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BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS  
FACULTY OF CHEMICAL AND BIOENGINEERING  
GEORGE OLÁH DOKTORAL SCHOOL

# STABLE CARBENES AND THEIR REACTIONS – NEW POSSIBILITIES

## Theses of the Doctoral Dissertation

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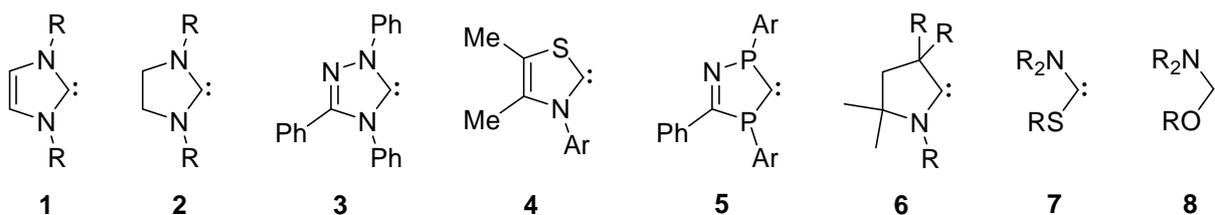
## 1. Introduction

Carbenes are of great current interest, due to their specific structural properties, and their catalytic reactions in transition-metal complexes, or as metal-free catalysts. Their significance can be represented by the great number of related industrial applications, and also by the two Nobel-prizes that can be connected to these species (Fisher - 1973; Schrock, Chauvin, Grubbs - 2005).

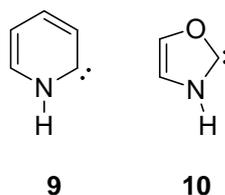
The investigation of free carbenes may pursue two goals: firstly, aiming the design of novel carbenes may contribute to the development of novel catalytic processes, or the improvement of the already existing ones. Secondly, the better understanding of the reactions of the hitherto synthesized carbenes can also result in the improvement of catalytic applications. The group of Prof. László Nyulászi has remarkable experience in both fields, thus, the research I was conducting during my doctoral studies in the Group also focused on these areas.

## 2. Background

Carbenes are hypovalent species, containing a divalent carbon atom.<sup>1</sup> Although several derivatives have triplet ground state, these are rather unstable compounds, which can be decomposed by e.g. dimerization. Thus, the stabilization of the singlet ground state is essential to stabilize carbenes. This can be achieved by  $\pi$ -electron withdrawing or  $\pi$ -electron donating substituents, of which stabilizing effect can be further increased by aromaticity and the steric effects provided by bulky groups. Based on these considerations many stable carbenes have been synthesized (e.g. **1-8**).<sup>1</sup>



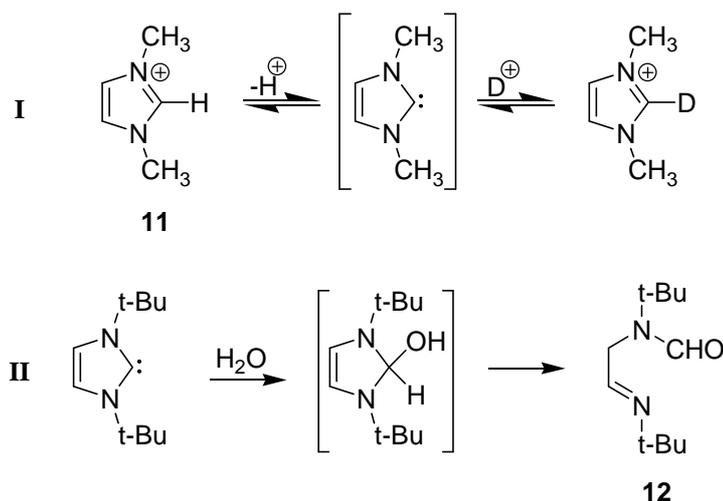
Considering the stabilizing factors in stable carbenes, together with some early data<sup>2</sup> regarding the presence of pyridine-2-ylidene as intermediate in many reactions, and the stability of **7-8** carbenes, the question is apparent: can any derivative of **9** and **10** be synthesized? Investigation of the stability of these carbenes was one of the aims of my doctoral research.



