F. E. Hahn and M. C. Jahnke

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Heterocyclic Carbenes

Heterocyclic Carbenes: Synthesis and Coordination Chemistry

F. Ekkehardt Hahn and Mareike C. Jahnke*

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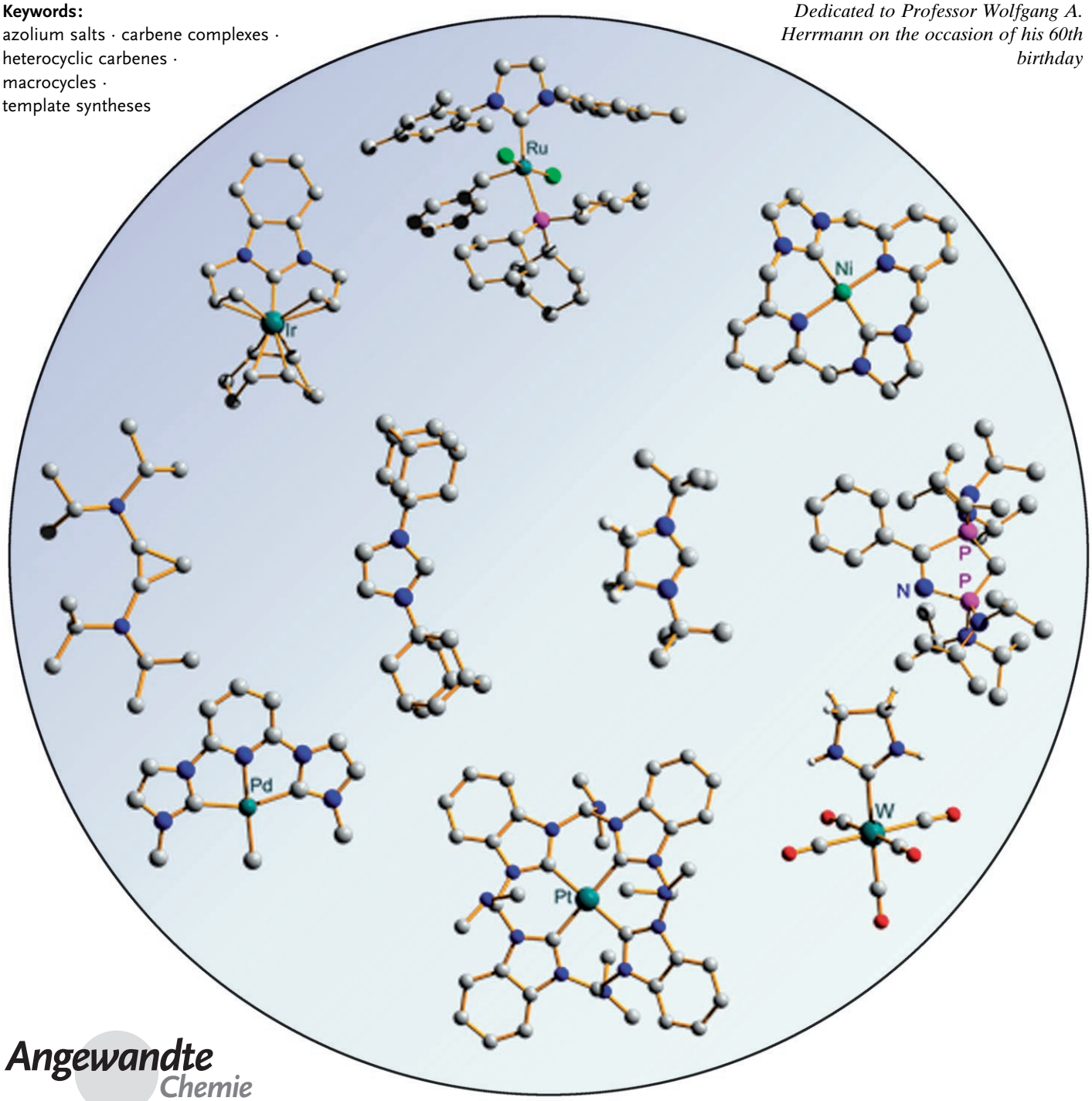
azolium salts · carbene complexes · heterocyclic carbenes · macrocycles · template syntheses

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday



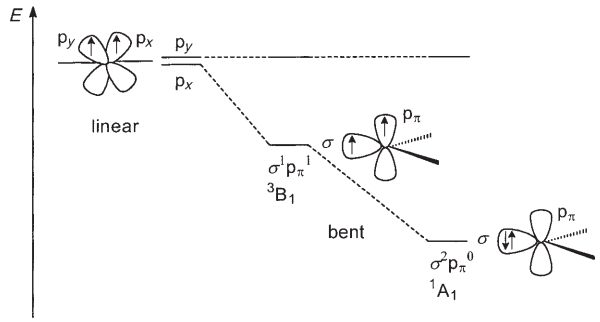
The chemistry of heterocyclic carbenes has experienced a rapid development over the last years. In addition to the imidazolin-2-ylidenes, a large number of cyclic diaminocarbenes with different ring sizes have been described. Aside from diaminocarbenes, P-heterocyclic carbenes, and derivatives with only one, or even no heteroatom within the carbene ring are known. New methods for the synthesis of complexes with N-heterocyclic carbene ligands such as the oxidative addition or the metal atom template controlled cyclization of β-functionalized isocyanides have been developed recently. This review summarizes the new developments regarding the synthesis of N-heterocyclic carbenes and their metal complexes.

From the Contents

1. Introduction

"*Now it will be my next task to prepare methylene or derivatives of it which are free of nitrogen; a number of observations already suggest that such substances can exist…*" wrote J. U. Nef in 1895.[1] Based on today's knowledge, this endeavor appears naive and, as expected, did not meet with success.

Methylene is the simplest conceivable carbene. Carbenes are defined as neutral compounds of divalent carbon where the carbon atom has only six valence electrons. The geometry at the carbene carbon atom can be linear or bent. The linear geometry is based on an sp-hybridized carbene carbon atom which has two energetically degenerated p orbitals (p_x, p_y). This geometry constitutes an extreme case, most carbenes contain an sp^2-hybridized carbon atom and the geometry at the carbene carbon atom is not linear. The energy of one p orbital, conventionally called p_π, practically does not change upon transition from the sp- to the sp^2-hybridization state. The newly formed sp^2-hybrid orbital, normally described as a σ orbital, exhibits partial s character and is thereby energetically stabilized relative to the original p orbital (Scheme 1).



Scheme 1. Frontier orbitals and possible electron configurations for carbene carbon atoms.

The two nonbonding electrons at the sp^2-hybridized carbene carbon atom can occupy the two empty orbitals with a parallel spin orientation. This situation leads to a triplet ground state ($\sigma^1 p_\pi^1$, $^3B_1$ state, Scheme 1). Alternatively, the two electrons occupy the σ orbital with an antiparallel spin orientation leading to the singlet ground state ($\sigma^2 p_\pi^0$, $^1A_1$). An additional, generally less-stable singlet state ($\sigma^0 p_\pi^2$, $^1A_1$) and an excited singlet state with an antiparallel occupation of the p_π and σ orbitals ($\sigma^1 p_\pi^1$, $^1B_1$) are conceivable but of no significance for the discussion herein.

The multiplicity of the ground state determines the properties and the reactivity of a carbene.[2] Singlet carbenes have a filled σ and an empty p_π orbital and therefore show an ambiphilic behavior. Triplet carbenes can be considered as diradicals because of their two unpaired electrons. The multiplicity of the ground state is determined by the relative energies of the σ and p_π orbitals as depicted in Scheme 1. The singlet ground state is observed if there is a large energy difference between the σ orbital and the p_π orbital. Quantum chemical calculations have shown that an energy difference of about 2 eV is required for the stabilization of the singlet ground state ($^1A_1$).[3] An energy difference of less than 1.5 eV between the relative energies of the σ and p_π orbitals favors the triplet ground state ($^3B_1$).[3]

Steric and electronic effects of the substituents at the carbene carbon atom control the multiplicity of the ground state. It is generally accepted that the singlet ground state is stabilized by σ-electron withdrawing, generally more electronegative substituents.[4] This negative inductive effect causes a lowering of the relative energy of the nonbonding σ orbital, while the relative energy of the p_π orbital remains essentially unchanged. Substituents with σ-electron donating properties decrease the energy gap between the σ and the p_π orbital and thus stabilize the triplet ground state.

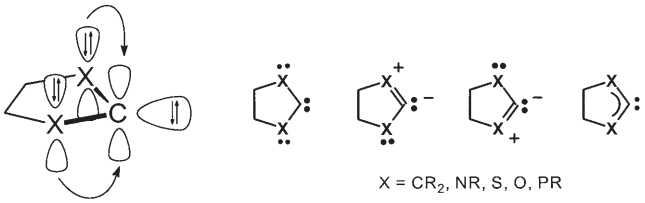
In addition to the inductive effects, mesomeric effects play a crucial role.[3,5] The substituents at the carbene carbon atom are classified into the three categories (X,Z,C): substituents (X) which provide π electrons for the carbene carbon atom, substituents (Z) which withdraw π electrons from the

[*] Prof. Dr. F. E. Hahn, Dr. M. C. Jahnke
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstrasse 30, 48149 Münster (Germany)
Fax: (+49) 251-833-3108
E-mail: fehahn@uni-muenster.de
Homepage:
http://www.uni-muenster.de/chemie.ac/hahn/welcome/html

carbene center, and substituents (C) which are carbon atoms that are part of a conjugated system.[6] The majority of the π-acceptor-substituted carbene centers Z_2C: (for example Z = Li, BH_2, BeH) are in the singlet ground state although they are linear or almost linear.[7] The combination of a π acceptor with a σ donor at the carbene carbon atom XZC: leads to compounds that are almost linear about the carbon atom. Bertrand's almost linear phosphanyl(silyl)carbene $(R_2N)_2P$-C-SiR_3,[8] (phosphanyl)(phosphonio)carbenes,[9] and trifluoroethylidynesulfur trifluoride[10] are among these derivatives.

