Carbenoid Compounds

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Alkali Metal Carbenoids: A Case of Higher Stability of the Heavier Congeners

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***Abstract:** As a result of the increased polarity of the metal–carbon bond when going down the group of the periodic table, the heavier alkali metal organyl compounds are generally more reactive and less stable than their lithium congeners. We now report a reverse trend for alkali metal carbenoids. Simple substitution of lithium by the heavier metals (Na, K) results in a significant stabilization of these usually highly reactive compounds. This allows their isolation and handling at room temperature and the first structure elucidation of sodium and potassium carbenoids. The control of stability was used to control reactivity and selectivity. Hence, the Na and K carbenoids act as selective carbene-transfer reagents, whereas the more labile lithium systems give rise to product mixtures. Additional fine tuning of the M−C interaction by means of crown ether addition further allows for control of the stability and reactivity.*

The ambiphilicity of main group element and metal systems has led to the revelation of remarkable applications, such as in bond activation chemistry or catalysis.[1] Prominent examples are singlet carbenes and frustrated Lewis pairs.[2,3] Similar to carbenes, metal carbenoids exhibit an ambiphilic character.[4] However, despite of their unique reactivity, which has found renewed interest in recent years, most applications are still limited to cyclopropanation, homologation, and lithiation/borylation reactions.[5–7] This limitation is mainly due to the high reactivity and thermal sensitivity of these systems. Thus, only few carbenoids, particularly examples of the extremely reactive lithium halogen systems, have been isolated so far. The first isolation of a lithium/halogen (Li/Hal) carbenoid was reported in 1993 by Boche et al. (Figure 1).[8] Although this carbenoid **I** was only stable up to −60 °C, Le Floch and co-workers later successfully isolated the room-temperature-stable system **II** employing anion-stabilizing substituents.[9] Such stabilized carbenoids finally led to the revelation of novel reactivity patterns, such as an application in bond activation and coupling reactions.[10] Very recently, a catalytic transformation was realized by Mézailles and co-workers.[11] In this context, electronic stabilization was found to be pivotal for an enhanced reactivity and selectivity control and the development of new applications. Although many reports have appeared focusing on the influence of the substitution pattern[12] and the M/X combination[13] on the carbenoid reactivity, virtually no studies on the heavier alkali metal systems have been reported.[14,15] In the case of simple alkali metal reagents, an increase in reactivity is generally observed when going down the group of the periodic table.[16] The increasing polarity and reactivity of the M−C bond often leads to side-reactions, such as solvent degradation or decomposition via β-elimination.[17] Thus, organosodium and organopotassium reagents are by far less employed than their lithium congeners. Herein, we report the preparation and isolation of the first heavier alkali metal carbenoids. In contrast to simple alkali metal organyl compounds, an unexpected increase of stability is observed for the sodium and potassium carbenoids, which was utilized to control reactivities and selectivities.

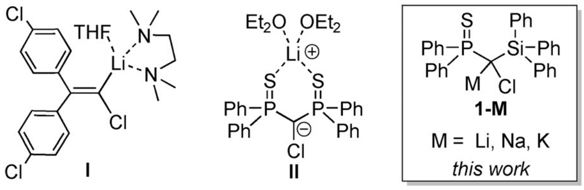
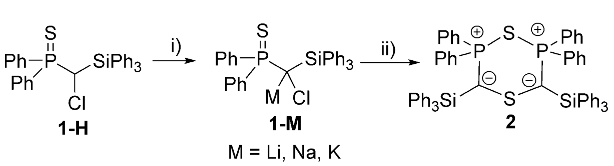


Figure 1. Examples of isolated alkali metal carbenoids.

