical methods,[16–34] and in recent years the Simmons–Smith reagents **2-X** were also studied by such means.[35–39] The difference between *lithium* (**1-X**) and *zinc* carbenoids **2-X** can be traced back to an analysis of the carbon–metal and the carbon–X bond as, e.g. in the case



Scheme 1. Cyclopropanation of ethene **3** with carbenoids MCH_2X.



Scheme 2. The lithiated (zincated) oxazoles **5** (**6**) and the products of the α-elimination **5′** and **6′**, respectively.

Keywords: theoretical studies; cycloadditions; carbenoids; olefins; transition states.

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of the 2-lithiated (zincated) oxazoles **5** and **6**, respectively, see Scheme 2.[37]

Oxazole **5** undergoes facile α-elimination to give **5′**, while **6** does not form **6′**. According to the calculations, the high s-character of the C-orbital of the C–Li bond in **5** ($sp^{1.0}$) is accompanied by a high p-character of the C-orbital in the carbenoid C–O bond ($sp^{3.3}$). In contrast, in the more covalent C–ZnCl bond in **6** the C-orbital is $sp^{2.2}$-hybridized which leads to a hybridization of the C-orbital in the C–O bond of $sp^{2.4}$. Thus, the weaker C–O bond in **5** is more easily broken (especially if a lithium-assisted ionization is involved) than the C–O bond in **6**; **5′** is also 15.2 kcal/mol more stable than **5**, while **6′** is 11.8 kcal/mol less stable than **6**. As will be shown in this work similar differences of the hybridizations of the C–Li(ZnX) and C–X bonds are characteristic for the behaviour of the carbenoids $LiCH_2X$ **1-X** and $XZnCH_2X$ **2-X**.

Although the number of theoretical investigations of **1-X** and **2-X** has increased lately there is only one work which allows a direct comparison of species **1-X** and **2-X**. Nakamura et al.[39] recently studied the transition states of the reactions of **1-Cl** and **2-Cl** with ethene **3** to give cyclopropane **4**. In agreement with the experimental results the energy of the transition state of the reaction of **3** with **1-Cl** amounts only to 3.8 kcal/mol, while it is 17.3 kcal/mol in the case of **2-Cl**. The calculations are in accord with the facile C–O bond cleavage in **5** as compared to **6**, see Scheme 2. The influence of the metal M in carbenoids $M–CH_2–X$ is thus well documented, at least for M=Li, **1-X,** and M=ZnCl, **2-X**.

In the following we are concerned with the question about the influence of the *leaving group X, X=F, Cl, Br, I and OH (as a model for OR),* on structure and reactivity in the carbenoid series **1-X** and **2-X**. With regard to **1-X**, it is known experimentally that Li/Hal carbenoids are much more reactive than Li/OR carbenoids.[26,27,40,41] Investigations comparing the reactivities of the different Li/Hal carbenoids **1-Hal** are not known. Furthermore, the most widely used Li/Hal carbenoids **1-Hal** are $LiCH_2Br$ **1-Br** and $LiCH_2I$ **1-I**, which have not been studied theoretically. An influence of X on zinc carbenoids **2-X,** although not studied theoretically, was found by Wittig:[42] reaction of $(PhCO_2CH_2)_2Zn$ with ZnF_2 ($ZnCl_2$; $ZnBr_2$; ZnI_2) and cyclohexene led under comparable conditions to norcarane in 0 (12; 36; 91)% yields.

Results and Discussion

Carbenoids $LiCH_2X$ 1-X, X=F, Cl, Br, I, OH

In Table 1 are summarized significant data of the structures of the most stable isomers of the carbenoids **1-X**, X=F, Cl, Br, I and OH, in which the C–X bond is bridged by lithium.[43–52]