Some surprisingly persistent triplet carbenes (half-lives of several μs up to 9 min) have been obtained by substitution at the carbene center by two carbon atoms which are part of a conjugated system (alkenes, alkynes, aryl groups). Crucial parameters for stability are the type and steric demand of the substituents (to prevent dimerization to olefins) and their ability to prevent the reaction with elemental oxygen.[11]

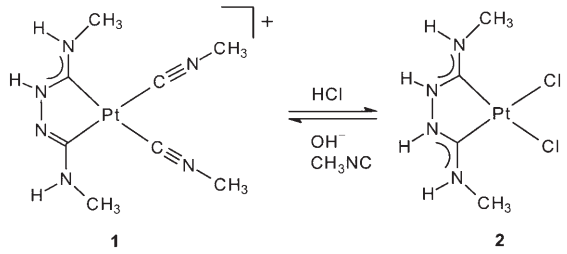
Singlet carbenes which are substituted with two π donors of type X_2C: are strongly bent at the carbene carbon atom. The interaction of the π-electron pairs at the substituents with the p_π orbital at the carbene carbon atom raises the relative energy of the p_π orbital. The relative energy of the σ orbital at the carbene carbon atom is not affected by the π interaction. Consequently, the σ–p_π energy gap becomes larger resulting in a further stabilization of the bent singlet ground state. The interactions of the π electrons of the substituents with the p_π orbital at the carbene carbon atom result in the formation of a four-electron–three-center π system in which the X–C bonds acquire partial multiple bond character (Scheme 2).



Scheme 2. Electronic configuration and resonance structures of heterocyclic five-membered carbenes containing an X_2C: carbene center.

Important members of this class of compounds are the dimethoxycarbenes[12] and the dihalocarbenes.[13] The N-heterocyclic carbenes which form the centerpiece of this review (for a theoretical treatment of N-heterocyclic carbenes with a five-membered carbene ring see reference [14]) contain for geometric and electronic reasons exclusively X_2C: singlet carbene centers (Scheme 2).

Early attempts to prepare stable carbenes always failed[15] or the isolation of the carbenes (for example Cl_2C:)[16] was impossible. However, complexes of X_2C: carbene ligands have been known for decades. The first complex with a heteroatom-stabilized carbene ligand, most likely unrecognized as such, was prepared as early as 1925 by Tschugajeff (the English transcription of his name is Chugaev). Tschugajeff's "red salt" **1** was formed by reaction of tetrakis(methylisocyanide) platinum(II) with hydrazine. The "yellow salt" **2** was obtained upon treatment of **1** with HCl in a reversible reaction (Scheme 3).[17] The molecular structures of **1** and **2**



Scheme 3. Tschugajeff's red (**1**) and yellow (**2**) complexes.

were determined in 1970 providing evidence for the formation of the diaminocarbene complexes.[18] Thus, the synthesis of carbene complexes by the Tschugajeff method was carried out almost 50 years before Fischer's seminal synthesis of heterocarbene complexes starting from metal carbonyl complexes.[19] The Tschugajeff method was recently employed for the preparation of a series of interesting palladium[20a,b] and platinum complexes[20c,d] with dicarbene ligands coordinated to the metal center in a chelating fashion. The intramolecular nucleophilic attack of proton bases at coordinated and therefore activated isocyanides has become a standard method for the preparation of complexes with heterocarbene ligands[21] and will be discussed in detail in Section 3.6.

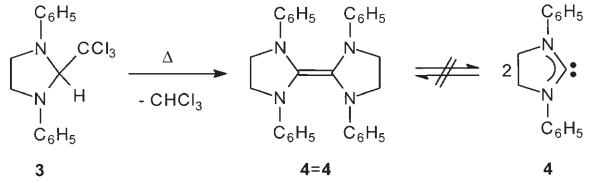
Discussions about N-heterocyclic carbenes were initiated in 1960 by Wanzlick's report about the α-elimination of chloroform from **3**.[22] Wanzlick, however, could never isolate

F. Ekkehardt Hahn, born 1955 in Jena, studied chemistry at the Technische Universität (TU) Berlin (Dipl.-Chem. 1983) and at the University of Oklahoma (M.S. 1982). After receiving a PhD with H. Schumann at the TU Berlin (1985) and a postdoctoral stay (1985–1988) with K. N. Raymond at the University of California, Berkeley, he returned to the TU Berlin (1988–1990) where he completed his habilitation. He was appointed Associate Professor at the Freie Universität Berlin in 1992 and moved to a chair of Inorganic Chemistry at the University of Münster in 1998.

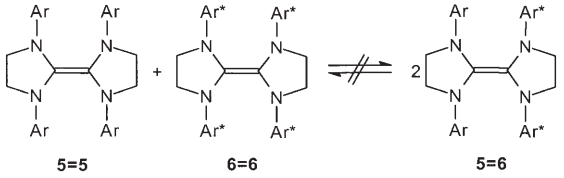
Mareike C. Jahnke, born 1978 in Münster, studied chemistry at the University of Münster (Dipl.-Chem. 2002). After completing her PhD on the preparation and catalytic properties of complexes with benzimidazolin-2-ylidene ligands under the supervision of Prof. F. E. Hahn in 2006, she started postdoctoral research with Prof. K. J. Cavell at the University of Cardiff.

the postulated imidazolidin-2-ylidene **4**, but always obtained its dimer the entetraamine **4=4** (Scheme 4).

Wanzlick's initially postulated cleavage of entetraamines according to **4=4**→2×**4** could not be demonstrated conclusively. Failed cross-metathesis experiments with the differently substituted entetraamines **5=5** and **6=6** excluded an equilibrium between the monomer and the dimer (Scheme 5).[23]

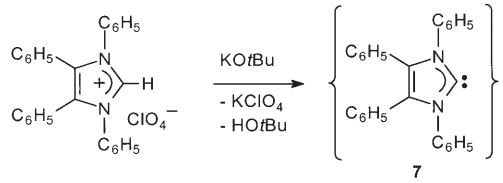


Scheme 4. Synthesis of the entetraamine **4=4** by α-elimination from **3**.



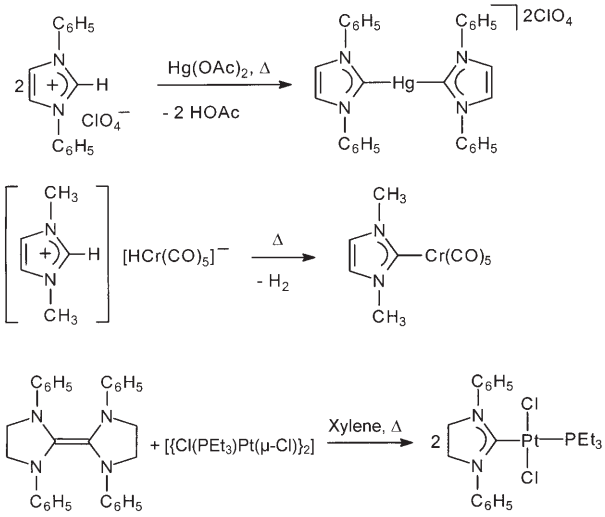
Scheme 5. Cross-metathesis experiments with entetraamines **5=5** and **6=6**.

Around 1960 it was already known that unsaturated heterocyclic azolium cations react in a base-catalyzed H,D-exchange reaction.[24] It was postulated that a delocalization of the six π-electrons in such derivatives helps to stabilize the intermediately formed carbene species. Consequently, Wanzlick attempted to prepare the free carbene **7** by deprotonation of tetraphenylimidazolium perchlorate with KO*t*Bu (Scheme 6). The free carbene could not be isolated. Its intermediate formation was demonstrated indirectly by identification of some of its reaction products with water or $Hg(OAc)_2$.[25] The free carbene **7** was, finally, prepared, isolated, and characterized crystallographically in 1998 by Arduengo et al. using a slightly modified synthetic approach for its preparation.[26]



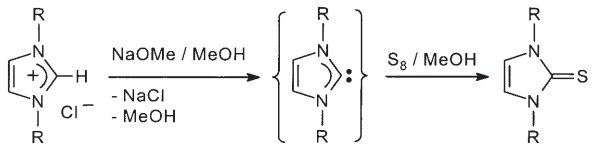
Scheme 6. Attempted synthesis of carbene **7** from tetraphenylimidazolium perchlorate.

Up to this point, all attempts to isolate a stable N-heterocyclic carbene either failed or gave the olefinic entetraamine. The stabilization of unsaturated imidazolin-2-ylidenes in metal complexes, on the other hand, was achieved as early as 1968 by deprotonation of an imidazolium salt in the presence of a suitable coordinatively unsaturated metal complex. Wanzlick treated an imidazolium salt with mercury(II) acetate,[27] and Öfele simply heated dimethylimidazolium hydridopentacarbonylchromate(−II)[28] (Scheme 7). In both cases, a ligand of the metal salt used acted as a base for the deprotonation of the imidazolium salt to the imidazolin-2-ylidene which was then stabilized by coordination to the metal center. Shortly thereafter, the stabilization of the saturated imidazolidin-2-ylidene in a metal complex was described. Lappert et al. treated the electron-rich entetraamines of type **4=4** described by Wanzlick et al. with transition-metal complexes and obtained new complexes with imidazolidin-2-ylidene ligands (Scheme 7).[29]



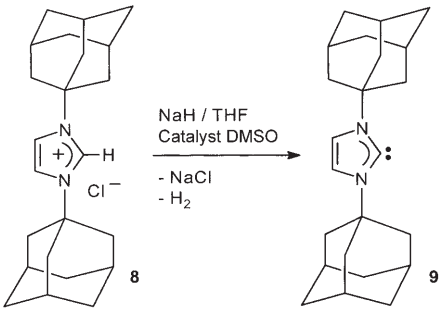
Scheme 7. Complexes with imidazolin-2-ylidene and imidazolidin-2-ylidene ligands.

About 100 years after the search for freely stable carbenes started, Arduengo et al. reached the finish line. The development of cross-linkers for the preparation of water-soluble car coatings required imidazolin-2-thiones, but no suitable synthesis for the preparation of these derivatives on an industrial scale was available. Arduengo et al. attempted to prepare the imidazolin-2-thiones starting from imidazolium salts which were deprotonated and the carbene intermediate was subsequently treated with elemental sulfur. It was assumed that the intermediate imidazolin-2-ylidene was highly reactive and consequently all reactions on a laboratory scale were carried out under a nitrogen atmosphere and under rigid exclusion of air and moisture (Scheme 8). The imidazolin-2-thione was obtained in good yield under these conditions. Furthermore these good yields were reproducible on an industrial scale where the exclusion of air and moisture was less rigid. Arduengo concluded correctly that the intermediate carbene must be much less reactive than originally assumed.[15a]



Scheme 8. Synthesis of imidazolin-2-thiones from imidazolium salts.