To study the influence of the nature of the metal on the carbenoid stability, we chose the silyl-substituted compounds **1-M** as starting systems. Carbenoids **1-M** (M = Li, Na, K) were prepared by treatment of a THF solution of the chlorinated precursor **1-H** with different alkali metal bases (Scheme 1). Addition of the base to **1-H** at −78 °C resulted in the instantaneous selective metalation (with no substitution reaction or double metalation) to form the corresponding carbenoids **1-M**, as evidenced by NMR spectroscopic studies at low temperatures (see the Supporting Information). The carbenoids are characterized by a singlet in the ^{31}P{^{1}H} NMR spectrum between $\delta_P = 45$ and 48 ppm as well as by the disappearance of the resonance signal of the central hydrogen atom in the ^{1}H NMR spectrum. The ^{13}C{^{1}H} NMR signal of the carbenoid carbon atom experiences only a slight shift



Scheme 1. Preparation and decomposition of M/Cl carbenoids **1-M**; i) THF, −78 °C, MeLi or NaN(SiMe$_3$)$_2$ or KN(SiMe$_3$)$_2$, quantitative formation as determined by NMR spectroscopy (see the text for the yields of the isolated products); ii) −78 °C→RT, −MCl.

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relative to the starting material **1-H** ($\delta_C = 42.3$ ppm): in case of **1-Li** towards higher field ($\delta_C = 37.6$ ppm), for **1-Na** and **1-K** towards lower field ($\delta_C = 42.9$ and 42.6 ppm).[18,19] The increased $^1J_{PC}$ coupling constant of approximately 70 Hz indicates a higher s character of the P−C bond and an approximately sp^2 hybridization of the carbenoid carbon atom. This is in line with the magnetic equivalence of the phosphorus-bonded phenyl groups, which gave rise to diastereotopic sets of signals for **1-H**.

The thermal stability of the carbenoids in THF solution was studied by variable temperature (VT) NMR spectroscopy using the $^{31}P\{^1H\}$ NMR signal as probe. Thereby, carbenoid decomposition upon warming could be traced by disappearance of the carbenoid signal ($\delta_P \approx 46$ ppm) and the appearance of the signal of the decomposition product **2** ($\delta_P = 37.8$ ppm), which is formed after MCl elimination.[10b] The decomposition processes (see the Supporting Information for NMR spectra) revealed a remarkable difference in the stability depending on the metal. Surprisingly, the lithium compound **1-Li** turned out to be the least stable system, decomposing at approximately 0 °C (Table 1). In contrast, the sodium carbenoid was found to be stable up to 30 °C, thus exhibiting, in contrast to simple alkali metal organyls, a higher thermal stability than its lighter congener. No significant further increase in stability was detected for **1-K**. Thus, **1-Na** and **1-K** can be handled at room temperature in solution as well as in the solid state for a couple of hours and could be isolated as yellow solids in excellent yields of 96 % and 91 %, respectively. Storage at room temperature for a longer period of time (several days) also resulted in partial decomposition.

Table 1: Comparison of the X-ray crystallographic and NMR spectroscopic properties of **1-H**, **1-Li**, **1-Na**, and **1-K**.

	1-H[a]	**1-Li**	**1-Na**	**1-K**	**1-Li**·(12-crown-4)
T[b] [°C]	–	0	30	30	20
δ_P [ppm]	46.3	45.4	48.0	47.6	46.1
δ_C [ppm]	42.3	37.6	42.9	42.6	39.9
$^1J_{PC}$ [Hz]	38.9	75.9	71.4	70.5	70.4
C1−Cl [Å]	1.798(2)	–	1.845(3)	1.824(2)	1.818(2)
C1−P [Å]	1.843(2)	–	1.729(3)	1.721(2)	1.715(2)
C1−Si [Å]	1.937(2)	–	1.828(3)	1.815(2)	1.810(2)
M−Cl [Å]	–	–	2.887(1)	3.308(1)	–
P-C1-Si [°]	119.6(1)	–	127.9(2)	137.8(1)	128.8(1)
Σ∡(C1)	–	–	342.4(2)	356.3(1)	351.0(1)

[a] Data taken from Ref. [20]. [b] Decomposition temperature in THF solution (determined by VT NMR spectroscopy, see the Supporting Information for spectra).