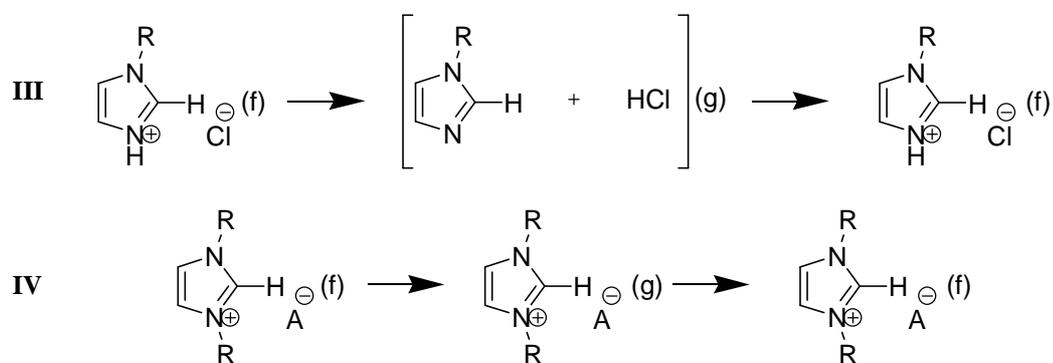
<sup>1</sup> Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chemical Reviews* **2000**, *100*, 39.

<sup>2</sup> Dyson, P.; Hammick, D. L. *J. Chem. Soc.* **1937**, 1724.

The reactivity of imidazole-2-ylidenes is greatly influenced by their lone electron pair, providing Lewis base character for these species. This can be represented by the remarkable stability of their complexes, which are formed even with silicon-derivatives.<sup>3</sup> Although with other electron donors (such as amines or phosphines) silicon derivatives have been shown to form not only penta-, but also hexacoordinate silicon derivatives, the latter type of complexes has not yet been reported with carbene ligands. The investigation of the stability, structure and synthesizability of these structures was another aim of my work.



Due to the basicity of **1**, the formation of imidazolium cation (**11**) in its reaction with proton donors, such as water is obvious. Although this process in aqueous solutions has not yet been directly examined, the H/D exchange at position 2 of the imidazolium ring could only be rationalized by the formation of **1**, followed by its immediate protonation (reaction I).<sup>4</sup> However, interestingly, the reaction of **1** (R = t-Bu) in THF with equimolar amount of water has been reported to yield an open-chain product (**12**, reaction II).<sup>5</sup> This reaction is surprisingly slow, for the complete decomposition of **1** three months were needed. Despite the importance of the understanding the hydrolysis of **1**, no thorough studies have been devoted to this apparently complex reaction, thus, it was investigated in my doctoral research.



<sup>3</sup> Kuhn, N.; Kratz, T.; Blaser, D.; Boese, R. *Chem. Ber.* **1995**, *128*, 245.

<sup>4</sup> Amyes, T. L.; Diver, S. T.; Richard, J. P.; Rivas, F. M.; Tóth, K. *J. Am. Chem. Soc.* **2004**, *126*, 4366.

<sup>5</sup> Denk, K. D.; Rodezno, J. M.; Gupta, S.; Lough, A. *J. Organomet. Chem.* **2001**, *617-618*, 242.

