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# Imidazolium Dicyanomethylides as N-Ylide Precursors of Anionic N-Heterocyclic Carbenes

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In the past, the use of nitrogen ylides focused primarily on cycloadditions, where the 1,3-dipole was used as a building block for the formation of heterocycles such as pyrroles or pyrrolinones. In this work, we present a new perspective on imidazolium dicyanomethylides with their synthesis and utilization as anionic N-heterocyclic carbenes (NHCs). The values of relative carbene formation energies (CREF) for a wide range of

substituted imidazolium ylides unknown in the literature showed promising properties. In situ trapping reactions of these anionic NHCs with selenium led to anionic, water-soluble compounds that exhibited remarkable coordination behavior according to X-ray structure analyses. In addition, the <sup>77</sup>Se shifts of the investigated compounds were measured to draw conclusions about their  $\pi$ -acceptance.

## Introduction

Arduengo's pioneering work to isolate the first stable crystalline N-heterocyclic carbene (NHC) in 1991<sup>[1]</sup> laid the foundation for a class of compounds that became one of the most intensively researched areas of modern organometallic chemistry.<sup>[2]</sup> Nowadays, applications in catalysis,<sup>[3–5]</sup> in the chemistry of main group elements<sup>[6,7]</sup> and in complexation, among others, are extensively researched. It is certainly no exaggeration to say that N-heterocyclic carbenes surpassed the classical electrophilic singlet or triplet carbenes<sup>[8,9]</sup> in importance in preparative chemistry. By varying the heterocyclic ring system or the substituents, countless structures of N-heterocyclic carbenes are conceivable, which can be used to tailor the electronic or steric properties. The variations also allow the introduction of charged substituents, which influence the electronic properties of the entire molecule or selectively of the carbene carbon atom. Thus, the addition of an anionic moiety to an otherwise neutral NHC ligand is an efficient way to directly influence its

(electro)chemical behavior, and the chemistry of the resulting anionic N-heterocyclic carbenes has aroused great research interest in recent years.<sup>[10–13]</sup> Depending on their structure, anionic N-heterocyclic carbenes can be divided into isolated and  $\pi$ -conjugated systems, and it is evident that conjugation within the NHC system plays a crucial role for its properties.<sup>[14]</sup> While the isolated negative charge of sulfonate **2**,<sup>[15]</sup> formed from zwitterion **1**, is not involved in conjugation within the heterocycle, the negative charge in carbene **4**, which is formed from the conjugated mesomeric betaine imidazolium-4-olate **3**,<sup>[16,17]</sup> is conjugated with the remaining  $\pi$ -system (Scheme 1, possible mesomeric sites of negative charge are marked in black). This is shown by the delocalization of the negative charge within the molecule in the mesomeric structures. These even make it possible to formulate the carbene carbon atom with two negative charges, as displayed in Scheme 1.

In contrast to the previously described case, the negative charge in the carbene **6**,<sup>[18]</sup> which is formed by deprotonation of the cross-conjugated mesomeric betaine **5**,<sup>[19]</sup> is not in  $\pi$ -

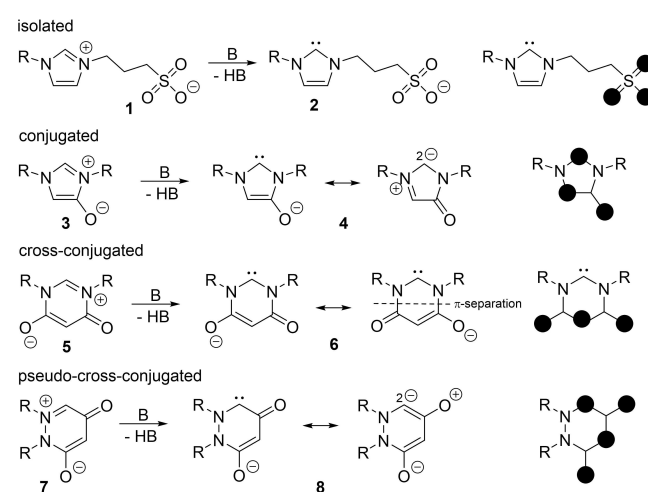
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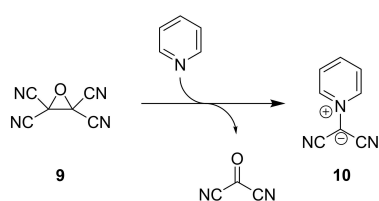
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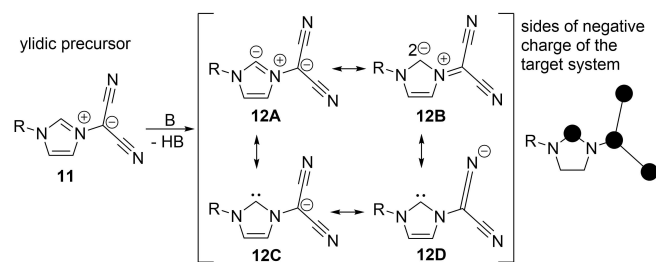
Scheme 1. Different types of conjugation in N-heterocyclic carbenes.

conjugation with the carbene position. The separation of the charge at the level of the rules of mesomerism is indicated by a dashed line. The same applies to the carbene **8** which is derived from the pseudo-cross-conjugated mesomeric betaine **7**,<sup>[20]</sup> with the difference that although there is an effective separation of the negative charge similar to the aforementioned CCMB, the positive charge of the NHC precursor can also be delocalized into the carbonyl groups according to the rules of resonance. Although this leads to a mesomeric structure of low relevance, which shows both a double negatively charged carbene position and an electron sextet structure at the oxygen, this is permitted according to the rules of mesomerism. Due to the increasing importance of anionic heterocyclic carbenes<sup>[10–13]</sup> and in continuation of our interest in mesomeric betaines and *N*-heterocyclic carbenes,<sup>[5,13,21]</sup> we became aware of ylides composed of a diazolum unit and an anionic dicyano moiety since literature regarding anionic NHCs derived from nitrogen ylides is scarce.<sup>[22]</sup> The synthesis of such ylides was first described almost simultaneously by Linn, Webster and Benson<sup>[23]</sup> and by Rieche and Dietrich.<sup>[24]</sup> The desired ylides were derived from the reaction of an azole with the electrophile tetracyanoethylene oxide<sup>[25]</sup> (TCNEO, **9**). Addition of **9** to pyridine led to the formation of the pyridinium dicyanomethylide **10** and the by-product carbonyl cyanide (Scheme 2).