As one can see from Table 1, the C–Li bonds are in the range of 192.4–196.7 pm. This corresponds to minimal changes if compared with the C–Li bond length in $H_3C–Li$ (a positive change [%] means an elongation, a negative change [%] a shortening with regard to the bond of comparison). Not unexpectedly, the hybridizations of the C-orbitals in the C–Li bonds show strong s-character. As a consequence, the C-orbitals of the C–X bonds have high p-character. This goes along with the C–X bonds in **1-X** being strongly elongated as compared to those in $CH_3–X$: in **1-F** the C–F bond (155.8 pm) is 17.1 pm longer than in $CH_3–F$ (138.7 pm) which corresponds to an elongation of 12.3%. In the case of **1-Cl** the elongation of the C–Cl bond amounts to 12.5 pm (177.5→190.0 pm), corresponding to 7.0%. Smaller elongations are found for **1-Br** (193.6→206.6 pm, Δ=13.0 pm, 6.7%) and **1-I** (214.7→226.6 pm, Δ=11.9 pm, 5.5%). In **1-OH** the situation is comparable to that in **1-Cl**: C–OH elongates from 142.1 to 152.2 pm, which corresponds to Δ=10.1 pm and 7.1%. Concerning the Li–X bonds in the Li-bridged **1-X**, the elongations, as compared to the bond lengths in the salts LiX, are between 8.2 and 11.9%, see Table 1.

The data of Table 1, especially those of the C–X bond elongations, which are confirmed by X-ray crystallography at least for the cases **1-Cl**[53–55] and **1-OR**,[26,27,40,56–59] might indicate that **1-F** is by far the 'strongest carbenoid', followed by **1-Cl** and **1-OH** (which are essentially equal), **1-Br**, and **1-I**, the 'weakest carbenoid'. Interestingly, **1-I** is one of the most widely used carbenoids of the $LiCH_2X$ type, and **1-Cl** is clearly much more reactive than α-lithiated ethers of the type $LiCH_2OR$.[26,27,40,41] It thus turns out that a comparison of the *structural properties* of the *carbenoids $LiCH_2X$ **1-X** with those of $CH_3–X$* is not in agreement with a scale of the 'carbenoid character' resulting from a comparison of the *reactivities of **1-X** with **3***.

Therefore we calculated the transition state structures and energies of the reactions of $LiCH_2X$ **1-X**, X=F, Cl, Br, I and

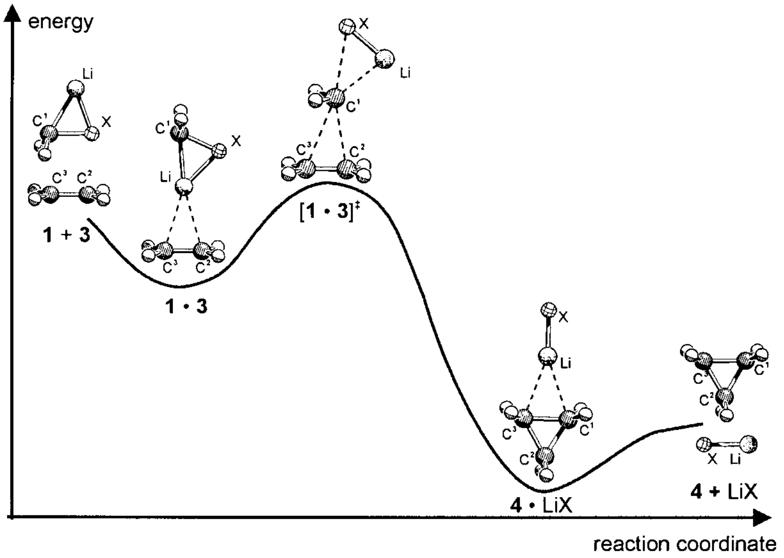
Table 1. Calculated bond lengths [pm] and bond elongation [%] in the carbenoids $LiCH_2X$ **1-X** as compared to the bond lengths of $CH_3–Li$, $CH_3–X$ and Li–X, respectively

	C–Li			C–X			Li–X	
1-X	*r* [pm]	Elong.[a] [%]	Hybr. C[1]	*r* [pm]	Elong.[b] [%]	Hybr. C[1]	*r* [pm]	Elong.[c] [%]
1-F	192.4	−2.9	$sp^{1.8}$	155.8	12.3	$sp^{8.5}$	178.5	11.9
1-Cl	194.7	−1.8	$sp^{1.9}$	190.0	7.0	$sp^{9.3}$	219.7	8.2
1-Br	196.7	−0.8	$sp^{1.8}$	206.6	6.7	$sp^{10.2}$	238.1	9.0
1-I	196.6	−0.8	$sp^{1.7}$	226.6	5.5	$sp^{11.8}$	261.9	8.7
1-OH	194.2	−2.0	$sp^{2.6}$	152.2	7.1	$sp^{5.1}$	177.4	10.7

[a] $CH_3–Li$ 198.2 pm.

[b] CH_3F 138.7 pm, CH_3Cl 177.5 pm, CH_3Br 193.6 pm, CH_3I 214.7 pm, CH_3OH 142.1 pm.