As it is indicated above, the chemistry of imidazole-2-ylidene derivatives is highly related to that of imidazolium salts. The latter compounds are often form so-called ionic liquids (ILs), which are also of great interest, due to their promising performance in many industrial applications.<sup>6</sup> ILs can be classified as protic and non-protic derivatives. Since protic ILs contain acidic proton, a proton transfer from the cation to the anion may occur, yielding the neutral, thus volatile acid-base pair (reaction **III**).<sup>7</sup> As a result, these compounds can be distilled under relatively mild conditions. In case of non-protic ILs, however, this proton transfer is regarded not feasible, thus, only the highly polar ion pairs can be evaporated from the liquid (reaction **IV**), which results in much lower vapor pressures.<sup>8</sup>

Although imidazole-2-ylidenes are very strong bases, it is likely, that with sufficiently basic anions a **III**-like proton transfer might be feasible in case of 1,3-dialkylimidazolium salts, yielding imidazole-2-ylidenes. Thus, the investigation of the effects of differently basic anions on the isomerisation of non-protic IL ion pairs was also pursued during my research.

### 3. Applied Methods

Addressing the issues described above, quantum chemical calculations have been carried out by the Gaussian 03 program package. The topological analysis of the electron density have been performed by the AIM 2000 program.

All the structures have been fully optimized, followed by the verification of the second derivative matrix, to establish the nature of the obtained stationary point. Calculations have usually been done at different DFT levels (often at the B3LYP/6-311+G\*\* level), and the results have been verified at other levels, such as other DFT functionals, MP2 and CCSD(T) methods with basis sets of different kind and size. Moreover, the results have also been compared to the available experimental data.

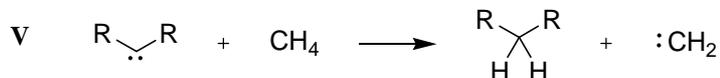
During the investigation of the stability of **9** and **10**, the aromaticity of these structures has been characterized by applying ISE<sub>c</sub>-type isodesmic reactions, comparing the energy of the aromatic species to that of its non-aromatic isomer. Bird-indeces have also been calculated, referring to the (normalized) scatter of the bond orders within the ring. Aromaticity has been examined according to magnetic properties as well: the magnetic shielding has been calculated at the center of the ring (NICS(0)), and 1 Å above that point (NICS(1)).

<sup>6</sup> Wasserscheid, P. ; Welton, T. *Ionic Liquids in Synthesis* 2. Edition, Wiley-VHC Verlag, Weinheim, 2007.

<sup>7</sup> Greaves, T. L.; Drummond, C. J. *Chem. Rev.* **2008**, *108*, 206.

<sup>8</sup> Earle, M. J.; Esperanca, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegreen, J. A. *Nature*, **2006**, *439*, 831.

The isodesmic reaction **V** has been shown to perform well in the evaluation of the stability of carbenes against dimerization. This reaction provides an underestimated stability value, since it does not account for steric hindrance, which also affects the dimerization energy.

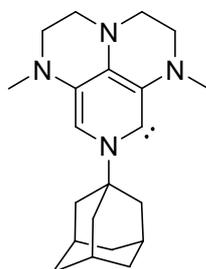


## 4. Results

### 4.1. Stabilizing the Pyridine-2-ylidene **9**

The stability of **9** has been examined by calculating the energy of the corresponding reaction **V**. at the B3LYP/6-311+G\*\* level. Although its value has been found to be significantly smaller than that for **1**, it is comparable to the stabilization energy of **2**, suggesting that this carbene can also be stabilized by proper substitution. As a main stabilizing factor, the aromaticity of **9** is smaller than that of the isomer pyridine by only ca. 20%.

Substitution at the ring carbons by amino groups and at the nitrogen by a bulky adamantyl group have been found to increase the stability of this compound by a few kcal/mol, which is presumably completed by the extended steric hindrance. Considering that the simplest potential synthetic approach to the derivatives of **9** is the deprotonation of the corresponding pyridinium salts, the possibility of competitive deprotonation reactions has also been examined. Interestingly, in the presence of  $\alpha$ -hydrogens at the side chain attached to the nitrogen, not the pyridine-2-ylidene, but its isomer pyridinium-ylide is the most stable deprotonation product, showing the importance of the quaternary carbon atom at that position. Since kinetic control may result in the deprotonation at positions 3 and 4 at the ring, the introduction of amino groups to those positions is highly desirable. Thus, considering all the aspects described above, **13** can be suggested as a potential candidate for synthesis.