1-Na and **1-K** are the first isolated and also structurally characterized sodium and potassium carbenoids. Single crystals of both compounds were grown by diffusion of pentane into saturated solutions (**1-Na**: THF; **1-K**: THF/pentane) at −28 °C. **1-Na** forms a monomeric structure (Figure 2 a) with three coordinating THF ligands. In contrast, **1-K** crystallizes as centrosymmetric dimer, in which each potassium is coordinated by the chloro and thiophosphoryl substituent, one THF, and one silicon-bound phenyl group via η^6-coordination (Figure 2 b).[21] In both structures, the carbenoid carbon atom C1 is only three-coordinate with no direct contact to the metal ion. Although the C1 center in **1-K** exhibits an almost planar geometry (sum of angles: Σ∡ = 356.3(1)°), a pronounced pyramidalization (Σ∡ = 342.4(2)°) is observed in **1-Na** in the solid state (Table 1). However, the NMR data of both carbenoids suggest that no stable pyramidal configuration is present in solution (as indicated by the absence of diastereotopic splitting and the $^1J_{PC}$ coupling constant).[22] The shortening of the C1−P and C1−Si bonds relative to the precursor **1-H** is in line with the increased charge at the C1 center and the electrostatic interactions involved.

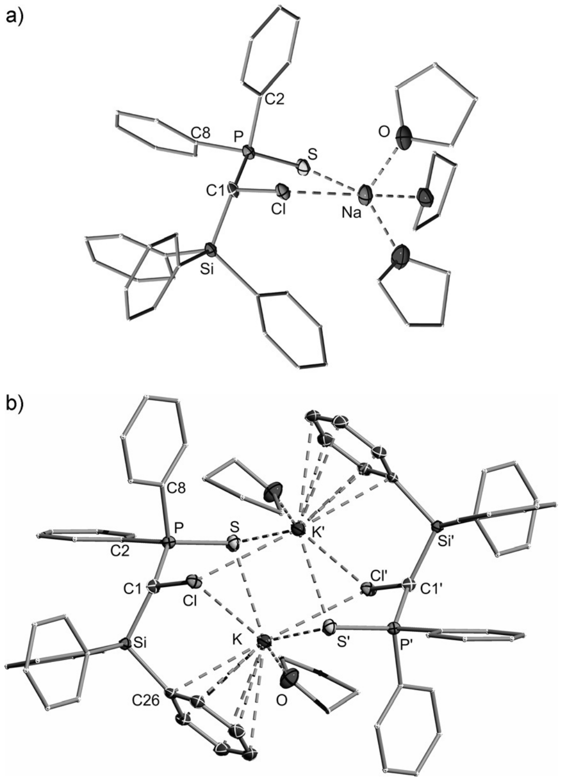


Figure 2. Molecular structures of a) sodium carbenoid [**1-Na**·(THF)$_3$] and b) potassium carbenoid (**1-K**·THF)$_2$. Displacement ellipsoids are set at 50% probability. Hydrogen atoms omitted for clarity.

It is interesting to note that both carbenoids exhibit a contact between the metal and the chloro substituent, but no M−Cl interaction. Such a structural motif has been described as a carbene donor complex RC:←XM (Figure 3), but never been structurally authenticated for a metal halogen carbenoid.[4a] The bridged coordination mode **A** with M−X and C−M contacts and the classical nonbridged structure **B** with a M−C interaction are generally thermodynamically favored

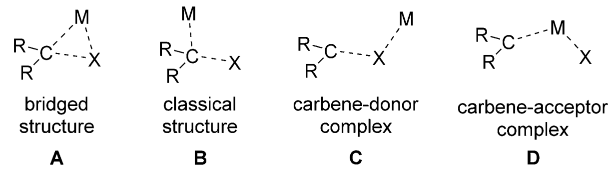


Figure 3. Structural motifs of Li/X carbenoids.