[c] LiF 159.5 pm, LiCl 203.1 pm, LiBr 218.4 pm, LiI 241.0 pm, LiOH 160.2 pm.



Scheme 3. Reaction profile of the cyclopropanation of ethene **3** with the carbenoids $LiCH_2X$ **1-X** to give cyclopropane **4**+LiX.

OH, with ethene **3** to give cyclopropane **4** and LiX, see Scheme 1. It was of interest to see whether the results are in agreement with the experimentally observed differences between the carbenoids Li/Hal and Li/OR. Furthermore, how is the reactivity scale within the Li/Hal series?

A reaction profile of the cyclopropanation of ethene **3** with $LiCH_2F$ **1-F** was first disclosed by Houk and Schleyer et al. (HF/3-21G).[60] The reactions investigated in our work similarly lead from the starting materials **1-X**+$CH_2{=}CH_2$ **3** (**1-X**+**3**) first to the complexes $LiCH_2X{\cdot}CH_2{=}CH_2$ [**1-X**], see Scheme 3. Via the transition states $[LiCH_2X{\cdot}CH_2{=}CH_2]^‡$ [**1-X·3**]‡ and the cyclopropane product complexes $C_3H_6{\cdot}LiX$ [**4**·LiX], the products C_3H_6 **4** and LiX are reached.

The relative energies of the complexes [**1-X·3**], transition states [**1-X·3**]‡, product complexes [**4**·LiX] and products **4**+LiX, as compared to the starting materials **1-X**+**3**, are summarized in Table 2.

Two results are of interest: (1) the transition state energy of the model reaction **1-OH**+**3** is roughly 2.5 times higher (19.2 kcal/mol) than the values of the carbenoids **1-Hal**, Hal=F, Cl, Br, I; (2) the transition state energies of the reactions of the different carbenoids **1-Hal** are rather similar. The low tendency of the carbenoids **1-OR** for cyclopropanation reactions is well documented. Schöllkopf et al.,[41] e.g. found in the reactions of **7** with the olefins **8** and **9**, respectively, the cyclopropanes **10** and **11** only in very low yields, see Scheme 4.

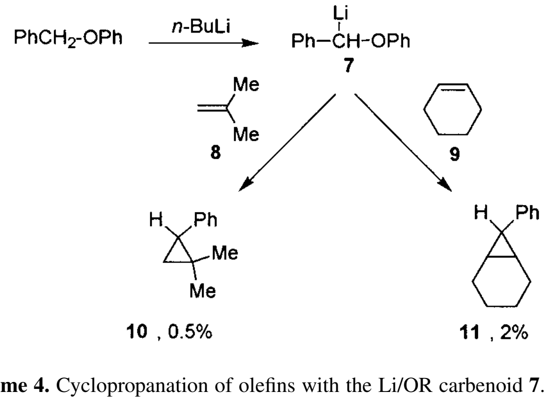
Table 2. Relative energies (values in parentheses include ZPE energy correction) [kcal/mol] of the complexes [**1-X·3**], transition states [**1-X·3**]‡, product complexes [**4**·LiX], and products **4**+LiX, as compared to the starting materials **1-X**+**3**[a]

	F	Cl	Br	I	OH
[**1-X·3**]	−10.4	−11.1	−11.3	−11.7	−9.8
[**1-X·3**]^{‡a}	7.4	6.9	6.5	6.1	19.2
	(10.1)	(7.9)	(7.7)	(7.4)	(19.8)
[**4**·LiX]	−78.0	−75.9	−75.1	−74.1	−60.1
4+LiX	−66.5	−63.0	−61.6	−60.0	−49.6
	(−62.9)	(−59.0)	(−57.4)	(−55.6)	(−47.2)

[a] MP2 calculations with two different all electron basis sets for the atoms F and Cl (6-311++G(d,p)//6-311++G(d,p) and cc-pVTZ//cc-pVDZ, respectively) yield lower transition state energies for [**1-F·3**]‡ (7.4 and 5.0 kcal/mol) than for [**1-Cl·3**]‡ (8.1 and 6.2 kcal/mol).