Reaction towards other heterocycles enables the formation of a variety of dicyanomethylides such as triazole- and imidazole-systems.<sup>[26]</sup> However, usage of this substance class was almost exclusively limited to 1,3-dipolar cycloadditions.<sup>[27,28]</sup> This work deals with the characterization of imidazolium dicyanomethanides as NHCs. As shown in Scheme 3, these are conjugated systems, as the charges are delocalized within the common  $\pi$ -electron system. Thus, the negative charge can be localized in both the methanide moiety and the imidazole ring. Through deprotonation of **11**, an anionic carbene can be



Scheme 2. Preparation of the pyridinium ylide **10**.



Scheme 3. Possible sites of localization of the negative charge within the imidazolium ylide **12**.

formulated, which is represented in the following four exemplary canonical forms (Scheme 3).

Through deprotonation of **11** at the 2-position in the presence of a base B, an anionic heterocyclic carbene **12** is formed which can be described by a number of canonical forms. Examples are the structures **12A–12D**. The formation of a double bond from the methanide carbon of **12A** to the nitrogen of the imidazole framework yields a carbene position with a doubly negative charge according to the rules of resonance (**12B**). As mentioned before, this behavior is typical for conjugated anionic carbenes.<sup>[13,14,21]</sup> In addition to the most common representation **12C**, where the stabilizing effect of the nitrile groups located in the  $\alpha$ -position is evident, the negative charge may also be localized on the two nitrogen atoms of the nitrile groups (**12D**). Overall, the negative charge of the anionic carbene is delocalized both in the substituent and at the carbene position, resulting in analogous behavior to the carbene derived from CMB **3** (see Scheme 1). Here, we present the examination of these *N*-ylides as precursors for the preparation of anionic *N*-heterocyclic carbenes (NHCs).

For characterization of the general electronic parameters of (anionic) carbenes, various techniques have been established in the literature. These include, among others, the Tolman electronic parameter (TEP)<sup>[29]</sup> or the Huynh electronic parameter (HEP)<sup>[30]</sup> of NHC-palladium-complexes. Complementary to these, computational values such as Carbenes Relative Energy of Formation (CREF),<sup>[17,31,32]</sup> molecular electrostatic parameters (CEP),<sup>[33]</sup> or calculated proton affinities<sup>[34]</sup> may be used to classify  $\sigma$ -donor or  $\pi$ -properties. In contrast to the methods mentioned so far, the  $\pi$ -accepting character of NHCs can be determined through <sup>31</sup>P NMR and <sup>77</sup>Se NMR shifts of phosphinidene- and selenium-carbene adducts. The examination of phosphorus shifts represents the method established by Bertrand,<sup>[35]</sup> while Ganter<sup>[36]</sup> opened a perspective on selenium shifts in 2013 as a more versatile approach. The idea of using selenoureas as probes for the characterization of NHC-properties becomes evident through the imidazolium-2-ylidene **13**, revealing an electronic bivalency through two types of representation **13A** and **13B**.

As apparent in Figure 1, in carbene systems with pronounced  $\pi$ -acidity preferentially the canonical structure **13A** gains in importance, which translates into downfield shifts of the <sup>77</sup>Se signal due to backbonding of a lone pair from selenium to the NHC, resulting in deshielding of the NMR-active nucleus.<sup>[36,37]</sup> In contrast, systems that cannot effectively accommodate  $\pi$ -electrons, commonly referred to as having poor  $\pi$ -accepting properties,<sup>[36]</sup> are better described by representation **13B**. With the increased electron density on the selenium and the associated shielding from the magnetic field in NMR-

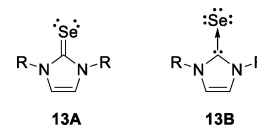


Figure 1. Two representations of the imidazol-2-ylidene **13**.

spectroscopy, more high-field-shifted selenium signals are observed.

## Results and Discussion

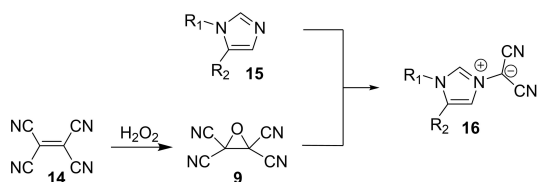
### Synthesis and Characterization of Various N-ylides

The synthesis of the target molecules was achieved through the reaction of a range of substituted imidazoles with the electrophile tetracyanoethylene oxide (**9**). *N*-Substitution of the imidazoles is accessible through coupling reactions (Chan-Lam coupling for *N*-arylated systems<sup>[38]</sup>), substitutions of 1*H*-imidazoles with benzyl halides<sup>[39]</sup> or Debus-Radziszewski reactions.<sup>[40]</sup> *N*-Alkylated derivatives are also synthesized through substitution reactions,<sup>[41]</sup> while compounds with derivatization at the 5-position in the backbone are prepared via Van-Leusen reactions.<sup>[42]</sup> Tetracyanoethylene oxide (TCNEO, **9**) is synthesized by the addition of hydrogen peroxide to the corresponding alkene tetracyanoethylene (TCNE, **14**).<sup>[25]</sup> The substituted imidazoles were dissolved in diethyl ether (Et<sub>2</sub>O) and treated dropwise with a solution of TCNEO in Et<sub>2</sub>O under ice-cooling. After a reaction time of 15 to 30 minutes, including the addition of the epoxide, the resulting betaines precipitated from the reaction solution and, following filtration and washing, were usually obtained in spectroscopically pure form. If necessary, the isolated polar substances can be recrystallized from predominantly alcoholic solutions. The well-explored conditions for the synthesis of the desired imidazoles **15** within the scope of this work, along with the straightforward addition of the epoxide **9** to the corresponding azoles to obtain the ylides **16**, provide an easily implementable synthetic route that allows a variety of modelling of the target systems with regards to the *N*-substituents and the backbone of the (benzo-)imidazoles (Scheme 4).