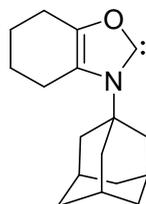
**13**

### 4.2. Stabilizing the Oxazole-2-ylidene **10**

The stability of **10** has also been investigated at the B3LYP/6-311+G\*\* level, and has been found to be bigger than that of all carbenes substituted by nitrogen or chalcogen atoms except for **1**, including the already synthesized **2**, **4**, **7** and **8**. This finding indicates the

possible stabilization of oxazole-2-ylidenes by proper substitution. Interestingly, despite the increased stability and the presence of six  $\pi$ -electrons, the aromaticity of **10** is only a minor contributor to its stability. Substitution at the nitrogen or at the carbons effects the stability only by a few kcal/mol. However, steric effects might be beneficial in this case as well; hence the bulky adamantyl group has been suggested for N-substitution.

According to literature data the fragmentation reaction of the derivatives of **10** yielding isocyanates and acetylenes should also be investigated, as an additional decomposition reaction. For **10** the reaction energy and Gibbs free energy indicated exothermic reaction, but the obtained high barriers suggest kinetic hindrance. However, destabilization of the forming acetylene derivative by closing it into a ring can switch the reaction energy to a positive value, providing thermodynamic prevention for such decompositions. Considering the aforementioned effects, **14** has been suggested to be a promising target of synthesis.

**14**

#### 4.3. Structure and Stability of Carbene Derived Penta- and Hexacoordinate Silicon Compounds

Both penta- and hexacoordinate structures derived from silicon-tetrahalides and a variety of carbenes could be localized at the potential energy surface at the B3LYP/6-311+G\*\* level. In the pentacoordinate  $\text{SiF}_4$  derivatives the carbene ligand generally occupies axial, while in the analogous  $\text{SiCl}_4$  structures usually equatorial position. This finding is in good agreement with the structure of experimentally investigated pentacoordinate derivative obtained in the reaction of **1** ( $\text{R} = i\text{-Pr}$ ) and  $\text{SiCl}_4$ .

In case of the most important aminocarbenes the complexation energies were found to be remarkably high: 20-30 kcal/mol in case of  $\text{SiF}_4$ , and 17-19 kcal/mol in case of  $\text{SiCl}_4$ . These values are much higher than those for the amine or phosphine complexes (e.g. -8,5 kcal/mol for  $(\text{NH}_3)\text{SiF}_4$ ).

In the most stable hexacoordinate derivatives the ligands are in trans position, and again, the energies of the formation of the complexes (30-60 kcal/mol for both halides) are significantly higher than those for the corresponding amine derivatives (e.g. -21,6 kcal/mol for  $(\text{NH}_3)_2\text{SiF}_4$ ). Since the  $(\text{NH}_3)_2\text{SiF}_4$  species has already been synthesized,<sup>9</sup> it is very

<sup>9</sup> Guy-Lussac, J. L.; Thenard, L. J. *Mem. Phys. Chim. Soc. Arcueil* **1809**, 2, 317.

likely that the analogous hexacoordinate silicon complexes derived from carbenes can also be prepared.

Considering the stability of the carbenes, and that of the complex they form with silicon-tetrahalides we suggested the synthesis of the hexacoordinate derivatives with 1,3-dimethylimidazol-2-ylidene ligands. Three months after the publication of these results, the successful synthesis and the crystallographic characterization of both penta- and hexacoordinate species have been reported. In agreement with the computational data, in the pentacoordinate complexes derived from  $\text{SiF}_4$  the carbene ligand occupies the axial position, while the conformation of the hexacoordinate derivative is trans.