Cyclopropanation reactions with **1-Hal**, on the other hand, are rather fast even at low temperatures, as mentioned earlier. The similar transition state energies of the reactions of the different **1-Hal** with **3** lead to the conclusion that the 'carbenoid character' of all four carbenoids **1-Hal** is essentially the same, *at least in the cyclopropanation reaction*. This is an interesting result considering the different C–X bond energies in $H_3C–X$ (C–F 110.9 kcal/mol; C–Cl 81.0 kcal/mol; C–Br 70.2 kcal/mol; C–I 58.2 kcal/mol).[43–52] Therefore it is necessary to look in more detail into the structures of the transition states [**1-Hal·3**]‡. In Table 3 are listed C–Li, C–X and Li–X bond lengths [pm] as well as differences in bond lengths [%] in the transition states [**1-X·3**]‡ as compared to those in $CH_3–Li$, $CH_3–X$ and Li–X.

The C–Li bonds are now slightly longer than in $H_3C–Li$. The hybridizations in the C-orbitals of the C–Li bonds are between $sp^{1.2}$ and $sp^{1.4}$. Significant differences to the



Scheme 4. Cyclopropanation of olefins with the Li/OR carbenoid **7**.

Table 3. Calculated bond lengths [pm] and bond elongation [%] in the transition states [**1-X·3**]‡, X=F, Cl, Br, I, OH, as compared to the bond lengths of CH_3–Li, CH_3–X and Li–X (bond lengths of CH_3–Li, CH_3–X and Li–X, see Table 1. Since the geometries of $LiCH_2X$ **1-X** have not much changed in the complexes [**1-X·3**] (see Appendix) we refer the transition state geometries of [**1-X·3**]‡, as those of **1-X**, see Table 1, to CH_3–Li, CH_3–X and Li–X)

	C–Li			C–X			Li–X	
[**1-X·3**]‡	*r* [pm]	Elong. [%]	Hybr. C^1	*r* [pm]	Elong. [%]	Hybr. C^1	*r* [pm]	Elong. [%]
[**1-F·3**]‡	199.7	0.8	$sp^{1.3}$	192.8	39.0	p	167.9	5.3
[**1-Cl·3**]‡	200.6	1.2	$sp^{1.2}$	233.2	31.4	p	212.5	4.6
[**1-Br·3**]‡	200.8	1.3	$sp^{1.2}$	246.5	27.3	p	227.9	4.3
[**1-I·3**]‡	201.0	1.4	$sp^{1.2}$	265.9	23.8	p	250.9	4.1
[**1-OH·3**]‡	202.4	2.1	$sp^{1.4}$	193.7	36.3	p	167.6	4.6

situation in the carbenoids **1-X**, however, are not observed (see Table 1). This is completely different in the case of the C–Hal bonds: they are strongly elongated with C–F showing the largest elongation and C–I the smallest; C–OH is also rather long. Thus, C–F is elongated from 138.7 to 192.8 pm (39.0%), and C–I from 214.7 pm to 265.9 pm (23.8%); C–OH is 36.3% longer than in CH_3–OH. The Li–X bond lengths are shorter than in **1-X**. They are only slightly longer than in the salts LiX: Li–F (5.3%), Li–Cl (4.6%), LiBr (4.3%), LiI (4.1%), Li–OH (4.6%). With regard to the very long C1–C2 (204.0–227.8 pm) and C1–C3 bonds (243.4–253.4 pm) in the transition states [**1-X·3**]‡, see Scheme 3 and Appendix—the C–C bonds in cyclopropane are only 150.8 pm long—the transition states are best described as a *carbenoid $LiCH_2X$ **1-X** with strongly decomplexed LiX, approaching $CH_2{=}CH_2$ **3***. It thus seems that the rather different energies required for the cleavage of the C–X bonds in the transition states [**1-X·3**]‡ (which are already elongated in the carbenoids **1-X**, see Table 1) are essentially compensated by the formation of the Li–X bonds. A calculation of the bond (dissociation) energies as shown in Scheme 5 leads to the results summarized in Table 4.