Through fine-tuning of the reaction conditions, a broad variety of imidazolium ylides **16a–o** with different electronic properties have been isolated in satisfactory yields (59–90%, Table 1).

To classify the structural properties of the isolated ylides, X-ray measurements were conducted on a representative compound. Single crystals of dicyano(1-(4-methylbenzyl)-1*H*-imidazolium-3-yl)methanide (**16i**) were obtained through vapor diffusion crystallization<sup>[43]</sup> of *n*-pentane into a solution of **16i** in ethanol (EtOH). The structure with crystallographic numbering is depicted in the following Figure 2.

Bond lengths of approximately 133 pm for C2–N1 and C2–N3 and a bond length of the triple bonds C7–N7 and C8–N8 of 116 ppm were measured, and these values are as expected.<sup>[44,45]</sup>



Scheme 4. General reaction approach for the isolation of ylides **16**.

Table 1. Reaction scope for the isolated ylides.

	R <sub>1</sub> =	R <sub>2</sub> =	Yield [%]
<b>16a</b>	methyl	H	87
<b>16b</b>	butyl	H	71
<b>16c</b>	isopropyl	H	59
<b>16d</b>	phenyl	H	89
<b>16e</b>	<i>p</i> -tolyl	H	82
<b>16f</b>	4-methoxyphenyl	H	86
<b>16g</b>	2-methoxyphenyl	H	79
<b>16h</b>	benzyl	H	76
<b>16i</b>	4-methylbenzyl	H	90
<b>16j</b>	3-methylbenzyl	H	89
<b>16k</b>	4-methoxybenzyl	H	88
<b>16l</b>	methyl	annulated	78
<b>16m</b>	benzyl	annulated	80
<b>16n</b>	methyl	methyl	65
<b>16o</b>	methyl	phenyl	89

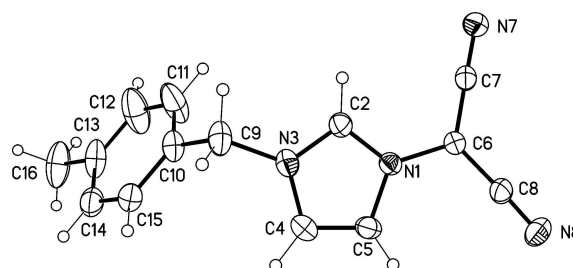


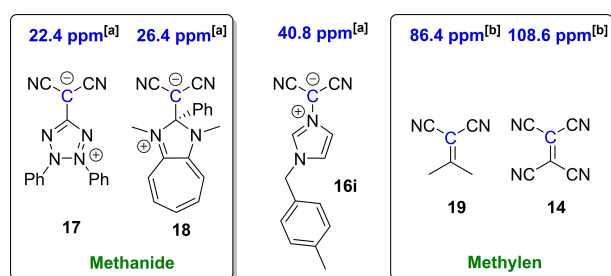
Figure 2. Molecular structure of **16i** with displacement parameters drawn at 50% probability level. Selected bond lengths in pm (crystallographic numbering): N1–C2: 132.98(14), N1–C5: 138.20(13), N1–C6: 143.18(13), N3–C2: 133.48(14), N3–C4: 137.11(15), N3–C9: 147.67(15), C4–C5: 135.23(17), C6–C7: 138.91(15), C6–C8: 139.31(15), C7–N7: 115.91(15), C8–N8: 115.89(16). Dihedral angle [°]: C2–N1–C6–C7: –14.07(16), C5–N1–C6–C8: –9.53(16).

The small torsion angle between the imidazole and the dicyano-moiety reveals a potential conjugation between the two parts of the ylide,<sup>[46]</sup> whereas the bond length N1–C6 was detected to be 143.18(13) pm which is longer than the values of the C(sp<sup>2</sup>)=N(sp<sup>2</sup>) bond of imines (128 pm) and the C(sp<sup>2</sup>)–N(sp<sup>2</sup>) bond of formamide (138 pm).<sup>[47]</sup> The chemical shifts of C6 provide insight into the delocalization of the negative charge. Its resonance frequency was measured at 40.8 ppm in *d*<sub>6</sub>-DMSO and its assignment was confirmed by 2D-HMBC experiments, demonstrating coupling of the methanide carbon with the imidazolium protons in the 2- and 4-positions. As exemplary representatives of methanides for the interpretation of the shift of **16i**, the corresponding values of tetrazolium ylide **17**<sup>[48]</sup> and the diazaazulenium methanide **18**<sup>[49]</sup> are

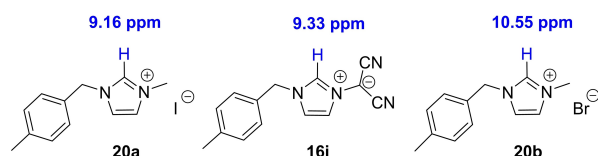
provided as comparison in Figure 3. As methylene compounds, the isopropylmalonitril **19**<sup>[50]</sup> and TCNE **14**<sup>[51]</sup> and their respective <sup>13</sup>C NMR shifts are also shown. The values reflect the conjugation types well. For example, ylide **17** is cross-conjugated with a formal charge separation between the molecular parts, as explained above. Ylide **18** is not conjugated but has oppositely charged, isolated molecular parts and can therefore be described as a zwitterion. The two representatives of methanides **17** and **18** exhibit typical shift values for this class of compounds at their respective carbon positions.<sup>[52,53]</sup> Due to the conjugation, the value of **16i** is shifted downfield in comparison to the values of the previously mentioned compounds. The value of **16i** clearly speaks against charge neutralization, as is the case in the methylene compounds **19** and **14**.

The value of ylide **16i** (40.8 ppm) therefore suggests a strong methanide character of this compound class. Notably, the <sup>13</sup>C NMR resonance frequency is only weakly influenced by the solvent used. Thus, ylide **16i** exhibits comparable resonance in *d*<sub>6</sub>-THF at 45.2 ppm. The <sup>1</sup>H NMR spectrum of the examined zwitterionic species **16i** displays a significant deshielding of the proton in the 2-position of the imidazolium framework. The imidazolium iodide **20a**<sup>[54]</sup> and the imidazolium bromide **20b**,<sup>[55]</sup> known to be easily converted to the corresponding carbenes by treatment with a base, exhibit comparable values, although they belong to different compound classes (Figure 4).