#### 4.4. The Hydrolysis of Imidazole-2-ylidenes

As it was described above, the hydrolysis of imidazole-2-ylidenes is different in moist organic solvents, and in aqueous solutions. The hydrolysis in predominantly organic media has been modeled by the reaction of **1** ( $\text{R} = \text{Me}$ ) with one, two and three water molecules in the gas phase, at the B3LYP/6-311+G\*\* level. The reaction energy profile has been found to be similar with both one and two water molecules. The first step of the reaction is the formation of a remarkably strong H-bond between the carbene and the water(s), followed by the concerted insertion of the carbene into the O-H bond, yielding the adduct intermediate in reaction **II**. Interestingly, the energy of the adduct, and the H-bonded structure is similar. From the adduct, first a Schiff-base isomer of **12** forms, which then rearranges to **12**. The latter two structures are similarly stable, providing the driving force for the reaction.

Interestingly, in case of three reacting water molecules the imidazolium-hydroxide structure could be obtained, thus, the concerted insertion has been split into a protonation –  $\text{OH}^-$  addition stepwise mechanism. Although the barriers are considerably lower, than those in the presence of one and two water molecules, the ring opening step still has a gap of 21,6 kcal/mol, explaining the experimentally found low rate.

The aqueous solution was modeled by explicit models. Firstly, the intermediates and products of the reaction were optimized in the presence of the first solvate shell (consisting of 30 water molecules). Secondly, ab initio molecular dynamic simulation was performed for the system containing **1** ( $\text{R} = \text{Me}$ ) and 105 water molecules. Both approaches indicate the lack of ring opening, due to the stabilization of aromaticity and solvation, which make the imidazolium-hydroxide the lowest energy structure.

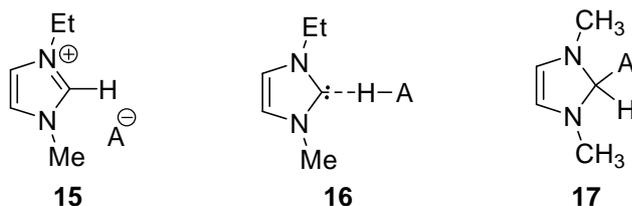
In cooperation with the group of Prof. Dietrich Gudat (University of Stuttgart), the reaction of **1** ( $\text{R} = \text{bis}(\text{diisopropyl})\text{phenyl}$ ) with 0,5-300 equivalents of water has been followed by NMR spectroscopy. In contrast to the previous findings, both open chain products could be identified in the solution in the presence of small amounts of water. The changes in chemical shifts, those in the water content of the reaction mixture, and also those

in the IR peaks, could only be explained by the presence of the carbene-water H-bonded complex.

However, in the presence of big excesses of water the signals of the open chain products did not appear in the NMR spectrum, in accordance with the calculations. It is also a notable result that in the presence of 60 equivalents of water, there is still a considerable amount of unreacted carbene in the solution.

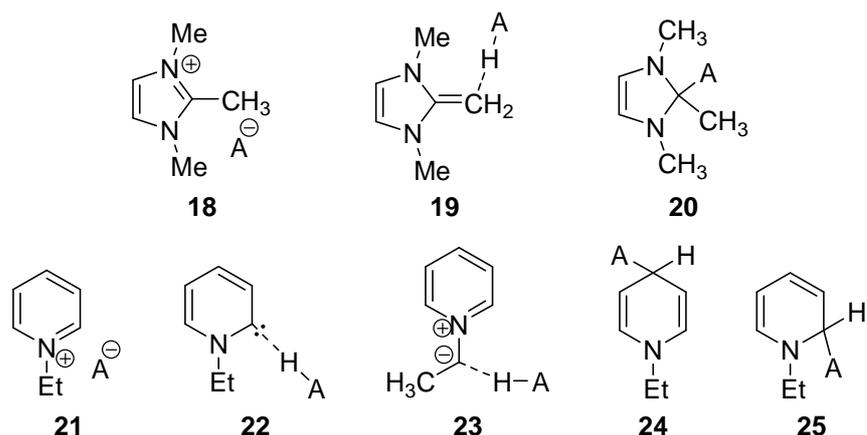
#### 4.5. Formation of Neutral Species in Ionic Liquids