It can be seen from Table 4 that the dissociation of $LiCH_2X$ **1-X** into $LiCH_2^+$ and X^- Eq. (1) requires a much higher energy in the case of **1-F** (194.8 kcal/mol) than in the case of **1-I** (156.3 kcal/mol). **1-OH** is even higher than **1-F** (217.9 kcal/mol). The formation of a Li–X bond between Li^+ and X^- Eq. (2), however, is much more favorable with X=F (−183.1 kcal/mol) than with X=I (−137.3 kcal/mol). The Li–OH bond energy (−189.2 kcal/mol) does not much exceed the Li–F bond energy. Eq. (3) $LiCH_2X+Li^+\rightarrow LiCH_2^+ + LiX$ summarizes the energies of Eqs. (1) and (2). One notices first that in the case of **1-OH** the energy is clearly higher (28.7 kcal/mol) than in the cases of the Li/Hal carbenoids **1-F**, **1-Cl**, **1-Br** and **1-I**, in agreement with the higher energy of the transition state of the reaction of **1-OH** with **3**, see Table 2. Secondly, the difference within the halide series **1-Hal** amounts only to 7.3 kcal/mol, which is in agreement with the similar transition state energies for the reactions of the carbenoids **1-Hal** with **3**, see Table 2. It is interesting to mention that in the transition states [**1-F·3**]‡ and [**1-OH·3**]‡ in which cases strong C–X bonds have to be cleaved, the C1–C2 and C1–C3 bonds are somewhat shorter than in the transition states [**1-Cl·3**]‡, [**1-Br·3**]‡ and [**1-I·3**]‡, see Appendix. In conclusion, according to the calculations outlined above, there is no special halide effect in the reactions of the carbenoids **1-Hal** with $CH_2{=}CH_2$ **3** because the energy of the cleavage of the C–Hal bonds in the transition states is essentially compensated by the energy of the formation of the Li–Hal bonds. In contrast, the reaction of **1-OH** with $CH_2{=}CH_2$ is comparatively unfavorable because of the strong C–O bond.[61]

$$\begin{array}{llll}
LiCH_2X & \longrightarrow & LiCH_2^+ \ + \ X^- & (1)\\
Li^+ \ + \ X^- & \longrightarrow & LiX & (2)\\
\hline
LiCH_2X + Li^+ & \longrightarrow & LiCH_2^+ \ + \ LiX & (3)
\end{array}$$

Scheme 5. Model reactions for the bond cleavage and bond formation steps of the leaving groups X in the transition states of the cyclopropanation reactions of **3** with $LiCH_2X$ **1-X**.

Table 4. Bond (dissociation) energies (kcal/mol) of the reactions **1**–**3**, see Scheme 5

	Reaction		
1-X	(1)	(2)	(3)
1-F	194.8	183.1	11.7
1-Cl	170.1	154.8	15.2
1-Br	164.1	147.5	16.6
1-I	156.3	137.3	19.0
1-OH	217.9	189.2	28.7

Carbenoids $XZnCH_2X$ 2-X, X=F, Cl, Br, I, OH

In order to get further insight into the reactions of carbenoids MCH_2X with olefins to give cyclopropanes we also studied the reactions of the zinc carbenoids $XZnCH_2X$ **2-X**, X=F, Cl, Br, I and OH, with ethene **3**. The C–Zn, C–X and Zn–X bond lengths of **2-X** as well as their differences with respect to the corresponding bonds in H_3C–Zn–CH_3, H_3C–X and X–Zn–X are summarized in Table 5.

The bond lengths C–ZnX in **2-X** are essentially the same as in $Zn(CH_3)_2$, see Table 5. One registers a dependence of the s-character in the C–ZnX bond of the nature of the X bound to carbon: the highest s-character in the C–Zn bond is observed in the case of X=I ($sp^{2.4}$), while the others are in the range between $sp^{3.1}$ and $sp^{3.7}$.

The C–X bonds in **2-X** are only marginally longer (1.4–2.3%) than in H_3C–X. This agrees perfectly with the results of the solid state structure investigations of Zn-carbenoids.[64] It is also significant that the 'bond' of the Zn atom to the leaving group X in **2-X**, as compared to the bond length in X–Zn–X, is exceptionally long because in the most stable XZn/X carbenoid structures the C–X bonds are not Zn-bridged. The differences in the Zn–X bond lengths

Table 5. Calculated bond lengths [pm] and bond elongation [%] in the carbenoids $XZnCH_2X$ **2-X** as compared to the bond lengths of CH_3–Zn–CH_3, CH_3–X and X–Zn–X, respectively

	C–Zn			C–X			Zn–X	
2-X	*r* [pm]	Elong.[a] [%]	Hybr. C^1	*r* [pm]	Elong.[b] [%]	Hybr. C^1	*r* [pm]	Elong.[c] [%]
2-F	192.2	0.1	$sp^{3.4}$	140.8	1.5	$sp^{3.6}$	272.8	56.4
2-Cl	191.9	−0.1	$sp^{3.2}$	181.6	2.3	$sp^{3.8}$	302.4	45.2
2-Br	191.9	−0.1	$sp^{3.1}$	196.4	1.4	$sp^{4.1}$	313.5	41.3
2-I	192.0	−0.1	$sp^{2.4}$	217.7	1.4	$sp^{5.6}$	330.2	36.2
2-OH	191.8	−0.2	$sp^{3.7}$	144.1	1.4	$sp^{3.1}$	270.0	52.5

[a] $Zn(CH_3)_2$ 192.1 pm.