This highlights the suitability of these substances as precursors for the generation of anionic NHCs, as such acidic positions may be easily deprotonated with the use of a base. In addition to the <sup>1</sup>H NMR shift, literature has established other probes for quantifying the tendency of a compound to form an NHC from the corresponding precursors. As a computational method, Ramsden and Oziminski introduced the carbene relative energy of formation (CREF value<sup>[17,31,32]</sup>) as a quantitative index for determining the tendency of NHC-formation from their respective precursors. The heterolytic cleavage of the C–H



**Figure 3.** Methanide and methylene representatives for comparison of the <sup>13</sup>C-NMR shift of **16i**. [a]: spectra measured in *d*<sub>6</sub>-DMSO,<sup>[48,49]</sup> [b]: spectra measured in CDCl<sub>3</sub>.<sup>[50,51]</sup>



**Figure 4.** <sup>1</sup>H NMR shifts of **16i** and **20a** in *d*<sub>6</sub>-DMSO and **20b** in CDCl<sub>3</sub>.

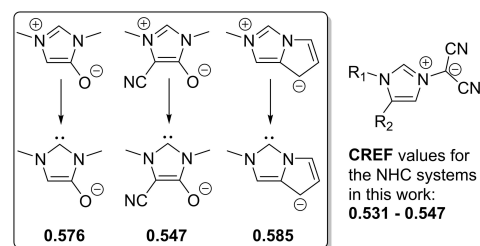
bond at the carbene position involves the transfer of both bonding electrons into a free  $\sigma$ -orbital. A reduction in the energy of the  $\sigma$ -orbitals accordingly facilitates deprotonation. The following Figure 5 illustrates a selection of precursors and their associated anionic NHCs along with their respective CREF values for comparison to the investigated compound class of this work.<sup>[17,32]</sup>

The CREF values of the ylides in this work were calculated at the B3LYP/6-311++G\*\* level in accordance with literature<sup>[17,31,32]</sup> and resulted in a range between 0.531 and 0.547, depending on the substituents on the nitrogen and the backbone of the imidazole. Comparison with the values shown in Figure 5 indicated promising results. A full list of the calculated values is given in the Supporting Information. In addition to the CREF values, the computational representation of the distribution of electron density within the ylides is another important characteristic for understanding the electronic properties of NHCs.<sup>[56]</sup> Two exemplary compounds are discussed for this purpose (one benzylated- and an arylated-imidazolium ylide). The HOMOs, which are located in the imidazolium as well as in the methanide moieties, respectively, of dicyano(1-(4-methylbenzyl)-1*H*-imidazolium-3-yl)methanide (**16i**) and dicyano(1-(*p*-tolyl)-1*H*-imidazolium-3-yl)methanide (**16e**) are shown in Figure 6. These HOMO profiles are characteristic of conjugated mesomeric betaines, because atomic orbital coefficients are localized in both formally oppositely charged parts of the molecule.

The anionic carbenes **16i<sub>c</sub>** and **16e<sub>c</sub>**, derived from deprotonation of **16i** and **16e** respectively, are shown in Figure 7. As expected, the HOMO of the anionic carbenes **16i<sub>c</sub>** and **16e<sub>c</sub>** are  $\pi$ -orbitals, with their strongest coefficients, however, localized in the anionic, exocyclic substituent. Accordingly, the carbene carbon showed virtually no coefficients of the HOMO. In the HOMO-1, on the other hand, the dominant  $\sigma$ -electron pair of the carbene was visible. The lowest unoccupied molecular orbital (LUMO, Figure 7) showed no coefficient at the carbene position, the LUMO+1 and LUMO+2 displayed only neglectable coefficients at this position (see SI).

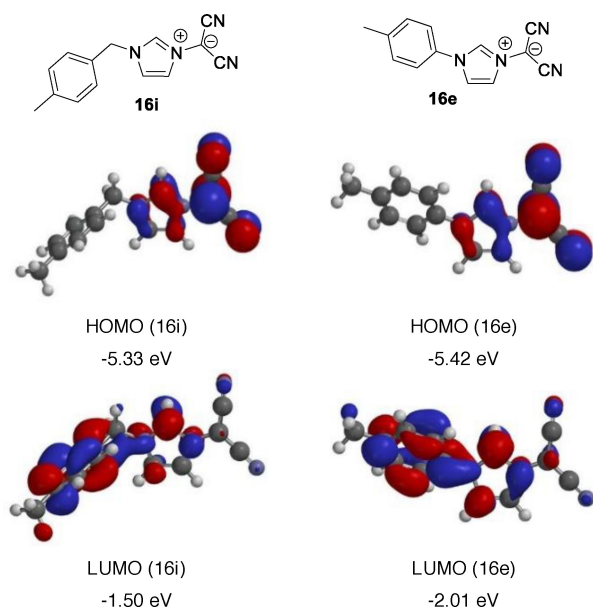
## Synthesis and Properties of the Anionic NHCs and their Behaviour Towards Selenium in Interception Reactions

With the knowledge gained regarding NMR spectra and CREF values, we then investigated ways to prepare and characterize the anionic carbenes and the potential influence of the dicyano

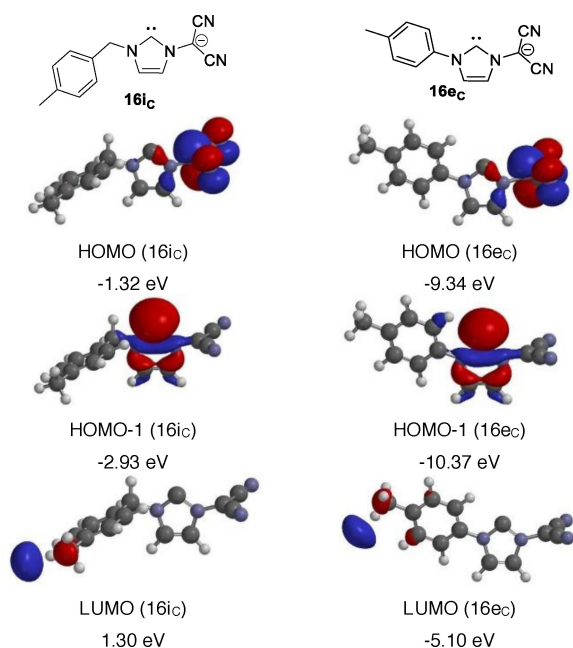


**Figure 5.** CREF values and their pictorial representation.





**Figure 6.** HOMO- and LUMO-profiles of the ylides **16i** and **16e** with their corresponding energies in electron volt [eV] were calculated at the B3LYP/6-311++G\*\* level.