Afterwards, Arduengo et al. studied the deprotonation reaction of imidazolium salts in detail initially using the sterically demanding substituted *N*,*N*′-diadamantyl imidazolium salt **8**. Sodium hydride and a catalytic amount of dimethyl sulfoxide were used as base. The by-products hydrogen and sodium chloride were easily separated and a colorless THF solution was obtained which upon concentration yielded a large amount of colorless crystals.[30] An X-ray diffraction analysis of these crystals (mp. 240 °C) showed unambiguously that compound **9**, the first stable N-heterocyclic singlet carbene, had been obtained (Scheme 9).



Scheme 9. Arduengo's synthesis of the first stable N-heterocyclic carbene **9**.

The isolation of compound **9** demonstrated that free carbenes are not invariably reactive, unstable reaction intermediates. It marked the starting point of an intensive search for additional stable carbenes. A large number of N-heterocyclic carbenes (NHCs) and acyclic heteroatom-substituted free carbenes were isolated in the 15 years following the preparation of **9**. Even larger, is the number of complexes with NHC ligands, some of which show remarkable catalytic properties.

Selected aspects of the chemistry of N-heterocyclic carbenes have been reviewed. The first comprehensive description of synthetic methods for the preparation of N-heterocyclic carbenes and their coordination chemistry including rules for the nomenclature of the free carbenes was published by Herrmann and Köcher about 10 years ago.[31] All types of stable carbenes including acyclic derivatives are the subject of a review by Bertrand.[32] Catalytic applications of NHC complexes have been reviewed by Herrmann,[33] Crudden,[34a] Nolan,[34b] and Glorius.[34c] Particularly NHC complex catalyzed C–C cross-coupling reactions[35] and the use of carbene complexes as catalysts in olefin metathesis[36] have been the subject of comprehensive review articles over the last years. The development of catalysts for the olefin metathesis, among them some ruthenium carbene complexes,[37] proved to be an organometallic success story leading the award of the 2005 Nobel Prize to Chauvin,[38] Grubbs,[39] and Schrock.[40] Further reviews deal with reactions of imidazolin-2-ylidenes with main-group elements[41] or with chiral N-heterocyclic carbene ligands.[42] The important aspect of carbene dimerization has been discussed in detail by Alder and co-workers.[43]

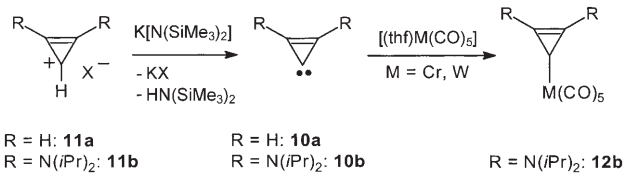
The reviews listed above deal almost exclusively with the properties and complexes of N-heterocyclic carbenes (NHCs) which contain a diamino-stabilized carbene center as part of a five-membered ring. However, today a number of stable carbenes are known which contain a carbene center as part of a larger or smaller heterocycle and diamino substitution has also proved not to be essential for the carbene stabilization. The synthesis of carbene complexes has also been developed further over the last few years. Up to 1991 almost all NHC complexes were prepared by the reaction of azolium salts with suitable transition-metal complexes,[27,28] or by the cleavage reaction of electron-rich entetraamines with transition metals.[29] Free, stable NHC ligands became available in 1991 and since then they could be used directly for the preparation of NHC transition-metal complexes. A number of new methods for the preparation of NHC complexes, such as the carbene transfer from silver NHC complexes or the metal-template-controlled generation of NHC ligands at transition-metal centers have been developed over the last years (see Section 3).

This review deals mainly with new synthetic methods for and the properties of stable heterocyclic carbenes and their metal complexes. Heterocyclic carbenes derived from heterocycles of different sizes and stabilized by various different heteroatoms are presented. In the last few years only one account has briefly summarized new developments in this rapidly expanding area[44] and we thus hope to fill a void.

2. Stable Heterocyclic Carbenes

2.1. Carbenes Derived from Three-Membered Cycles

The simplest singlet carbene derived from a cyclic precursor is cyclopropylidene (**10a**). In spite of the absence of a heteroatom within the ring it will be discussed herein together with its derivative **10b**. Cyclopropylidene (**10a**) was detected by radio astronomical methods in 1985 and has been inferred to be the most abundant cyclic hydrocarbon in interstellar space.[45] It is highly unstable in the condensed phase but can be detected for several hours in a solid argon matrix at 35–40 K.[46] The search for stable cyclopropylidenes was not limited to **10a**. It was known that amine substituents lead to a stabilization of the cyclopropylidenium salt **11b**.[47] Consequently, the deprotonation of the amine-substituted salt **11b** appeared as a promising strategy to obtain a cyclopropylidene, particularly since the carbene **10b**, formed as an intermediate, had previously been trapped and stabilized with metal complex fragments such as $\{PdCl(PR_3)_2\}$,[48a] $\{M(CO)_5\}$ (M = Cr, W, Scheme 10),[48b] or with complexes of type $M[N(SiMe_3)_2]_2$ (M = Ge, Sn, Pb).[49] Bertrand and co-workers



R = H: **11a**
R = N(*i*Pr)$_2$: **11b**

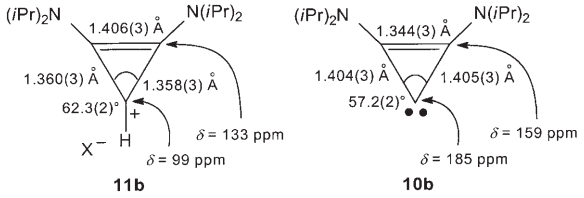
R = H: **10a**
R = N(*i*Pr)$_2$: **10b**

R = N(*i*Pr)$_2$: **12b**

Scheme 10. Synthesis and reactions of cyclopropylidenes.

deprotonated the cyclopropylidenium salt **11b** (X = BPh_4) with K[N(SiMe$_3$)$_2$] at −78 °C in diethyl ether and obtained, after recrystallization of the reaction product from hexane at −20 °C, yellow crystals of the cyclopropylidene **10b**.[50a]

Compound **10b** is air-sensitive but exhibits a remarkable thermal stability (m.p. 107–109 °C). In the ^{13}C NMR spectrum, the resonance signals for the ring carbon atoms are shifted downfield from $\delta = 99$ and 133 ppm for **11b** to $\delta = 185$ and 159 ppm for **10b** (Scheme 11). In the ^{1}H spectrum, two



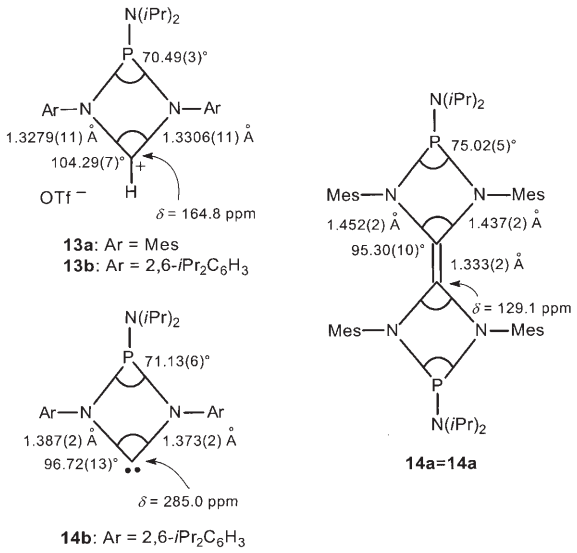
Scheme 11. Spectroscopic and molecular parameters of **11b** and **10b**.

sets of resonances were observed for the *i*Pr protons, which is consistent with a hindered rotation about the C_{ring}–N bonds, and was taken as indication for a π-donor interaction of the amine groups with the electron-deficient three-membered ring. This assumption is corroborated by the single-crystal X-ray analysis. The three-membered ring and the nitrogen atoms are arranged in a coplanar fashion both in **11b** and **10b** (Scheme 11). Since then the lithium adduct of **10b**, known as the Weiss–Yoshida reagent,[50b–e] has been isolated and crystallographically characterized.[50f]

2.2. Carbenes Derived from Four-Membered Heterocycles

The first heterocyclic carbene based on a four-membered heterocycle was described in 2004.[51] Attempts to deprotonate the iminium salt **13a** with KO*t*Bu, however, led to opening of the endocyclic P–N bond by nucleophilic attack at the phosphorus atom. Deprotonation of **13a** is possible with sterically more hindered, less nucleophilic bases, such as LiMes (Mes = mesityl) or K[N(SiMe$_3$)$_2$]. However, not the monomer, but the carbene dimer **14a**=**14a** was isolated from this reaction. Deprotonation of the iminium salt **13b** which has even bulkier substituents finally allowed the isolation of carbene **14b** with a four-membered heterocycle (Scheme 12).

Surprisingly, carbene **14b** exhibits no C_2 symmetry in the solid state. Two different $C_{carbene}$-N-C_{Ar} angles were observed. As expected, the endocyclic N–C bonds are short, but the nitrogen atoms are not perfectly planarized (sum of angles



Scheme 12. NMR-spectroscopic and molecular parameters for **13a**, **14a**=**14a**, and **14b**.

355.1° and 348.2°) which prevents an optimal stabilization of the carbene center. The drastic downfield shift of the resonance signal for the carbene carbon atom ($\delta = 285$ ppm, $^{2}J_{CP} = 13$ Hz) is remarkable.

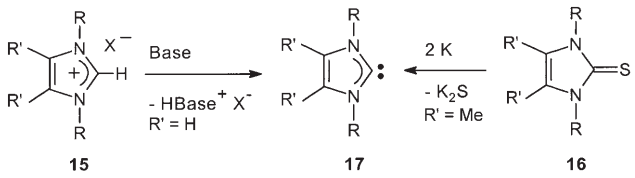
2.3. Carbenes Derived from Five-Membered Heterocycles

Most of the stable heterocyclic carbenes are derived from five-membered heterocycles with nitrogen, sulfur, or phosphorus present as heteroatoms. Stable carbenes with one up to four heteroatoms and saturated or unsaturated five-membered heterocycles are discussed in the following Sections.

2.3.1. Imidazolin-2-ylidenes

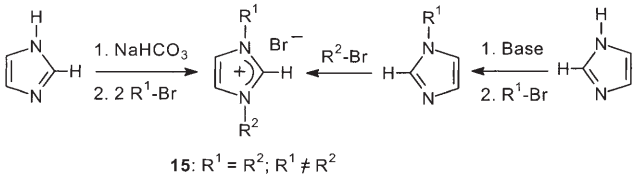
The unsaturated imidazolin-2-ylidenes probably constitute the largest group of stable heterocyclic carbenes. The first isolated stable N-heterocyclic carbene **9**[30] belongs also to this group. As early as 1970, Wanzlick had probably prepared the tetraphenylimidazolin-2-ylidene (**7**; Scheme 6). He was not able to isolate the free carbene but demonstrated its formation by quenching reactions.[25] Today a large number of differently substituted imidazolin-2-ylidenes of type **17** are known. In general they are obtained by deprotonation of imidazolium salts **15** or by reductive desulfurization of imidazolin-2-thiones **16** (Scheme 13).