The 1,3-dialkylimidazolium salts have been modeled by 1,3-dimethylimidazolium derivatives at the B3LYP/6-31+G\* level. The optimized structures and their relative energies are highly dependent on the basicity of the anion. While in case of the most frequently used, least basic anions (e.g. Cl<sup>-</sup>, TfO<sup>-</sup>, Tf<sub>2</sub>N<sup>-</sup>) only **15** could be optimized, in case of the moderately basic acetate, phenolate etc. also the H-bonded **16** and the adduct **17** could be obtained. By the increase of the basicity of the anion, the relative stability of **15** compared to **16** decreases, and in case of the most basic anions (hydroxide, methanolate) only **16** and **17** were found to be a minimum of the potential energy surface.



Dissociation to the carbene **1** (R = Me) and the corresponding acid is endoergic in case of the moderately basic anions, but considering the role of entropy it is likely to occur at higher temperatures and under low pressures. Among these structures the acetate deserves special attention, since the 1-ethyl-3-methylimidazolium-acetate (EMIM-acetate) is a widely used IL. In agreement with the calculations, photoelectron spectroscopic and mass-spectroscopic measurements indicated the occurrence of the proton shift for EMIM-acetate. While the photoelectron spectrum (measured by Tamás Veszprémi and Balázs Németh) could be assigned to **16**, the mass spectrum (measured by BASF) could only be rationalized by the presence of the free acetic acid and the carbene, formed prior to ionization. Assuming that the carbenes are present in the liquid phase as well (although in significantly smaller concentrations), these results indicate the possibility of the development of ILs, which can catalyze certain reactions themselves.

The possibility of the formation of neutral species in 1,3-dialkyl-2-methylimidazolium, and 1-butylpyridinium salts has also been examined. These compounds have been modeled by 1,2,3-trimethylimidazolium and 1-ethylpyridinium salts at the B3LYP/6-31+G\* level.



In both cases, the neutral species can be formed by the increase of the basicity of the anion, and in case of the most basic anions the ionic **18** and **21** isomers could not be optimized, similarly to the 1,3-dimethylimidazolium salts. Interestingly, in **19** the acid forms an H-bond with the methylene moiety, which can be rationalized by the known polarized nature of such exocyclic double bonds. However, this H-bond is rather weak, thus – apart from the most basic hydroxide and methanolate case – **18** was found to be the most stable structure. On the other hand, the dissociation energies to the acid and the double bonded structure are similar to those for 1,3-dimethylimidazolium salts, hence the dissociation of 1,3-dialkyl-2-methylimidazolium salts is presumably also likely under low pressures. Interestingly, in case of the pyridinium salts with moderately basic anions (e.g. acetate) **24** and **25** are usually far more stable than the other isomers, in agreement with the known electrophilicity of pyridinium cations. Since the dissociation of **24** and **25** to the carbene (via **22**) or to the pyridinium-ylidene (via **23**) is highly endoergic, it is rather unlikely to occur. However, the high stability of the adducts **24** and **25** indicate the possibility of the formation of these compounds, which needs to be taken into account if one is applying pyridinium-based ILs for reactions containing basic anions.