**Figure 7.** The profiles of HOMO, HOMO-1 and LUMO of the anionic carbenes **16ic** and **16ec** with the corresponding energies in electron volt [eV] and calculated at the B3LYP/6-311++G\*\* level. The subscript "c" stands for "carbene".

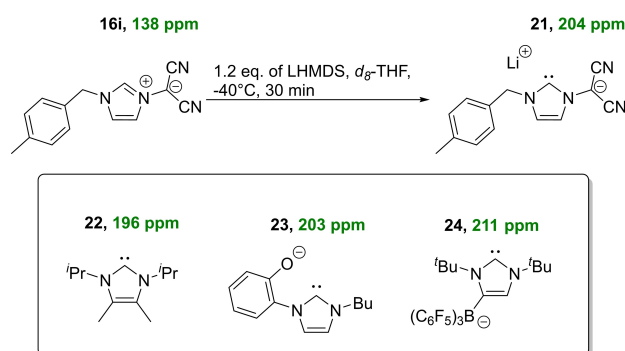
moiety.<sup>[57,58]</sup> First, the formation of an anionic carbene was proven *in situ* via NMR experiments. For this purpose, a solution of dicyano(1-(4-methylbenzyl)-1H-imidazolium-3-yl)methanide (**16i**) in deuterated tetrahydrofuran ( $d_8$ -THF) was treated with lithium bis(trimethylsilyl)amide (LHMDS, 1 M in dry THF, 1.2 eq.) at  $-40^\circ\text{C}$ . After 30 minutes, the  $^{13}\text{C}$  NMR spectrum of the solution revealed the development of a carbon signal at 204 ppm. This corresponds to the Li-adduct of the depro-

nated 2-position of **21**, with a  $\delta(\Delta)$  of 66 ppm in comparison to the chemical shift of the carbon at position 2 of the starting material **16i** which was detected at 138 ppm (Scheme 5).

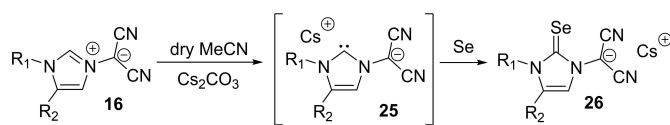
Based on the resonance frequency of the lithium-stabilized<sup>[59]</sup> carbene, its nucleophilicity can be classified in the series of derivatives known from literature. The carbene center of the lithium-stabilized, saturated imidazolin-2-ylidene **22**<sup>[60]</sup> exhibits a chemical resonance at 196 ppm for the free carbene in solution and shows analogous behavior to the novel compound **21**. Other anionic carbenes such as the imidazolium phenolate **23** (203 ppm in  $d_5$ -pyridine<sup>[61]</sup>) or the anion carrying derivative **24**<sup>[62]</sup> (211 ppm in  $d_8$ -THF) display a comparable resonance frequency. Due to the unstable nature of the Li-adducts of the anionic carbenes (measurement was only possible at  $-40^\circ\text{C}$ ), caesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) was employed as an alternative, mild base for the generation of the carbenes. In dry acetonitrile under a nitrogen atmosphere, the ylides were easily convertible to the corresponding carbenes in moderate reaction times in the presence of this base. For the investigation of their electronic properties concerning  $\pi$ -backbonding, the anionic carbenes generated from the ylides **16** (Table 1) were intercepted *in situ* with elemental selenium (Scheme 6).<sup>[36,63]</sup>

In this context, a series of salt-like, water-soluble products were isolated in satisfactory yields (64–93%, Table 2). They consist of an anionic, organic fragment and caesium(I) as the cation. The crude salts were recrystallized from aqueous or alcoholic solutions to remove traces of  $\text{Cs}_2\text{CO}_3$ . As a consequence of their polar structure, recrystallization of the salts was more feasible than column chromatography as a work-up procedure.

Upon examination of the  $^{77}\text{Se}$  NMR chemical shift values (measured in  $d_6$ -DMSO) of various derivatives, a grouping is possible based on the nitrogen-substituent in 1-position of the

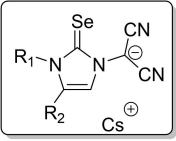


**Scheme 5.** Reaction conditions of the NMR-experiment to prove the presence of an anionic carbene *in situ* and some selected  $^{13}\text{C}$  NMR shifts of anionic Li-stabilized carbenes for comparison.



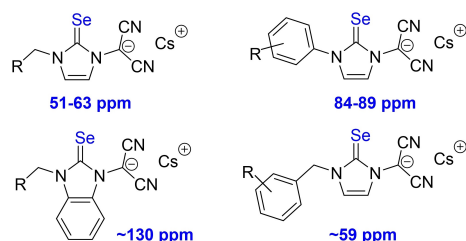
**Scheme 6.** Preparation of the anionic carbene **25** with  $\text{Cs}_2\text{CO}_3$  in dry MeCN yielded selenones with the general structure **26**.