Imidazolium salts of type **15** can be prepared by two different routes by 1) nucleophilic substitution at the nitrogen atoms of the imidazole or 2) multicomponent reactions for the generation of the N,N′-substituted heterocycle. The direct substitution of the nitrogen atoms of imidazole is initiated with the deprotonation of the nitrogen atom of the heterocycle. The resulting salt reacts with numerous alkyl halides under alkylation of the N^{1}-position.[52] The second alkylation



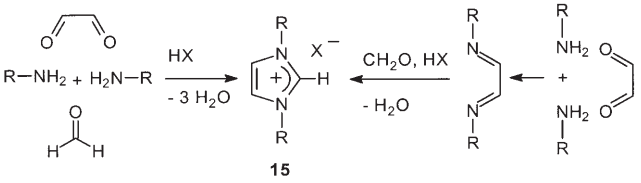
Scheme 13. Synthesis of imidazolin-2-ylidenes of type **17**.

resulting in the *N*,*N*′-dialkylimidazolium salt **15** proceeds by reaction with a second equivalent of an alkyl halide.[53] In general, this method is limited to the introduction of primary alkyl substituents, although some methods for the substitution of imidazole nitrogen atoms with aryl groups have been described.[54] The introduction of two different substituents proceeds in a stepwise alkylation whereas a symmetric substitution of both ring nitrogen atoms can be achieved in a one-pot synthesis in the presence of a suitable base (Scheme 14).[55]



Scheme 14. Symmetrically and unsymmetrically N,N′-substituted imidazolium salts.

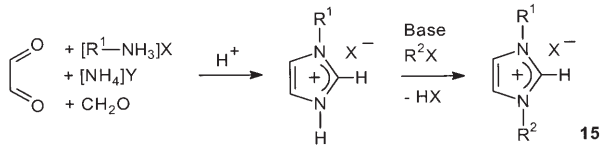
The multicomponent reaction of primary amines, glyoxal, and formaldehyde in the presence of a Brønsted acid has been developed for the introduction of reactive N,N′-substituents (Scheme 15).[56] This flexible reaction gives access to a



Scheme 15. Synthesis of imidazolium salts by multicomponent reactions.

multitude of symmetrically N,N′-substituted imidazolium salts. The initial condensation product between the primary amine and glyoxal can be isolated before the cyclization with formaldehyde. This allows the preparation of imidazolium salts with unusual or sterically very demanding nitrogen substituents (R = ferrocenyl[57a] or 2,6-*i*Pr$_2$C$_6$H$_3$[57b]).

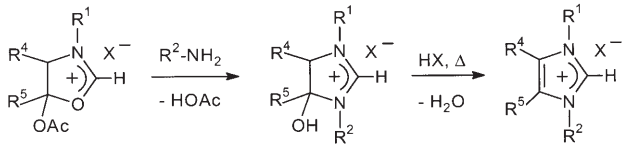
Unsymmetrically N,N′-substituted imidazolium salts can be obtained by combining a multicomponent cyclization with an N-alkylation reaction (Scheme 16).[58] An initial multicomponent cyclization at pH 1 yields an *N*-alkylimidazolium salt which is subsequently alkylated at the second ring



Scheme 16. Combination of multicomponent cyclization and N-alkylation.

nitrogen atom to give the unsymmetrically substituted derivative.

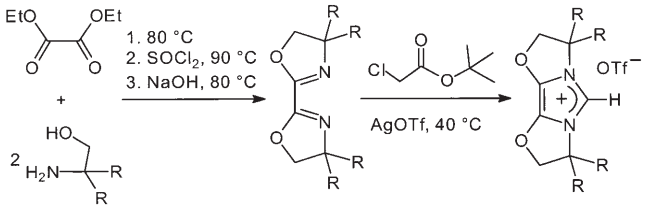
Imidazolium salts with unusual and previously inaccessible substitution patterns (e.g. derivatives with two different aryl substituents) were recently introduced by Fürstner et al. (Scheme 17).[59a] Initially, a suitable, substituted oxazolium



Scheme 17. Synthesis of imidazolium salts by heterocycle interconversion from oxazolinium salts.

salt was synthesized. With this salt a heterocycle interconversion strategy was followed in analogy to the low-yield conversion of 1,3,4-oxadiazolium precursors into *N*-aryltriazolium salts.[59b] The exchange of the oxygen atom in the oxazole heterocycle was achieved by the reaction with a primary amine. The resulting imidazolidinium salt eliminates water upon heating in an acid-catalyzed reaction to give of an unsymmetrically substituted imidazolium salt of type **15**.

Glorius and co-workers described imidazolium salts derived from bisoxazolines.[60] Their preparation starts with the synthesis of a bisoxazoline diimine from an amino alcohol and diethyl oxalate (Scheme 18). Standard methods for the

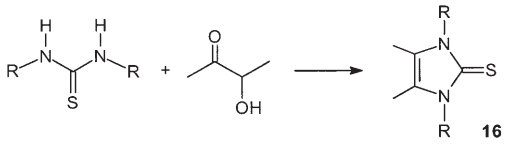


Scheme 18. Synthesis of bisoxazoline derived imidazolium salts.

ring-closing reaction of diimines to imidazolium salt failed in this case. However, the bisoxazoline-substituted imidazolium salt could be obtained in good yield by reaction of the bisoxazoline diimine with silver triflate/chloromethyl pivalate. The imidazolium salt can be deprotonated at the C^2-position to give an N-heterocyclic carbene ligand with "flexible steric demand".

Kuhn et al. described a method for the preparation of imidazolin-2-thiones **16** in 1993, which has become a standard

procedure for the preparation of such compounds (Scheme 19).[61] The cyclic thioureas are obtained in good yield by the condensation reaction of α-hydroxyketones, such as 3-hydroxy-2-butanone, with suitably N,N′-substituted thiourea derivatives.



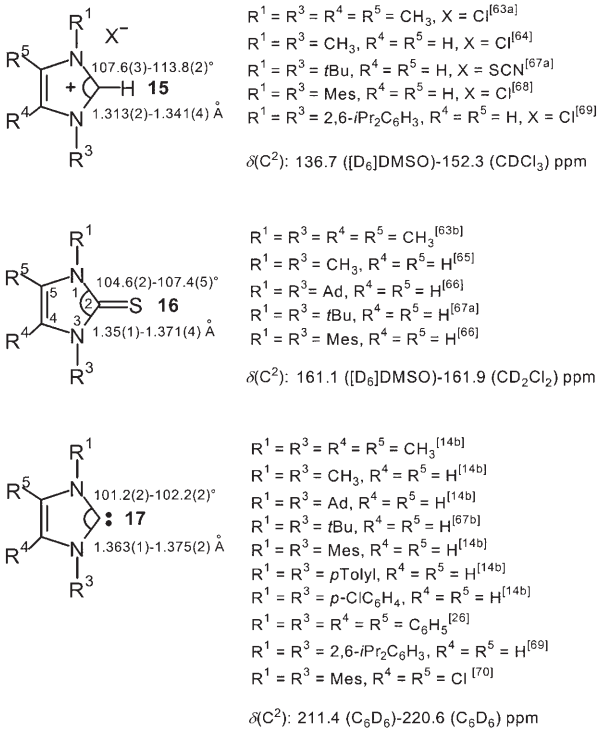
Scheme 19. Synthesis of imidazolin-2-thiones **16**.

Free and stable imidazolin-2-ylidenes of type **17** can be prepared from imidazolium salts **15** as well as from imidazolin-2-thiones **16** (Scheme 13). The first method requires that the proton at the C^2 carbon atom can be removed by a base. Bases such as NaH, KO*t*Bu, or deprotonated DMSO, have been employed successfully in THF for this reaction. Some imidazolium salts with acidic substituents require the use of sterically demanding bases, such as potassium hexamethyldisilazide (KHMDS), for a selective deprotonation of the C^2 carbon atom of the heterocycle. KH and NaH are insoluble in THF so their use requires the presence of a catalytic amount of KO*t*Bu or deprotonated DMSO to reach an acceptable reaction rate (Scheme 9).[30] Alternatively, a stoichiometric amount of KO*t*Bu can be used which, however, leads to the formation of *t*BuOH that is less volatile than hydrogen. An intelligent alternative to the procedures described above is the ammonia method proposed by Herrmann et al. in 1996.[62] In this procedure the imidazolium salt is dissolved or suspended in a mixture (5:1, v/v) of liquid ammonia and an aprotic polar solvent, such as THF. The deprotonation is initiated by addition of NaH and proceeds, depending on the imidazolium salt used, at temperatures between −80 °C and −30 °C within minutes. Important advantages of this method are the short reaction time, the low reaction temperatures, the high yields, and the straight forward isolation of the free carbene.

Imidazolin-2-thiones **16** are reduced to the free carbenes **17** within 4 h by potassium in boiling THF (Scheme 13). The thermal sensitivity of the free carbenes in solution, which depends strongly on the N,N′-substitution pattern, can develop into a problem under these reaction conditions. Similar problems have been observed for the deprotonation reaction **15**→**17**, again depending on the N,N′-substitution pattern.

Both N-aryl and N-alkyl substituted imidazolin-2-ylidenes are normally obtained as colorless, diamagnetic, crystalline solids which show remarkably high melting points. An exception is the *N,N′*-dimethylimidazolin-2-ylidene which was isolated as a colorless liquid. The imidazolin-2-ylidenes are stable under an inert gas atmosphere at −30 °C for months. Decomposition in solution at 50 °C takes several hours. The 1,3-dimesityl-4,5-dichloroimidazolin-2-ylidene, which was obtained by chlorination of 1,3-dimesitylimidazolin-2-ylidene with CCl_4, is even stable in air for some days at ambient temperature.[70]

Structural and ^{13}C NMR spectroscopic parameters for selected imidazolium salts **15**, imidazolin-2-thiones **16**, and imidazolin-2-ylidenes **17** are summarized in Scheme 20. For-



Scheme 20. Structural and spectroscopic parameters of selected compounds of types **15**–**17**.

mation of the carbenes is indicated by a significant downfield shift of the resonance for the C^2 carbon atom at $\delta = 210$–220 ppm relative to the C^2 resonances for imidazolium salts **15** or imidazolin-2-thiones **16**. A stabilization of the carbene center by sterically demanding N,N′-diadamantyl substituents is not necessary because even the sterically undemanding N,N′-dimethyl substituents lead to a stable imidazolin-2-ylidene. Clearly thermodynamic factors (electronic structure) contribute mostly to the stabilization of imidazolin-2-ylidenes while kinetic factors (steric protection of the carbene carbon atom) are less important.