## 5. Theses of Doctoral Dissertation:

1. The stability of the pyridine-2-ylidene was found to be greatly increased by its aromaticity, being ca. 80% of that for the isomer pyridine. The stability can be increased by the introduction of amino groups to the carbon atoms of the ring, and bulky substituents to the nitrogen. According to these data the synthesis of **13** has been suggested.<sup>PU1</sup>
2. The stability of oxazole-2-ylidene was found to be higher than that of the already synthesized imidazolidine-2-ylidene and thiazole-2-ylidene, but this stability could not be increased significantly by substitution.
3. The fragmentation of oxazol-2-ylidene to isocyanate and acetylene is exothermic, but kinetically hindered at room temperature. Furthermore, this reaction can be switched to endothermic by destabilizing the forming acetylene by closing the neighboring ring carbons into a ring. Considering these influential factors, **14** has been suggested for synthesis.
4. Carbenes form very stable penta- and hexacoordinated complexes with silicon-tetrahalides. The pyridine-2-ylidene forms the most stable complex, but the imidazole-2-ylidene-derived, hitherto unknown hexacoordinate compounds were also found to be stable and synthesizable. (it is worth to note that three months after the publication of these data this compound has been reported, exhibiting similar structure to those obtained by the calculations).<sup>PU2</sup>
5. The contradictive data regarding the hydrolysis of imidazole-2-ylidenes has been reconsidered according to a complex reaction mechanism. This process follows different paths depending on the amount of water being present in the reaction mixture. In case of traces of water the ring opens, and yielding a formamide derivative. The calculations predicted a hitherto undetected product, which was later verified by NMR spectroscopy. In case of big excess of water a single protonation occurs, without any ring opening. The lack of the cleavage of the ring could be rationalized according to aromaticity and solvation.<sup>PU4</sup>
6. imidazole-2-ylidenes form very strong H-bonds with acids and with water. The latter structure has been indicated by NMR and IR spectroscopies, while the one with acetic acid was identified in the gas phase by photoelectron spectroscopy.<sup>PU3-PU4</sup>
7. In imidazolium-based ionic liquids with moderately basic anions proton transfer may occur. This process yields imidazole-2-ylidenes (or their H-bonded derivatives) in 1,3-dialkylimidazolium salts, and 1,3-dialkyl-2-

methyleneimidazoles in 1,3-dialkyl-2-methylimidazolium salts. This process could be observed by photoelectron- and mass-spectroscopies.<sup>PU3</sup>

8. In case of pyridinium-based ionic liquids the more basic (and more nucleophilic) anions attach to the carbon atom at positions 2 or 4 of the pyridinium ring, rather than deprotonate that.

## 6. Publication Data

### 6.1. Publications Related to the Thesis

- PU1. **Hollóczki, O.**; Nyulászi, L. “Stabilizing the Hammick Intermediate” *J. Org. Chem.* **2008**, *73*, 4794. (IF: 3,952 I: 3)
- PU2. **Hollóczki, O.**; Nyulászi, L. “Stability and Structure of Carbene-Derived Neutral Penta- and Hexacoordinate Silicon Complexes” *Organometallics*, **2009**, *28*, 4159. (IF: 4,204 I: 3)
- PU3. **Hollóczki, O.**; Nyulászi, L.; Gerhard, D.; Massone, K.; Szarvas, L.; Németh, B.; Veszprémi, T. “Carbenes in Ionic Liquids” *New J. Chem. Accepted*. (IF(2009): 3,006)
- PU4. **Hollóczki, O.**; Terleczy, P.; Szieberth, D.; Mourgas, G.; Gudat, D.; Nyulászi, L. “The Hydrolysis of Imidazole-2-ylidenes” *J. Am. Chem. Soc., Submitted* (IF(2009): 8,580)

### 6.2. Other Publications

- PU5. Nyulászi, L.; **Hollóczki, O.**; Lescop, O.; Hissler, M. and Réau, R. “An aromatic–antiaromatic switch in P-heteroles. A Small Change in Delocalisation Makes a Big Reactivity Difference” *Org. and Biomol. Chem.*, **2006**, *4*, 996. (IF: 2,874 I: 10)
- PU6. Aluri, B. R.; Burck, S.; Gudat, D.; Niemeyer, M.; **Hollóczki, O.**; Nyulászi, L.; Jones, P. G.; Heinicke, J. “Ambident PCN<sup>-</sup> Heterocycles: *N*- and *P*-Phosphanylation of Lithium 1,3-Benzazaphospholides” *Chem. Eur. J.* **2009**, *15*, 12263. (IF: 5,382)
- PU7. Heinicke, J.; Aluri, B. R.; Niaz, B.; Bruck, S.; Gudat, D.; Niemeyer, M.; **Hollóczki, O.**; Nyulászi, L.; Jones, P. G. “Ambident Reactivity of P=CH-N-Heterocycles: Lithiation and Substitution Sites”. Phosphorus, Sulfur, and Silicon Re. Elem. Közlésre elfogadva. (IF: 0,586)