[b] Values of CH_3X, see Table 1.

[c] ZnF_2 174.4 pm, $ZnCl_2$ 208.3 pm, $ZnBr_2$ 221.9 pm, ZnI_2 242.5 pm, $Zn(OH)_2$ 177.0 pm.

Table 6. Relative energies [kcal/mol] of the complexes [**2-X·3**], transition states [**2-X·3**]‡, product complexes [**4**·ZnX_2], and products **4**+ZnX_2, as compared to the starting materials **2-X**+**3**[a,b]

	F	Cl	Cl[a]	Br	I	OH
[**2-X·3**]	−5.4	–	–	–	–	–
[**2-X·3**]‡	31.9	23.2	21.4	19.2	17.0	44.8
[**4**·ZnX_2]	−38.9	–	–	–	–	–
4+ZnX_2	−32.4	−40.0	−37.2	−40.6	−40.2	−26.9

[a] Calculated with the all-electron basis set 6-311++G(d,p)[45–48]

amount to 56.4% in the case of **2-F**, and to 36.2% in the case of **2-I** (see Table 5). The metal assisted ionization of the C–Hal bond in the case of the zinc carbenoids **2-X** is thus much less pronounced than in the case of the carbenoids $LiCH_2X$ **1-X**. The relative energies of the transition states in the reactions of **2-X** with **3** are summarized in Table 6.

The carbenoids **2-X** have a much higher transition state energy for their reactions with **3** than **1-X**, compare Tables 2 and 6. There is a further difference to the Li/Hal carbenoids **1-Hal** because in the zinc series **2-Hal** the energies of the transition states [**2-Hal·3**]‡ are clearly a function of Hal: **2-F** 31.9 kcal/mol, **2-Cl** 21.4 kcal/mol, **2-Br** 19.2 kcal/mol; **2-I** 17.0 kcal/mol. The iodine species **2-I** with the lowest activation energy are the most widely used Simmons–Smith reagents.[11–14] The reason for the halide-dependence is evident from a comparison of Tables 1,3,5 and 7.

The carbenoids **2-X** (see Table 5) (as similarly in the complexes [**2-X·3**], see Appendix and Refs. 35,38) the C–Zn bond does not cause a noticeable elongation of the C–X bonds which have to be cleaved in the cyclopropane forming process. As mentioned above, the C–X bonds in **2-X** are only between 1.4 and 2.3% longer than in CH_3–X. This is totally different in the Li-series **1-X**, in which case the C–X elongation, caused by the C–Li bonds, is between 12.3 and 5.5%, see Table 1. Since the C–X bonds in the transition states of the **2-X** (**1-X**) reactions with ethene **3** (see Tables 7 (3)) are almost equally elongated (F 40.9 (39.0)%; Cl 32.7 (31.4)%; Br 28.9 (27.3)%; I 25.9 (23.8)%; OH 40.4 (36.8)%), the activation energies of the reactions of **2-X** with ethene **3** are higher than of the reactions of **1-X** with **3**. Furthermore, in the **2-X** case, **2-F** must have a higher activaton energy than **2-I** because of the very different bond energies C–F 110.9 kcal/mol≫C–I 58.2 kcal/mol, which is in perfect agreement with the already mentioned findings of Wittig.[42] The almost equal activation energies in the **1-X** series, in contrast, result from the stronger elongation of the C–F bond (12.3%) as compared to the C–I bond (5.5%) in the carbenoids **1-X** and in the complexes [**1-X·3**].