The singlet ground state at the carbene carbon atom is stabilized by σ-electron withdrawing, that is, more-electronegative substituents.[4] Mesomeric effects play, next to the inductive ones, an important role in the stabilization of the ground state.[3–5] The relative energy of the p_π orbital at the carbene carbon atom increases through its interaction with the π-electron pairs at the nitrogen atoms (Scheme 2). This interaction leaves the relative energy of the σ orbital at the carbene carbon atom practically unchanged thus increasing the σ–p_π energy gap (Scheme 1) and further stabilizing the singlet ground state. The interaction of the π electrons of the substituents with the p_π orbital at the carbene carbon atom

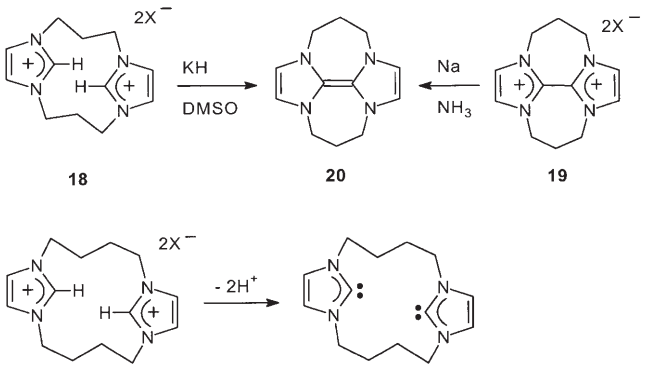
leads to the formation of a four-electron three-center π system in which the N–$C_{carbene}$ bonds acquire partial multiple-bond character.

The bond angles N^1-C^2-N^3 for the imidazolin-2-ylidenes listed in Scheme 20 fall in the narrow range of 101.5(2)–102.2(2)°. They are significantly smaller than in the parent imidazolium salts and match well the calculated N^1-C^2-N^3 angles for $^1A_1$ carbenes ($\sigma^2p_\pi^0$, Scheme 1).[4b] An expansion of the C^2–N^1(N^3) bond lengths of about 0.05 Å is observed upon deprotonation of the imidazolium salts to the free carbenes indicating less π delocalization in the imidazolin-2-ylidenes than in the imidazolium cations.

Arduengo et al. noted as early as 1991 that the unsaturated imidazolin-2-ylidenes of type **17** do not dimerize to give electron-rich tetraazafulvanes. Wanzlick, on the other hand, failed to isolate the stable saturated N-heterocyclic carbene **4** (Scheme 4) and instead always obtained the dimer **4**=**4** of the saturated imidazolidin-2-ylidenes. These reactivity differences are caused by differences in the stabilization of the $^1A_1$ singlet ground state by inductive and mesomeric effects which appear to be more pronounced for the unsaturated imidazolin-2-ylidenes than for the saturated imidazolidin-2-ylidenes.[43] This assumption is corroborated by quantum chemical calculations[14a,71,72c] which show that the energy gap between the singlet and triplet states amounts to about 85 kcal mol^{-1} for unsaturated imidazolin-2-ylidenes but only to 69 kcal mol^{-1} for the saturated imidazolidin-2-ylidenes. The larger singlet–triplet gap for the unsaturated heterocycles is possibly also caused by the aromaticity of the imidazolin-2-ylidenes (6 π electrons) although this is normally not considered a crucial factor for carbene stabilization.[14c,d]

Based on the quantum chemical calculations the strength of the C=C bond which would result from the dimerization of two unsaturated imidazolin-2-ylidenes was estimated to be approximately 2 kcal mol^{-1}.[72] This estimate is based on the model by Carter and Goddard.[73] According to the Carter and Goddard formulation, the strength of the central C=C bond in a dimer of two imidazolin-2-ylidenes should correspond to that of a canonical C=C bond (normally that of ethylene, 172 kcal mol^{-1}) minus the sum of the singlet–triplet energy difference for the two carbenes involved. For a tetraazafulvalene (the dimer of two imidazolin-2-ylidenes) a bond strength of $[172-(2\times85)] \approx 2$ kcal mol^{-1} would thus be expected. The significantly smaller singlet–triplet gap for the saturated imidazolidin-2-ylidene[71] should therefore energetically favor the dimerization under formation of C=C double bonds, if kinetic factors are disregarded. This behavior has been experimentally confirmed (see Section 2.3.2).

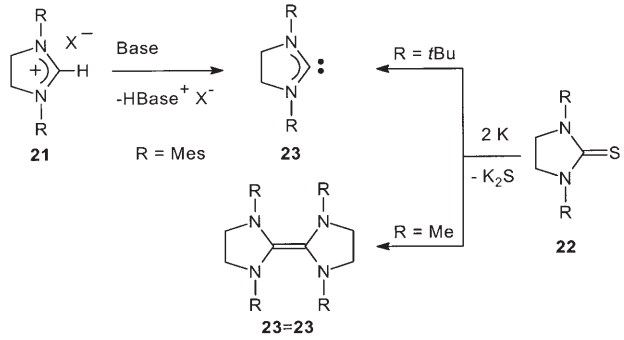
Convincing experimental evidence for the weakness of the C=C double bond in tetraazafulvalenes was presented by Taton and Chen (Scheme 21).[72a] Both, the deprotonation of the doubly propylene-bridged diimidazolium salt **18** as well as the two-electron reduction of the diimidazolium derivative **19**[72b] gave the doubly bridged tetraazafulvalene **20** with a true C=C double bond (*d*(C=C) 1.337(5) Å). Deprotonation of the doubly butylene-bridged analogue, however, always led to the bis(imidazolin-2-ylidene). A similar behavior has been observed for singly bridged diimidazolium salts and unbridged imidazolium salts.



Scheme 21. Attempted syntheses of tetraazafulvalenes.

2.3.2. *Imidazolidin-2-ylidenes*

Wanzlick et al. were the first to attempt the preparation of saturated imidazolidin-2-ylidenes by an α-elimination of chloroform from imidazolidine derivatives (Scheme 4).[22] They obtained exclusively the electron-rich entetraamines. Considering the smaller single–triplet energy gap relative to the imidazolin-2-ylidenes, today the preferred formation of these dimers of N-heterocyclic carbenes is not surprising anymore.[73] It was again Arduengo et al. who presented the first stable crystalline imidazolidin-2-ylidene (R = Mes) **23** which was obtained by deprotonation of the imidazolidinium salt **21** (Scheme 22).[74]



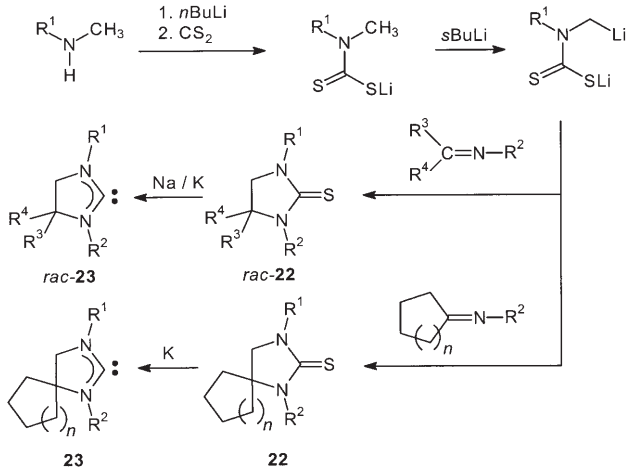
Scheme 22. Synthesis of imidazolidin-2-ylidenes **23** and entetraamines **23**=**23**.

Denk et al. described the reductive desulfurization of imidazolidin-2-thione **22** with potassium in boiling THF as an alternative method for the preparation of stable imidazolidin-2-ylidenes.[75] This method had been previously employed successfully for the preparation of imidazolin-2-ylidenes.[61a] The reductive desulfurization of an imidazolidin-2-thione with sterically demanding N,N′-substituents (such as, R = *t*Bu) resulted in the formation of the stable carbene **23** while the derivative with the sterically less-demanding methyl substituents reacted in the reductive desulfurization to give the entetraamine **23**=**23** (Scheme 22).[75] From these data it is clear that the kinetic stabilization of the carbene center by sterically demanding N,N′-substituents is much more impor-

tant for the saturated imidazolidin-2-ylidenes of type **23** than for the unsaturated imidazolin-2-ylidenes of type **17**.

Symmetrically substituted imidazolidinium salts **21** are obtained by N,N′-alkylation of dihydroimidazole or by cyclization of *N*,*N*′-dialkylethylenediamines with orthoesters.[76] This method was used to prepare the precursor for 1,3-bis(*N*,*N*′-dialkylamino)imidazolidin-2-ylidene[76b] and an acenaphthylene-annulated imidazolidinium salt.[76c] A similar reaction sequence was used for the preparation of thiones **22** from *N*,*N*′-dialkylethylenediamines and CS_2.[77]

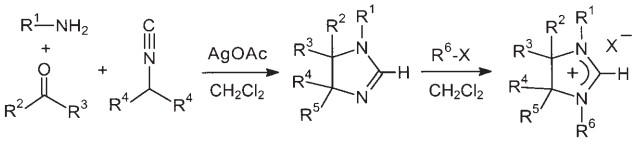
Over the last years some new methods for the preparation of unsymmetrically substituted imidazolidin-2-thiones have emerged. The racemic compounds *rac*-**22**[78a] as well as spirocyclic compounds of type **22**[78b] were obtained by the reaction of lithium-*N*-lithiomethyldithiocarbamates with aldimines and ketimines, respectively (Scheme 23). The use of an



Scheme 23. Synthesis of unsymmetrically substituted imidazolidin-2-thiones **22** and -ylidenes **23**.

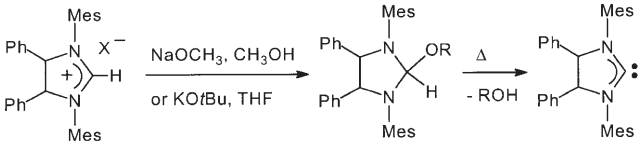
aldimine ($R^4 = H$) or of an unsymmetrically substituted ketimine ($R^3 \neq R^4$) leads to the formation of heterocycles with a chiral center, and the thione is obtained as a racemate. To avoid the racemate formation, ketimines derived from cyclic ketones were subsequently used. These react under formation of a spiro center at the heterocycle. The imidazolidin-2-thiones which were obtained by these reactions undergo reductive desulfurization with potassium or a potassium/sodium alloy under formation of the imidazolidin-2-ylidenes of types *rac*-**23** and **23**. The substituents R^1 (originating from the secondary amine used for the preparation of the lithium-*N*-lithiomethyldithiocarbamates) and R^2 (originating from the primary amine used for the preparation of the aldimines or ketimines) can be varied over a wide range, thus giving access to a large number of differently substituted imidazolidin-2-ylidenes. In addition, the use of different cyclic ketones for the preparation of the ketimines allows the preparation of spirocyclic systems with differently sized rings.