and have also been experimentally observed for different M/X combinations.[14,23] The carbene donor complex **C** has been confirmed by Boche et al. and Steinborn and co-workers in the case of a Li/OR and Li/S(O)R carbenoid,[24] whereas the carbene acceptor species **D** has been reported above all for NHCs.[25] The M−Cl contact in **1-Na** and **1-K** suggests facile formation of the metal chloride salt and thus reflects the still present carbenoid character. Accordingly, the C1−Cl bond in **1-Na** and **1-K** is slightly elongated compared to **1-H** (**1-Na**: $\Delta d = 0.05$ Å; **1-K**: $\Delta d = 0.03$ Å). This elongation is typical for carbenoid species and indicative of the increased polarization of the C−Cl bond.[18a] Computational studies (M062X/6-311+G(d)) on **1-Na** and a model system (with H instead of Ph groups) show that the carbene-donor structure is only maintained in the case of the real system. Energy optimization of the model system always led to rearrangement to the bridged structure (see the Supporting Information for details). Thus, the heavier alkali metal carbenoids seem to prefer similar structures than their lithium analogues. However, steric effects as well as weak noncovalent interactions (for example π- or dispersive interactions, which are more important for the larger atoms) probably lead to the break of the C−M interaction in **1-Na** and **1-K**.

We hypothesized that the increased stability of **1-Na** and **1-K** is due to the lower Lewis acidity of the heavier metals and the higher polarity of the M−C interaction. This should decrease the polarization of the C−Cl bond and thus hamper MX elimination.[26] This assumption suggested that manipulation of the M−C interaction, for example by the use of strong donor ligands, can be used as tool to control the carbenoid stability. This hypothesis was tested by means of lithium carbenoid **1-Li**. To this end, **1-Li** was prepared in the presence of 12-crown-4 and its stability was studied by VT NMR experiments. Indeed, the THF solution of the carbenoid **1-Li**·(12-crown-4) showed an increased stability with no decomposition occurring up to 20 °C (compared with **1-Li** at 0 °C without 12-crown-4). Thus, isolation of **1-Li**·(12-crown-4) as a yellow crystalline solid in yields of up to 81 % was possible (Figure 4; Table 1). In the molecular structure, **1-Li**·(12-crown-4) forms a separated ion pair and thus a "metal-free" carbenoid, in which lithium is solely coordinated by the crown ether. The central carbon atom remains slightly pyramidalized with a sum of angles around C1 of 351.0(1)°. The bond lengths in the carbenoid are comparable to those found in the **1-M** and **1-K** with the C−Cl bond elongation being somewhat less pronounced.

The systematic control of the stability of highly reactive species has often allowed for a control of reactivity and the development of novel applications. With the established stability control of the carbenoids **1-M** by employment of the heavier alkali metals and strong coordinating ligands, we addressed the impact on the reactivity. First, we focused our studies on the application of **1-Na** and **1-K** in the dehydrocoupling of secondary phosphines to test their propensity to still react under salt elimination. This unique transformation has only recently been established in our group and was found to selective occur only in case of stabilized lithium carbenoids.[10d] Employing **1-Na** and **1-K** under the same reaction conditions that were used for the lithium systems selectively led to the formation of the diphosphines ($2\,Ar_2PH \rightarrow Ar_2PPAr_2$, with Ar = p-MeC$_6H_4$), thus confirming their ambiphilic nature and their ability to eliminate MCl (see the Supporting Information for details). A further important yet underdeveloped application of carbenoids is their use as carbene transfer reagents, particularly to access carbene complexes that are difficult to prepare through alternative routes (for example nucleophilic carbene complexes with late transition metals).[9,27] However, this method has often been limited by side-reactions associated with the high reactivity and low stability of carbenoids.[12c] For example, lithium carbenoid **1-Li** reacts with [Pd(PPh$_3$)$_4$] to form an approximately 1:1 mixture of the desired carbene complex **3** and thioketone complex **4** formed by sulfur transfer from phosphorus to carbon (Table 2, entry 1). The more reactive SiMe$_3$-substituted Li/Cl carbenoid exclusively delivered the thioketone species.[28] Thus, this transformation offers an excellent model reaction to examine the stability–reactivity relationship of compound series **1-M**. Fortunately, treatment of sodium or potassium carbenoid, **1-Na** or **1-K**, with 1 equiv [Pd(PPh$_3$)$_4$] in THF at RT provided selective access to carbene complex **3**, with no thioketone formation observed. Consistent with the increased stability of the lithium carbenoid in the presence of crown ether, the use of **1-Li**·(12-crown-4) also resulted in a marked increase in selectivity. Instead of forming a 1:1 mixture of **3** and **4** as in the case of the uncomplexed **1-Li**, the crown ether adduct gave 93 % conversion into the carbene complex. This clearly demonstrates a stability–selectivity relationship and a possible