Conclusions

The reactions of the lithium carbenoids **1-X**, X=F, Cl, Br, I and OH, with ethene **3** to give cyclopropane **4**+LiX, profit from the weakening of the C–X bonds by the C–Li bonds in the carbenoids **1-X** and in the complexes [**1-X·3**]. The C–F bond is more affected than C–I. Since in the transition states [**1-X·3**]‡ LiHal is strongly decomplexed, the cleavage of the C–Hal bonds is essentially compensated by the formation of the Li–Hal bonds. This leads to almost equal activation energies for the reactions of **1-Hal** with **3**. The higher energy for the reaction of **1-OH** with ethene **3** to cyclopropane **4** results from the high C–OH bond energy. In the **2-X** reactions with ethene **3**, the C–ZnX bond causes almost no elongation of the C–X bonds. This leads to higher

Table 7. Calculated bond lengths [pm] and bond elongation [%] in the transition states [**2-X·3**]‡, X=F, Cl, Br, I, OH, as compared to the bond lengths of H_3C–Zn–CH_3, CH_3–X and X–Zn–X (bond lengths of H_3C–Zn–CH_3, CH_3–X and X–Zn–X, see Table 5. Since the geometries of $XZnCH_2X$ **2-X** have not much changed in the complexes [**2-X·3**] (see Appendix and Refs. 35,38) we refer the transition state geometries of [**2-X·3**]‡, as those of **2-X**, see Table 5, to H_3C–Zn–CH_3, CH_3–X and X–Zn–X)

	C–Zn			C–X			Zn–X	
[**2-X·3**]‡	*r* [pm]	Elong. [%]	Hybr. C^1	*r* [pm]	Elong. [%]	Hybr. C^1	*r* [pm]	Elong. [%]
[**2-F·3**]‡	194.3	1.1	$sp^{1.6}$	195.4	40.9	p	198.5	13.8
[**2-Cl·3**]‡	195.2	1.6	$sp^{1.5}$	235.6	32.7	p	232.6	11.7
[**2-Br·3**]‡	195.4	1.7	$sp^{1.5}$	249.6	28.9	p	245.6	10.7
[**2-I·3**]‡	195.7	1.9	$sp^{1.5}$	270.3	25.9	p	265.6	9.5
[**2-OH·3**]‡	200.7	4.5	$sp^{1.6}$	199.5	40.4	p	191.9	8.4

activation energies of these reactions, which is in agreement with experimental observations. The calculations also show that the compound with X=F (**2-F**) has a much higher activation energy than the normally used iodine species **2-I**, again in agreement with experiments.

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Appendix

Table A1. Calculated bond lengths [pm] and bond elongations [%] in the complexes [**1-X·3**], X=F, Cl, Br, I, OH, as compared to the bond lengths of H_3C–Li, CH_3–X and Li–X, see Table 1

[**1-X·3**]	C–Li		C–X		Li–X	
	r [pm]	Elong. [%]	*r* [pm]	Elong. [%]	*r* [pm]	Elong. [%]
[**1-F·3**]	193.4	−2.4	155.2	11.9	179.8	12.7
[**1-Cl·3**]	196.3	−1.0	192.7	8.6	223.8	10.2
[**1-Br·3**]	196.9	−0.7	206.4	6.6	239.6	9.7
[**1-I·3**]	196.9	−0.7	226.0	5.3	252.2	4.6
[**1-OH·3**]	195.0	−1.6	151.7	6.8	178.6	11.5

Table A2. Calculated bond lengths [pm] and bond elongations [%] in the complex [**2-F·3**], as compared to the bond lengths of H_3C–Zn–CH_3, CH_3–F and F–Zn–F, see Table 5

	C–Zn		C–X		Zn–X	
	r [pm]	Elong. [%]	*r* [pm]	Elong. [%]	*r* [pm]	Elong. [%]
[**2-F·3**]	192.5	0.2	140.8	1.5	276.7	58.7

Table A3. Calculated C1–C2 and C1–C3 bond lengths [pm] in the transition states $[\mathbf{1\text{-}X\cdot 3}]^{\ddagger}$ and $[\mathbf{2\text{-}X\cdot 3}]^{\ddagger}$, X=F, Cl, Br, I, OH

X	$[\mathbf{1\text{-}X\cdot 3}]^{\ddagger}$		$[\mathbf{2\text{-}X\cdot 3}]^{\ddagger}$	
	C1–C2 *r* [pm]	C1–C3 *r* [pm]	C1–C2 *r* [pm]	C1–C3 *r* [pm]
F	225.5	249.8	225.3	240.5
Cl	227.8	252.1	231.2	249.0
Br	227.2	252.5	230.4	249.8
I	226.8	253.8	229.2	251.2
OH	204.0	243.4	218.6	237.7