Another interesting method for the preparation of unsymmetrically substituted imidazolidines has been developed by Orru and co-workers.[79] This multicomponent reaction[80] is particularly suitable for the introduction of substituents at the C^4 and C^5 carbon atoms of the imidazolidine heterocycle. A primary amine, an aldehyde or ketone, and an isocyanide with an acidic α-proton are allowed to react. The method is only limited by the reactivity of the isocyanide used. With selected C^4 substituents (*p*-nitrophenyl isocyanide) the initial reaction product is not stable but is rapidly oxidized to the imidazole. The reaction of less-reactive ketones is enabled by catalysis with silver acetate. All the synthesized imidazolidines were converted into the imidazolidinium salts by standard methods (Scheme 24).[79c]



Scheme 24. Synthesis of unsymmetrically substituted imidazolidinium salts.

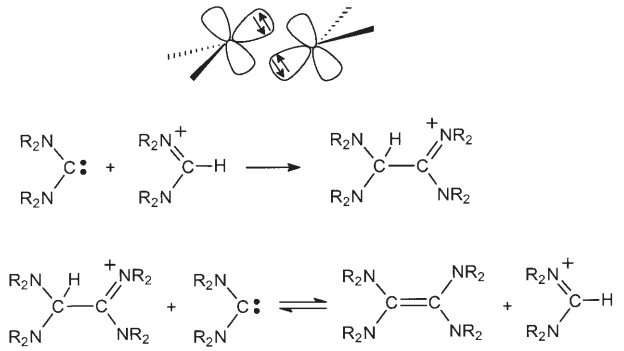
It has been reported that certain imidazolidinium salts of type **21** with particularly bulky N,N′-substituents are not easily deprotonated with the strong base NaH. In such cases the reaction of the imidazolidinium salt with NaOMe or KO*t*Bu to give the 2-alkoxyimidazolidines **24** proved helpful. Compounds of type **24** react upon heating (60–80 °C) under elimination of alcohols to the free carbenes **23** (Scheme 25).[81a] A variation of this method proceeding under α-elimination of fluoroaryls from 2-(fluorophenyl)imidazolidines has also been described.[81b,c]



Scheme 25. Synthesis of imidazolidin-2-ylidenes by thermal α-elimination.

The isolation of the imidazolidin-2-ylidenes **23** clearly demonstrates that an aromatic 6π-electron system is not required for the stabilization of an N-heterocyclic diaminocarbene. The stabilization of the singlet carbene center in these derivatives is based on the inductive (−I) effect and the mesomeric (+M) effect which causes N^1-C^2-N^3 π delocalization. The smaller energy gap between the singlet and triplet states relative to the imidazolin-2-ylidenes of type **17**, however, often leads to the dimerization of the imidazolidin-2-ylidenes **23** to give entetraamines of type **23**=**23** if this process is not inhibited by kinetic factors, such as the introduction of sterically demanding substituents on the nitrogen atoms.

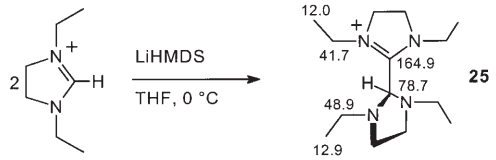
Alder and co-workers have studied the dimerization of acyclic diaminocarbenes.[43] It was found that the classical dimerization mechanism for a singlet carbene in which the filled sp^2 orbital of each carbene interacts with the formally empty p_π orbital of the other (Scheme 26, top) is probably



Scheme 26. Direct (top) and proton-catalyzed dimerization (bottom) of diaminocarbenes.

extremely rare and remains to be established experimentally. Alternatively, a proton-catalyzed dimerization can be envisaged (Scheme 26, bottom) where a formamidinium ion and a free carbene coexist. This situation can be expected to occur during the deprotonation of formamidinium salts. The dimerization is further influenced by factors such as the N^1-C^2-N^3 angle at the carbene carbon atom (size of carbene ring for N-heterocyclic carbenes), the basicity of the carbene carbon atom, and the steric influence of the substituents at the nitrogen atoms. Deprotonation of imidazolidinium salts with bulky substituents (R = Mes,[74] *t*Bu[75]) leads to stable monomeric carbenes. For imidazolidinium salts with sterically less demanding N,N′-substituents the proton-catalyzed formation of the electron-rich entetraamines occurs.[75]

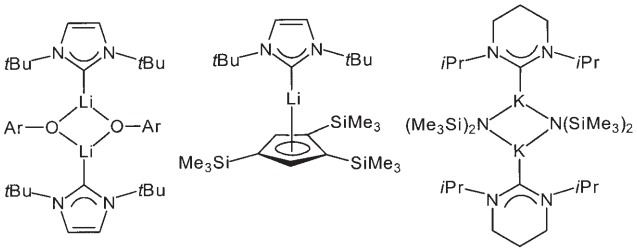
Alder et al. were able to isolate and characterize spectroscopically a protonated dimer **25** from the reaction of *N*,*N*′-diethylimidazolidinium hexafluorophosphate with 0.5 equivalents of lithium bis(trimethylsilyl)amide (LiHMDS) (Scheme 27).[43] In the ^{13}C NMR spectrum they observed, as



Scheme 27. Formation of the protonated dimer **25** and selected ^{13}C NMR spectroscopic parameters (δ [ppm] in CD_2Cl_2).

expected, two different resonance signals for the carbon atoms of the C–C bond (δ = 164.9 and 78.7 ppm) in addition to different resonances for the N-ethyl substituents of the two heterocycles. DFT calculations confirmed that the two heterocycles are orientated more or less mutually perpendicular which is a typical conformation for a C^2-protonated tetraaminoethylene derivative.

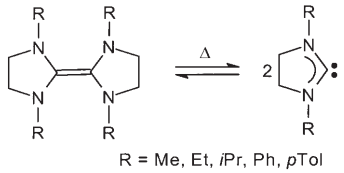
Probably not only protons but also other Lewis acids such as alkali-metal ions are able to catalyze the dimerization of imidazolidin-2-ylidenes. Carbene lithium adducts have been described for cyclopropylidene[50b–f] and some imidazolin-2-ylidenes (Scheme 28)[82] while a carbene potassium adduct is



Scheme 28. Alkali-metal adducts of some N-heterocyclic carbenes.

known for an N-heterocyclic carbene with a six-membered carbene ring[83] (see Section 2.4 and Scheme 28). The interactions between the alkali metal and the carbene center are weak and the bond lengths within the heterocycle change only marginally upon adduct formation whereas significant changes in these parameters are observed upon formation of carbene transition-metal complexes. Even the observed weak interaction of alkali-metal ions with the carbene center could, however, be sufficient to catalyze the dimerization reaction of saturated imidazolidin-2-ylidenes.

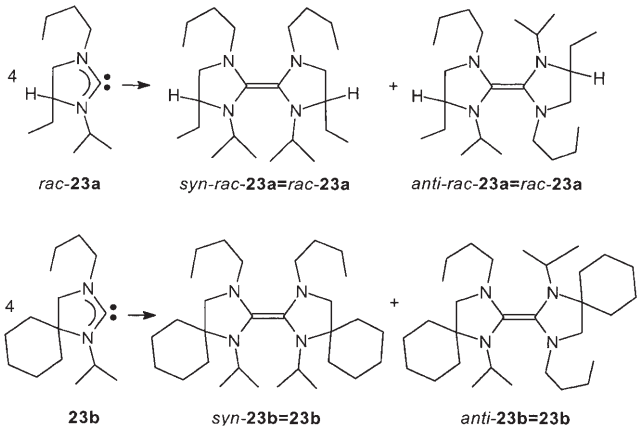
In this context the question of an equilibrium between an imidazolidin-2-ylidene and its entetraamine, postulated by Wanzlick et al., can be posed again (Scheme 4).[22] Contrary to Wanzlick, today we know there are some stable imidazolidin-2-ylidenes with bulky N,N′-substituents (R = Mes,[74] *t*Bu[75]). Imidazolidin-2-ylidenes with sterically less demanding N,N′-substituents, on the other hand, dimerize to the electron-rich entetraamines, in a process that is most likely proton-catalyzed as depicted in Scheme 26.[43] The formation of an equilibrium between the carbene and its entetraamine dimer has been ruled out based on cross-metathesis experiments more than 40 years ago (Scheme 5).[23] Denk et al. have reported an equilibrium between entetraamine and imidazolidin-2-ylidene (Scheme 29) at 150 °C which, however, can also be rationalized by a [2+2]-cycloaddition/[2+2]-cycloreversion mechanism.[84] Subsequent studies by Lemal and Liu showed that no equilibrium exists if the reaction is carried out in the presence of potassium hydride, which prevents proton catalysis.[85] It was concluded that the formation of the equilibrium observed by Denk et al. was most likely caused by



Scheme 29. Postulated equilibrium between entetraamine and imidazolidin-2-ylidene.

traces of an electrophilic contamination in the reaction mixture.

Both, stable imidazolidin-2-ylidenes as well as the entetraamines formed from them can be observed depending on the steric demand of the N,N′-substituents. It was therefore attempted to vary the steric demand of the N,N′-substituents in a way that the carbene and its dimeric entetraamine can coexist. For this purpose unsymmetrically substituted imidazolidin-2-ylidenes, such as *rac*-**23a** and **23b**,**c** (Scheme 30, Figure 1) were developed.[78,86] The carbene *rac*-**23a** ($\delta(C^2)=$



Scheme 30. Dimerization of unsymmetrically substituted imidazolidin-2-ylidenes.