**Table 2.** Selenones derived from the corresponding ylides. [a]: spectra measured in  $d_6$ -DMSO.

	R <sub>1</sub> =	R <sub>2</sub> =	Yield [%]	<sup>77</sup> Se-shift [ppm] <sup>[a]</sup>
				
<b>26a</b>	methyl	H	78	62.9
<b>26b</b>	butyl	H	88	53.7
<b>26c</b>	isopropyl	H	89	51.0
<b>26d</b>	phenyl	H	78	89.3
<b>26e</b>	<i>p</i> -tolyl	H	90	88.8
<b>26f</b>	4-methoxyphenyl	H	70	86.8
<b>26g</b>	2-methoxyphenyl	H	85	83.7
<b>26h</b>	benzyl	H	93	59.0
<b>26i</b>	4-methylbenzyl	H	89	59.5
<b>26j</b>	3-methylbenzyl	H	92	59.4
<b>26k</b>	4-methoxybenzyl	H	83	59.5
<b>26l</b>	methyl	annulated	63	134.3
<b>26m</b>	benzyl	annulated	79	130.0
<b>26n</b>	methyl	methyl	64	71.8
<b>26o</b>	methyl	phenyl	79	86.6

imidazolium ylide (Figure 8). While the alkylated compounds exhibited shift values in the range of 51 to 63 ppm, the arylated selenones displayed values between 84 and 89 ppm. Benzylated adducts showed selenium resonances similar to the alkylated derivatives mentioned before. Therefore, it is apparent that no secondary effects such as non-classical hydrogen bonding (NCHB<sup>[64]</sup>) or direct electronical influence of the anisotropy cone of the substituted benzyl group to selenium occurred in solution. As expected, the benzimidazole-selenones showed the highest degree of deshielding of the <sup>77</sup>Se NMR shifts due to the enhanced  $\pi$ -backbonding facilitated by the extended  $\pi$ -system.

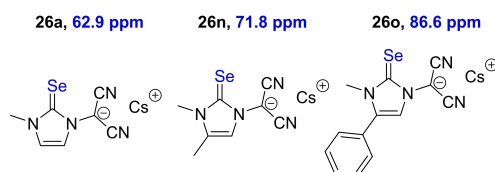
The modification of the backbone of the *N*-methylated imidazolium ylide by a methyl group in position 5 resulted in a downfield shift of the <sup>77</sup>Se NMR signal. Analogous to two benzannulated systems **26l** and **26m** (see Table 2), arylation at



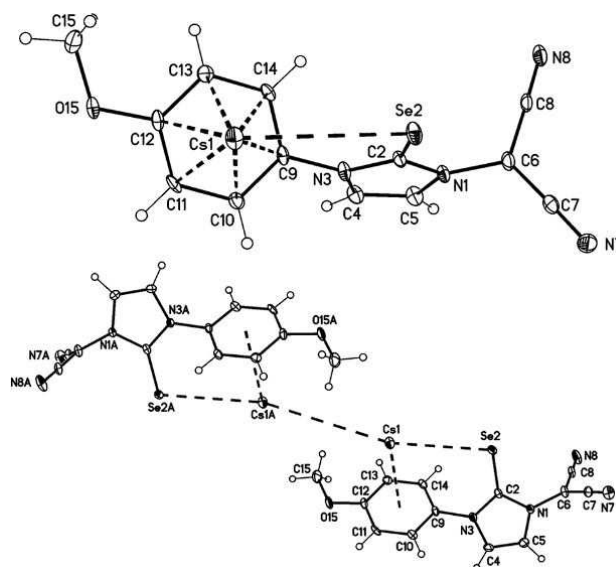
**Figure 8.** Grouping of the <sup>77</sup>Se NMR chemical shifts based on their substitution pattern.

the 5-position of selenone **26a** leads to an extension of the  $\pi$ -system and an associated improved  $\pi$ -acceptance (Figure 9).

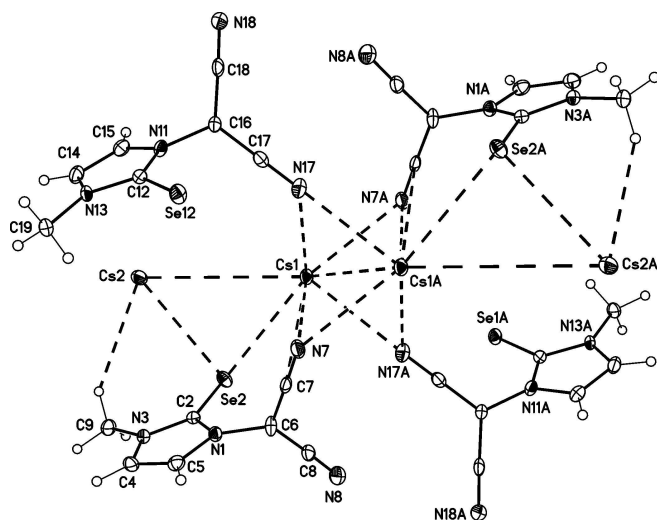
In the context of the existing literature on NHC-selenium adducts, the compounds isolated in this work can be categorized as moderate  $\pi$ -acceptors based on their <sup>77</sup>Se shifts ranging from 52 to 134 ppm.<sup>[36,37]</sup> A series of single crystals of selenones were isolated, and the bond lengths, dihedral angles of the compounds as well as the coordination behavior of caesium(I) will be exemplary discussed using the data of caesium dicyano(1-(4-methoxyphenyl)-2-selenoxo-1*H*-imidazol-3-yl)methanide (**26f**). As evident from Figure 10, the caesium cation resides in proximity to the *N*-substituted 4-methoxyphenyl ring, coordinating additionally to selenium (Cs1, **26fA**). In contrast to that, a spatial proximity to the dicyano subunit was expected. This coordination to selenium forces the imidazole backbone to protrude out of the coordination plane towards the aromatic ring. The torsion angle between C2–N3–C9–C14 is approximately 58°. In contrast to the ylide precursor, conjugation of the dicyano moiety with the imidazole core is strongly hindered with a torsion angle between C2–N1–C6–C8 of 84°.



**Figure 9.** Influence of the backbone-modification.



**Figure 10.** Molecular structure of monomeric (**26fA**) and dimeric (**26fB**) compound **26f** with displacement parameters drawn at 50% probability level. Selected bond lengths in pm (crystallographic numbering): N1–C2: 137.00(4), N1–C5: 139.70(4), N1–C6: 142.70(4), N3–C2: 136.30(4), N3–C4: 139.60(4), N3–C9: 142.80(4), C4–C5: 134.90(5), C2–Se2: 183.90(3), C6–C7: 139.30(5), C6–C8: 139.90(5), C7–N7: 115.90(5), C8–N8: 115.90(5), C9–Cs1: 376.20(3), Z(Ar)–Cs1: 344.10(1). Dihedral angle [°]: C2–N3–C9–C14: 58.10(5), C2–N1–C6–C8: –83.60(4).