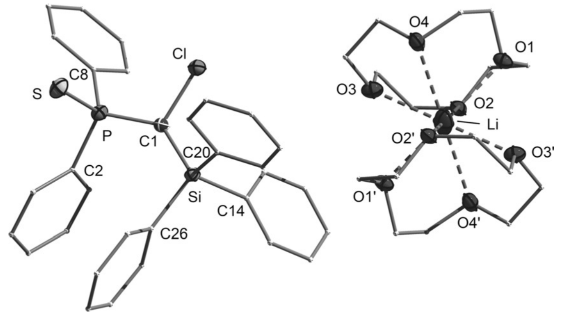
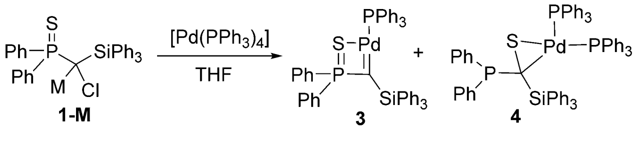


Figure 4. Molecular structure of the lithium carbenoid [**1**][Li·(12-crown-4)$_2$]. Displacement ellipsoids are set at 50 % probability. Hydrogen atoms are omitted for clarity (only one Li position is shown).

Table 2: Application of alkali metal carbenoids for the synthesis of **3**.



Entry	Carbenoid **1-M**	Solvent/ additive	Reaction temp.	Yield of **3** [%]	Yield of **4** [%]
1	**1-Li**	THF	−78 °C	48	52
2	**1-Li**	THF/ 12-crown-4	RT	93	7
3	**1-Na**	THF	RT	>99	<1
4	**1-K**	THF	RT	>99	<1

tuning of carbenoid reactivity by variation of the metal and/or the use of strong Lewis bases.

In conclusion, we have reported the preparation and isolation of alkali metal carbenoids, including the first structure elucidation of a sodium and a potassium carbenoid. Contrary to the general trend in the periodic table, the heavier alkali metal compounds showed a higher thermal stability than the usually more commonly applied lithium congener. This stability increase was attributed to the higher polarity of the M−C bond and the lower Lewis acidity of the larger metals. Further stabilization could be achieved by employment of crown ether to efficiently complex the metal and manipulate the M−C interaction. Studies on the stability–reactivity relationship by means of carbene transfer reactions demonstrated that the control in stability also allows for control of reactivity and selectivity. The use of the heavier alkali metals may provide a general tool for stability and reactivity manipulations in carbenoid chemistry and thus may lead to the development of novel applications.

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Keywords: alkali metals · carbanions · carbenoids · lithium · structure–activity relationships

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[19] The high-field shift of C1 in **1-Li** suggests a lower carbenoid character (Ref. [4a,c]). However, **1-Li** is the most reactive system

in the series **1-M** which indicates facile LiCl formation. NMR shifts are also influenced by several factors, which may cause the unexpected high-field shift in **1-Li**.

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