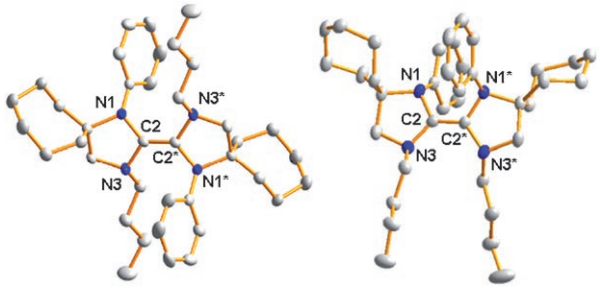
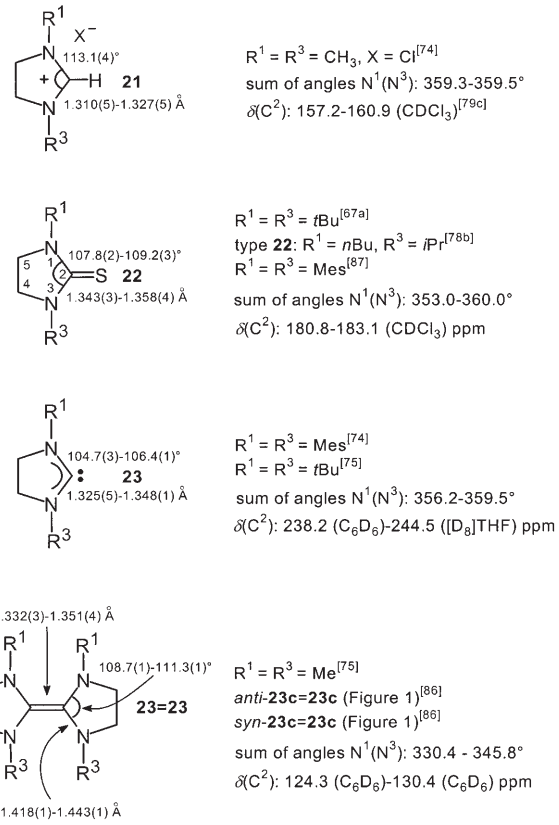


Figure 1. Molecular structures of *anti*-**23c**=**23c** and *syn*-**23c**=**23c**.

238 ppm in [D_8]THF) dimerizes only slowly over several weeks to give the entetraamine *rac*-**23a**=*rac*-**23a** (four resonances in the range $\delta(C^2)=126$–128 ppm for the *syn*- and *anti*-isomers, Scheme 30) and both species can be detected simultaneously by NMR spectroscopy during this period.[78a] Similar observations have been made for **23b** (carbene: $\delta(C^2)=236.0$ ppm, *syn*- and *anti*-entetraamine dimer: $\delta(C^2)=130.0$ and 128.6 ppm in [D_8]THF).[78b] If a THF solution of **23b** is prepared under rigorous exclusion of moisture and stored over a sodium/potassium alloy under argon, no dimerization was observed even after several weeks. This result was taken as another indication of a proton-catalyzed mechanism for the dimerization process.

The formation of *syn*- and *anti*-dimers was demonstrated for **23c**=**23c** by X-ray diffraction studies for both compounds (Figure 1).[86] DEPT NMR experiments allowed the assignment of the resonances for the C^2 carbon atoms for the *syn*- ($\delta=129.2$ ppm) and *anti*-isomers ($\delta=130.4$ ppm). As expected, the *anti*-isomer is formed as the main product during the reduction of the parent imidazolidin-2-thione (about 80%).

Structure data of saturated imidazolidin-2-ylidenes of type **23** (Scheme 31) show some differences to the unsatu-



Scheme 31. Structural and spectroscopic parameters for selected compounds of types **21**–**23**, and **23**=**23**.

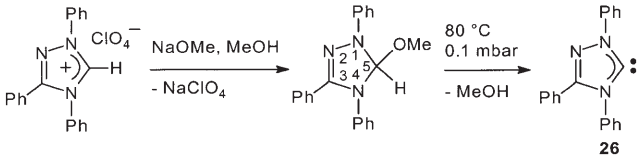
rated imidazolin-2-ylidenes of type **17** (Scheme 20). The N^1-C^2-N^3 angles of the imidazolidin-2-ylidenes (104.7(3)°, 106.4(1)°) are significantly enlarged in comparison to the unsaturated derivatives (101–102°). However, the N^1-C^2-N^3 angle becomes smaller upon carbene formation in comparison to the imidazolidinium salts or the imidazolidin-2-thiones. Deprotonation of imidazolidinium salts to imidazolidin-2-ylidenes causes only a small enlargement of the N–C^2 bond lengths, a behavior which is consistent with the observations made for unsaturated imidazolin-2-ylidenes. The nitrogen atoms in the imidazolidin-2-ylidenes of type **23** are essentially in a trigonal-planar environment. The five-membered heterocycle in carbenes of type **23** is not planar which is in contrast to the five-membered ring in the unsaturated imidazolin-2-ylidenes of type **17**.

The formation of imidazolidin-2-ylidenes can be detected by NMR spectroscopy. Carbene formation causes a significant downfield shift to $\delta\approx240$ ppm for the resonance for the C^2 carbon atom compared to imidazolidinium salts **21** and

imidazolidin-2-thiones **22**. Relative to imidazolin-2-ylidenes, a downfield shift of $\Delta\delta \approx 25$ ppm is observed for the C^2 carbon atom in imidazolidin-2-ylidenes. These shifts match the expectations and previous calculations of the chemical-shielding tensor for N-heterocyclic carbenes.[88] The dimerization of imidazolidin-2-ylidenes is also clearly detected in the ^{13}C NMR spectra and leads to an upfield shift of the resonance of the C^2 atom ($\delta \approx 130$ ppm). Both the C^2–N distances and the N^1-C^2-N^3 bond angles are enlarged in the entetraamines **23**=**23** relative to the parent imidazolidin-2-ylidenes **23** (Scheme 31) in accord with theoretical predictions.[71] The nitrogen atoms in the entetraamines are pyramidalized and the $N_2C{=}CN_2$ unit is not planar (torsion angle N^1-$C^2{=}C^2$*-N^1* 6°[75] and 11.2° for *anti*-**23c**=**23c**,[86] 14.5° and 15.7° for *syn*-**23c**=**23c**[86]).

2.3.3. Triazolin-5-ylidenes

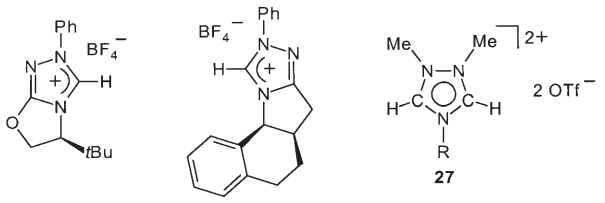
As early as 1995 Enders and co-workers isolated the first triazolin-5-ylidene **26**. This compound is not accessible by deprotonation of C^5 of the azolium ion with sodium methanolate because the triazolium cation reacts with the base to form 5-methoxytriazole. The 5-methoxytriazole decomposes at 80 °C under vacuum to give **26** in an endothermic ($\Delta H =$ 33 kJ mol^{-1}) methanol-elimination reaction (Scheme 32).[89]



Scheme 32. Synthesis of the triazolin-5-ylidene **26**.

Triazolin-5-ylidene **26** is stable up to a temperature of 150 °C. The ^{13}C NMR spectrum exhibits the resonance for the carbene carbon atom at $\delta(C^5) = 214.6$ ppm (in C_6D_6). This value falls in the range observed previously for the carbene carbon atoms in imidazolin-2-ylidenes **17** (Scheme 20). The free triazolin-5-ylidene **26** also behaves like an unsaturated N-heterocyclic carbene of type **17** and shows no tendency for dimerization. The important structural parameters of these two types of carbenes are also similar, such as the short C^5–N^1(N^4) bonds (1.351(3) Å and 1.373(4) Å) and the small N^1-C^5-N^4 bond angle (100.6(2)°) in **26**. Particularly the short C^5–N^1(N^4) bonds can serve as an indicator for a strong interaction between the filled p orbitals at the nitrogen atoms and the formally unfilled p_π orbital at the C^5 carbon atom in **26**. This type of interaction cannot exist in the 5-methoxytriazole which therefore exhibits longer C^5–N bonds (N^1–C^5 1.443(7) Å, N^4–C^5 1.443(7) Å).[89]

Triazolin-5-ylidene **26** can be reduced reversibly to the radical anion. DFT calculations show that the maximum spin density is located in the NBO-LUMO of the $N^2{=}C^3$ double bond and at the C^3-bound phenyl group.[90] 1,2,4-Triazolium salts have been used successfully as precatalysts in the benzoin condensation. Efficient chiral compounds of this type have been developed by Enders et al. (Scheme 33). After



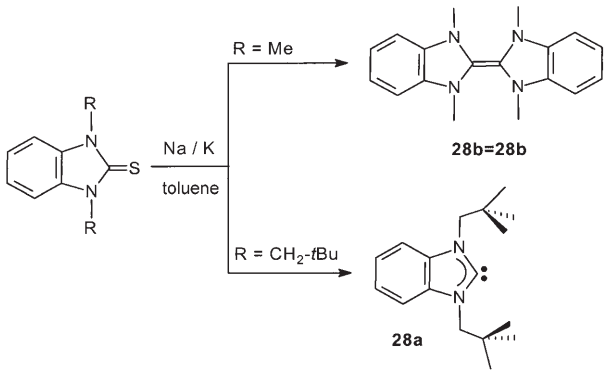
Scheme 33. Chiral 1,2,4-triazolium salts and the salt, **27**, containing the 1,2,4-triazolium dication.

deprotonation of C^5 to give the triazolin-5-ylidenes they act as chiral catalysts for inter-[91a] and intramolecular[91b] benzoin condensations.

Bertrand and co-workers succeeded with the preparation of the salt **27** with a 1,2,4-triazolium dication.[92a,b] All attempts to prepare the mono or dicarbene from this dication by single or double deprotonation, respectively, have failed to date. However, silver complexes with both carbene species could be isolated. Recently Peris and co-workers reported the preparation of homo- and heterobimetallic complexes of the triazolin-3,5-diylidene.[92c]

2.3.4. Benzimidazolin-2-ylidenes and Related Benzannulated Compounds

The first stable benzimidazolin-2-ylidene **28a** was described by Hahn et al. in 1999.[93] Compound **28a** was obtained by reductive desulfurization of the corresponding benzimidazolin-2-thione (Scheme 34). The reduction of such thiones leads, in analogy to the imidazolidin-2-thiones **22** and depending on the steric demand of the substituents at the nitrogen atoms, either to the free carbene **28a** (R = CH_2-*t*Bu) or to the dibenzotetraazafulvalene **28b**=**28b** (R = Me).