**Figure 11.** Molecular structure of the 3D polymer of **26a** with displacement parameters drawn at 50% probability level. Selected bond lengths in pm (crystallographic numbering): N1–C2: 136.20(5), N1–C5: 139.60(5), N1–C6: 143.90(5), N3–C2: 135.70(5), N3–C4: 138.50(6), N3–C9: 144.80(5), C2–Se2: 184.10(5), Se2–Cs1: 372.08(5), Se2–Cs2: 372.28(5), C6–C7: 139.20(6), C6–C8: 139.90(6), C7–N7: 115.70(6), C8–N8: 115.80(6), N7–Cs1: 315.70(4). Dihedral angle [°]: C2–N1–C6–C7: 102.90(5).

The C2=Se2 distance (183.90 pm) is in a typical range for selenium carbene adducts.<sup>[37]</sup> The caesium salts tend to form dimers, as evident from Figure 10 (**26fB**). The crystal structure of caesium dicyano(1-methyl-2-selenoxo-1*H*-imidazol-3-yl)methanide **26a** reveals, in addition to the coordination of caesium in the dimer *via* the nitrogen of the nitrile groups and selenium, the structural arrangement of the three-dimensional framework. In this structure, caesium(I) plays a stabilizing role between layers of the anionic fragments and is coordinated octahedrally (Figure 11).

A torsion angle of 103° between C2–N1–C6–C7 was observed in **26a**, indicating an interrupted conjugation with the imidazole backbone analogous to **26f**. The rotatable dicyano unit contributes to the stabilizing coordination to caesium(I). It may be concluded that while the dicyano unit in the ylide is still coordinated to the imidazole backbone, the formed selenones exhibit free rotation.

## Conclusions

An optimized synthesis of a variety of electronically distinct dicyanoimidazolium ylides was presented. These compounds are bench-stable ylides that can be easily converted into the corresponding anionic carbenes in the presence of a base such as caesium carbonate or LHMDs. This allowed the isolation of the first anionic dicyanoimidazolium carbenes derived from *N*-ylide precursors, characterized exemplarily for the dicyano(1-(4-methylbenzyl)-1*H*-imidazolium-3-yl)methanide (**16i**) by determining the <sup>13</sup>C NMR shift of the free carbene. The  $\pi$ -conjugated systems were further characterized by CREF values and the examination of their electron density distribution (HOMO/LUMO-profiles). The ylides were implemented in trapping

reactions with selenium to yield unique, salt-like and water-soluble adducts that can be classified as moderate  $\pi$ -acceptors based on their bonding behavior towards selenium. Crystal data of an exemplary azomethine ylide as well as a series of anionic, Cs(I)-stabilized NHC-selenium-adducts revealed the binding behavior of the discussed systems.

## Experimental Section

Commercially available materials were used without further purification unless noted otherwise. Solvents were dried according to established procedures and stored under nitrogen. The reaction progress was monitored by thin layer chromatography (TLC) on silica coated aluminum sheets from MERCK (60 F<sub>254</sub>). NMR spectra were measured on the FT-NMR Devices AVANCE NEO (400 MHz) and AVANCE III (600 MHz) from BRUKER and analyzed with TOPSPIN 3.5 from BRUKER. Chemical shifts ( $\delta$ ) are given in ppm relative to the residual solvent for CDCl<sub>3</sub> (<sup>1</sup>H (CDCl<sub>3</sub>):  $\delta$  = 7.26 ppm, <sup>13</sup>C (CDCl<sub>3</sub>):  $\delta$  = 77.16 ppm), *d*<sub>6</sub>-DMSO (<sup>1</sup>H (*d*<sub>6</sub>-DMSO):  $\delta$  = 2.50 ppm, <sup>13</sup>C (*d*<sub>6</sub>-DMSO):  $\delta$  = 39.52 ppm), *d*<sub>8</sub>-THF (<sup>1</sup>H (*d*<sub>8</sub>-THF):  $\delta$  = 1.72 and 3.58 ppm, <sup>13</sup>C (*d*<sub>8</sub>-THF):  $\delta$  = 6.21 and 25.31 ppm) and *d*<sub>3</sub>-MeCN (<sup>1</sup>H (*d*<sub>3</sub>-MeCN):  $\delta$  = 1.94 ppm, <sup>13</sup>C (*d*<sub>3</sub>-MeCN):  $\delta$  = 118.26, 1.32 ppm).<sup>[65]</sup> Coupling constants *J* are given in Hertz (Hz) and with the following abbreviations for multiplicity: s (singlet), d (duplet), t (triplet), q (quartet), qui (quintet), sext (sextet) and sept (septet). Signals without analyzable coupling are marked as m (multiplet). The prefix app. (apparent) is used to highlight that the observed multiplicity is a result of vague subordinated coupling. For the <sup>13</sup>C/DEPT-spectra, (+) is added for carbons bonded to one or three hydrogens and (–) for carbons bonded to two hydrogens. Quaternary carbon atoms are denoted with the symbol (o). The *N*-substituted imidazoles are synthesized by *N*-arylation,<sup>[38]</sup> *N*-benzylation<sup>[39]</sup> and *N*-alkylation<sup>[41]</sup> of 1*H*-imidazole or 1*H*-benzo[*d*]imidazole according to literature procedures or the heterocycles are formed by Debus-Radziszewski-reactions<sup>[40]</sup> or Van-Leusen reactions.<sup>[42]</sup> Alternatively, they are purchased directly from the supplier (TCI, Merck).

## General Procedure for the Synthesis of Imidazolium Ylides

A solution of TCNEO (1 equiv.) in Et<sub>2</sub>O was added dropwise to an ice-cooled and stirred solution of the corresponding imidazole (1 equiv.) in Et<sub>2</sub>O over the course of 15 min. After the complete addition, the solution was stirred for further 15 min. in the ice bath and diluted with half the volume of *n*-pentane. The resulting solid was filtered off and washed with Et<sub>2</sub>O and *n*-pentane to remove unreacted imidazole and TCNEO. If necessary, the crude product was purified by recrystallization. Alternatively, the ylides may be subjected to column chromatography (silica gel, DCM/MeOH 10:0.5 v/v).