### 6.3. Presentations in English

- PR1. 2008.02.10-11. **Hollóczki, O.**; Nyulászi, L. „Mechanistic investigations on the phosphine – phosphine-oxide redox system” 5<sup>th</sup> European Workshop on Phosphorous Chemistry, Regensburg an der Donau, Germany
- PR2. 2008.05.23-24 **Hollóczki, O.**; Nyulászi, L. „Mechanistic investigations on the phosphine – phosphine-oxide redox system” MTA Szervetlen és Fémorganikus munkabizottsági ülése, Pécs

### 6.4. Presentations in Hungarian

- PR3. 2004.11.19. **Hollóczki, O.**; Nyulászi, L. „” MTA Szervetlen és Fémorganikus munkabizottsági ülése, Budapest

- PR4. 2006.04.18. **Hollóczki, O.**; Nyulászi, L. „Hipervalens heterociklusos vegyületek aromaticitása” MTA Kemometriai és Molekulamodellezési Munkabizottságának, és az MKE QSAR és Modellezési Szakcsoportjának előadó ülése, Szeged
- PR5. 2006.09.30. **Hollóczki, O.**; Nyulászi, L. „Hipervalens heterociklusos vegyületek aromaticitása” MTA Szervetlen és Fémorganikus munkabizottsági ülése, Szekszárd
- PR6. 2006.10.03-08. **Hollóczki, O.**; Nyulászi, L. „Hipervalens heterociklusos vegyületek aromaticitása” XII. International Conference on Chemistry, Miercurea Ciuc, Romania
- PR7. 2007.02.07. **Hollóczki, O.**; Nyulászi, L. „A Piridin-2-ilidén stabilizálhatóságának vizsgálata” BME-VBK Oláh György Doktori Iskola Konferenciája
- PR8. 2007.05.07. **Hollóczki, O.**; Nyulászi, L. „Karbénekből származtatható, penta- és hexakoordinált szilíciumvegyületek stabilitása és előállíthatósága” MTA Szervetlen és Fémorganikus munkabizottsági ülése, Budapest
- PR9. 2009.02.04. **Hollóczki, O.**; Terleczy, P.; Szieberth, D.; Nyulászi, L. „Az imidazol-2-ilidén hidrolízise” BME-VBK Oláh György Doktori Iskola Konferenciája
- PR10. 2009.04.29. **Hollóczki, O.**; Terleczy, P.; Szieberth, D.; Nyulászi, L. „Karbének hidrolízise” MTA Kemometriai és Molekulamodellezési Munkabizottságának, és az MKE QSAR és Modellezési Szakcsoportjának előadó ülése, Szeged
- PR11. 2009.05.09 **Hollóczki, O.**; Terleczy, P.; Szieberth, D.; Nyulászi, L. „Karbének hidrolízise” MTA Szervetlen és Fémorganikus munkabizottsági ülése, Mezőkövesd

#### 6.5. *Poster presentations*

- PO1. 2006.06.24-28. **Hollóczki, O.**; Nyulászi, L. „Aromaticity of hypervalent five-membered heterocycles” Third Humboldt Conference on Computational Chemistry, Varna, Bulgaria
- PO2. 2008.02.08. **Hollóczki, O.**; Nyulászi, L. „Karbénekből származtatható magas koordinációjú szilíciumvegyületek stabilitásának vizsgálata” BME-VBK Oláh György Doktori Iskola Konferenciája
- PO3. 2008.09.23-27. **Hollóczki, O.**; Nyulászi, L. „Stability and structure of carbene derived penta- and hexacoordinate silicon compounds” 44<sup>th</sup> Symposium on Theoretical Chemistry, Ramsau am Dachstein, Austria