(1-Butyl-1*H*-imidazolium-3-yl)dicyanomethanide (**16b**). According to the general procedure, a solution of 1-butyl-1*H*-imidazole (0.250 g, 2.01 mmol) in Et<sub>2</sub>O (50 mL) was reacted with a solution of tetracyanoethylene oxide (**9**, 0.290 g, 2.01 mmol) in Et<sub>2</sub>O (50 mL) to give **16b** (0.272 g, 71 %) as a pale-yellow solid after recrystallization from isopropanol, m.p.: 83–85 °C. <sup>1</sup>H NMR (600 MHz, *d*<sub>6</sub>-DMSO):  $\delta$  = 9.21 (m, 1H, H-2), 7.76 (m, 1H, H-5), 7.66 (m, 1H, H-4), 4.10 (t, *J* = 7.4 Hz, 2H, H-9), 1.77 (qui, *J* = 7.4 Hz, 2H, H-10), 1.24 (sext, *J* = 7.4 Hz, 2H, H-11), 0.89 (t, *J* = 7.4 Hz, 3H, H-12) ppm. <sup>13</sup>C NMR (150 MHz, *d*<sub>6</sub>-DMSO):  $\delta$  = 136.8 (+, 1 C, C-2), 124.7 (+, 1 C, C-4), 123.1 (o, 2 C, C-7, C-8), 122.6 (+, 1 C, C-5), 48.7 (–, 1 C, C-9), 40.3 (o, 1 C, C-6), 31.2 (–, 1 C, C-10), 18.9 (–, 1 C, C-11), 13.22 (+, 1 C, C-12) ppm. IR (ATR)  $\nu$  = 3168, 3127, 3100, 3061, 2960, 2932, 2868, 2206, 2173, 2118, 2046, 1630, 1566, 1537, 1462, 1381, 1258, 1198, 1096, 1054, 940, 862, 762,



716, 664, 634, 544, 497 cm<sup>-1</sup>. HR-ESI-MS: calcd. for [C<sub>10</sub>H<sub>12</sub>N<sub>4</sub> + Na]<sup>+</sup>: 211.0954, found: 211.0962.

### General Procedure for the Trapping Reactions with Selenium

A stirred solution of the corresponding imidazolium ylide (1 equiv.) in abs. MeCN was treated with Cs<sub>2</sub>CO<sub>3</sub> (2 equiv.) and left to stir for 10 min. at rt. After the addition of selenium (1.2 equiv.), the suspension was stirred for 16–48 h at 40 °C. Excess selenium and base were filtered off and the solvent was removed under reduced pressure. The crude product was purified by recrystallization.

**Caesium dicyano(1-butyl-2-selenoxo-1*H*-imidazol-3-yl)methanide (26b).** According to the general procedure, a solution of (1-butyl-1*H*-imidazolium-3-yl)dicyanomethanide (**16b**, 0.100 g, 0.53 mmol) in dry MeCN (10 mL) was stirred with Cs<sub>2</sub>CO<sub>3</sub> (0.347 g, 1.06 mmol) and selenium (0.050 g, 0.64 mmol) for 48 h at 40 °C to give **26b** (0.187 g, **88%**) as a golden, crystalline solid after recrystallization from isopropanol, m.p. 91–93 °C. <sup>1</sup>H NMR (600 MHz, d<sub>6</sub>-DMSO): δ = 7.21 (d, *J* = 2.2 Hz, 1H, H-5), 7.07 (d, *J* = 2.2 Hz, 1H, H-4), 3.99 (t, *J* = 7.4 Hz, 2H, H-9), 1.65 (qui, *J* = 7.4, 2H, H-10), 1.26 (sext, *J* = 7.4 Hz, 2H, H-11), 0.89 (t, *J* = 7.4 Hz, H, H-12) ppm. <sup>13</sup>C NMR (150 MHz, d<sub>6</sub>-DMSO): δ = 159.9 (o, 1 C, C-2), 126.4 (o, 2 C, C-7, C-8), 124.3 (+, 1 C, C-4), 118.9 (+, 1 C, C-5), 49.1 (–, 1 C, C-9), 30.4 (–, 1 C, C-10), 19.2 (–, 1 C, C-11), 13.6 (+, 1 C, C-12) ppm.

<sup>77</sup>Se-NMR (114 MHz, d<sub>6</sub>-DMSO): δ = 53.7 (Se-13) ppm. IR (ATR) ν = 3465, 3172, 3140, 2949, 2866, 2216, 2172, 2101, 1645, 1568, 1451, 14220, 1387, 1280, 1236, 1196, 1119, 1099, 1029, 940, 883, 822, 754, 712, 667, 628, 566, 544, 467 cm<sup>-1</sup>. HR-ESI-MS: calcd. for [C<sub>10</sub>H<sub>11</sub>N<sub>4</sub>Se]<sup>–</sup>: 267.0154, found: 267.0153.

### Supporting Information

The authors have cited additional references within the Supporting Information. Deposition Numbers 2310733 (for **17**), 2310734 (for **32**), 2310735 (for **33**), 2310736 (for **1\_SI**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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### Conflict of Interests

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

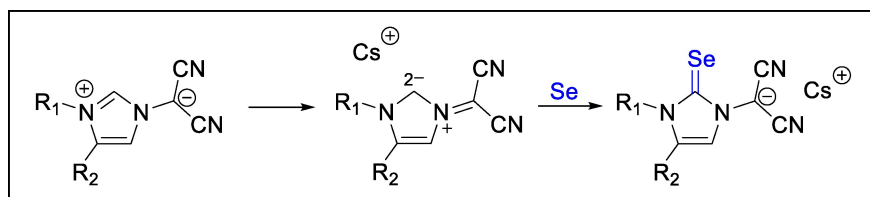
**Keywords:** mesomeric betaine · selenium · carbene · imidazol-2-ylidene · mesoion

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## RESEARCH ARTICLE



Imidazolium-ylides are conjugated mesomeric betaines with an exocyclic anionic carbon substituent. These ylides were converted by deprotonation into anionic N-heterocyclic carbenes, which can be formulated

with two negative charges on the carbene carbon atom due to their origin. Subsequent reaction with selenium gave anionic selenourea compounds.

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**Imidazolium Dicyanomethylides as N-Ylide Precursors of Anionic N-Heterocyclic Carbenes**