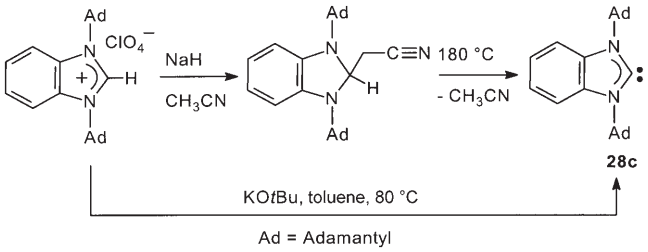


Scheme 34. Synthesis of the benzimidazolin-2-ylidene **28a** and the dibenzotetraazafulvalene **28b**=**28b**.

In analogy to the azolium salts described above, it should be possible to prepare benzimidazolin-2-ylidenes such as **28a**, more conveniently and faster by deprotonation of benzimidazolium salts. The preparation of suitable benzimidazolium salts is possible by N,N′-alkylation of benzimidazole[94] or by the cyclization reaction between N,N′-dialkyl substituted *ortho*-phenylenediamines and formaldehyde.[95] The first

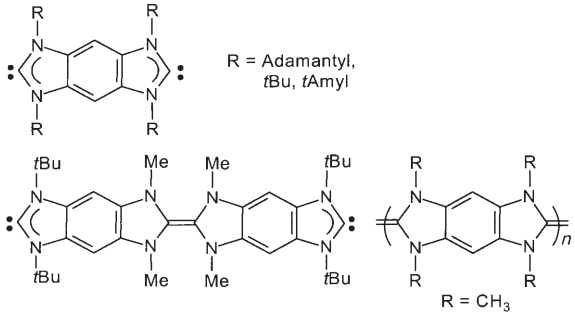
method was used for the preparation of the sterically demanding substituted *N*,*N*′-diadamantylbenzimidazolium bromide.[94c] The second method proved useful for the preparation of ferrocenyl substituted benzimidazolium salts.[95]

Upon attempts to deprotonate 1,3-diadamantylbenzimidazolium perchlorate[96] a reaction of the newly formed carbene with the solvent acetonitrile was noted and a derivative alkylated at C^2 was obtained. This compound decomposes upon heating to 180 °C in the absence of a solvent under α-elimination and formation of 1,3-diadamantylbenzimidazolin-2-ylidene **28c**. The α-elimination resembles that observed for 5-methoxytriazole upon heating (Scheme 32). Carbene **28c** is also directly accessible by deprotonation of 1,3-diadamantylbenzimidazolium perchlorate with KO*t*Bu in toluene at 80 °C (Scheme 35).



Scheme 35. Synthesis of 1,3-diadamantylbenzimidazolin-2-ylidene **28c**.

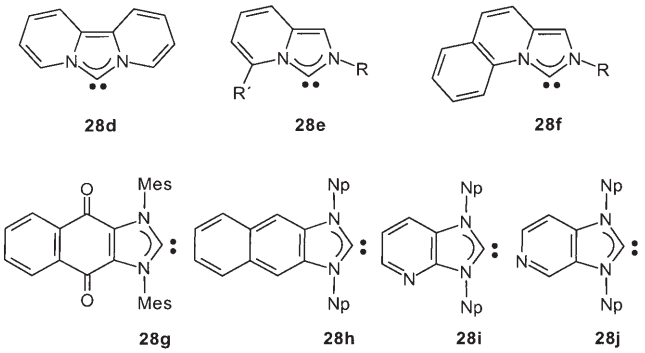
Bielawski et al. reported novel benzobis(imidazolin-2-ylidenes),[97] which were obtained by deprotonation of benzobis(imidazolium) salts[98] with lithium diisopropylamide. These dicarbenes can form monomeric,[97] dimeric,[98] or polymeric units[99] (Scheme 36) depending on the steric



Scheme 36. Benzobis(imidazolin-2-ylidenes) and their oligomerization products.

demand of the nitrogen substituents. The reaction of the benzobis(imidazolium) salts with suitable metal precursors allows the preparation of organometallic polymers.[100]

To vary the electronic situation at the carbene carbon atom a number of carbo- and heterocycle-annulated imidazolin-2-ylidenes have been prepared and studied. The doubly pyrido[*a*]-annulated carbene **28d** (Scheme 37) can be considered formally as the complex of 2,2′-bipyridine with a singlet carbon atom.[101,102] Singly pyrido[*a*]-annulated carbenes such

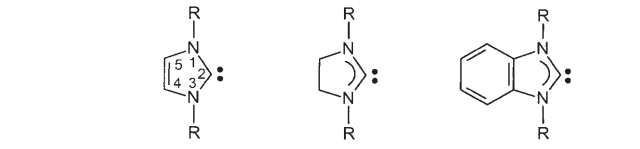


Scheme 37. Carbo- and pyrido-annulated imidazolin-2-ylidenes. Np = neopentyl, Mes = 2,4,6-trimethylphenyl.

as **28e** and **28f**,[103] have been obtained by deprotonation of the corresponding azolium salts.[103,104] The molecular structures of derivatives of type **28d** and **28e** were determined by X-ray diffraction.[105] The quinone-annulated carbene **28g** has been described recently.[106] Its complexes have been used in an intelligently conceived experiment to study the π backbonding in carbene complexes. The carbonyl stretching frequencies of the quinone moiety in these complexes served as a sensitive probe for the detection of electronic changes within the π system of the ligand. Heinicke et al. synthesized the naphtho-annulated carbene **28h**[107] and reported their attempts to prepare a quinoxaline-annulated carbene.[108] The preparation of the pyrido[*b*]- and pyrido[*c*]-annulated carbenes **28i** and **28j** has been reported recently.[107,109]

Annulation of imidazolin-2-ylidenes normally changes the electronic situation at the carbene carbon atom in a way that depends on the π-electron donor or acceptor capability of the annulated ring. Quantum mechanical calculations have demonstrated that annulation generally destabilizes N-heterocyclic carbenes.[110] This situation becomes apparent when the analogies between benzannulated N-heterocyclic carbenes and the saturated imidazolidin-2-ylidenes **23** (Scheme 22) are considered. Both, the saturated imidazolidin-2-ylidenes and the benzannulated derivatives, such as benzimidazolin-2-ylidene **28** (Scheme 34) dimerize rapidly to **28**=**28**, if the nitrogen atoms are functionalized with sterically less demanding substituents. No such dimerization was observed for imidazolin-2-ylidenes of type **17** although they have an unsaturated five-membered carbene ring like the benzimidazolin-2-ylidenes.

A detailed inspection of selected structural and ^{13}C NMR spectroscopic parameters provides additional evidence for the special properties of benzimidazolin-2-ylidenes of type **28** (Scheme 38). The ^{13}C NMR resonance for the C^2 carbon atom in compounds of type **28**, for example, is observed at a chemical shift which lies between the typical values for the C^2 resonance of saturated imidazolidin-2-ylidenes **23** and unsaturated imidazolin-2-ylidenes **17**. In spite of the unsaturated nature of the five-membered carbene ring in **28**, the N^1-C^2-N^3 angles determined crystallographically are in fact in the range typical for saturated imidazolidin-2-ylidenes of type **23** (Scheme 38). It appears that the five-membered ring in



	17	23	28
$\delta(C^2)$ [ppm]	211.4-220.6	238.2-244.5	**28a**: 231.5 ([D$_8$]THF) **28c**: 223.0 (C_6D_6)
Angle N^1-C^2-N^3 [°]	101.2(2)-102.2(2)	104.7(3)-106.4(1)	**28a**: 103.5(1), 104.3(1) **28c**: 103.5(1), 104.3(1)

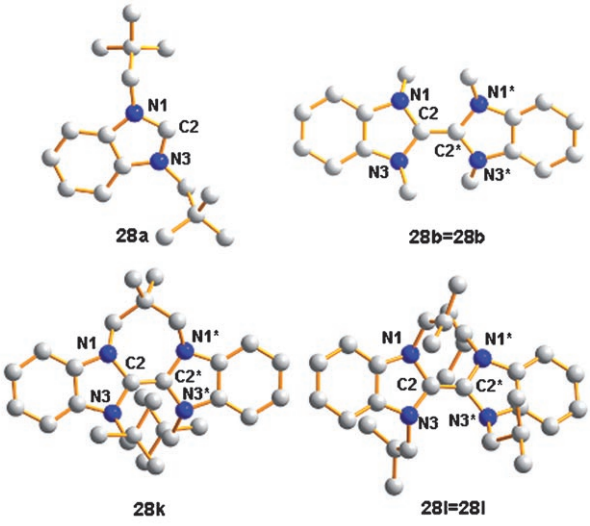
Scheme 38. Comparison of structural and ^{13}C NMR-spectroscopic parameters for compounds of types **17**, **23**, and **28**.

carbenes of type **28** has the topology of an unsaturated N-heterocyclic carbene (such as **17**) but exhibits spectroscopic and structural parameters which are similar to those observed for the saturated imidazolidin-2-ylidenes of type **23**.

This intermediate position of the benzimidazolin-2-ylidenes between unsaturated (**17**) and saturated (**23**) N-heterocyclic carbenes indicates, even in the absence of experimental data, that the energy-gap between the singlet and triplet states for compounds of type **28** should assume an intermediate position between the stable imidazolin-2-ylidenes **17** and the rapidly dimerizing imidazolidin-2-ylidenes **23**. Therefore the formation of a chemical equilibrium between the monomeric carbene and its entetraamine dimer as postulated by Wanzlick (Scheme 4) was reinvestigated using benzimidazolin-2-ylidenes.

The dimerization behavior of benzimidazolin-2-ylidenes is, as expected, determined by kinetic factors (steric demand of the N,N′-substituents). The first attempts to prepare *N*,*N*′-dimethylbenzimidazolin-2-ylidene by deprotonation of the corresponding benzimidazolium salt did not yield the free carbene but instead the dibenzotetraazafulvalene **28b**=**28b** (Scheme 34).[93a,c] Use of the sterically more-demandingly substituted *N*,*N*′-diadamantylbenzimidazolium salt in the deprotonation reaction yields the stable carbene **28c** (Scheme 35).[96] A monomeric benzimidazolin-2-ylidene (**28a**) was also obtained by reductive desulfurization of *N*,*N*′-dineopentylbenzimidazolin-2-thione.[93a] The molecular structures of **28a** and **28b**=**28b** have been determined by X-ray diffraction studies (Figure 2). A situation similar to that observed for imidazolidin-2-ylidenes **23** and their dimeric entetraamines **23**=**23** was found for compounds **28** and **28**=**28**. The geometry of the nitrogen centers in the carbene **28** is trigonal-planar whereas pyramidalized nitrogen centers are found in the entetraamines **28**=**28**. The C^2–C^{2*} distances in **28**=**28** are typical for normal C=C double bonds, but the N_2C=CN_2 units are not planar (Figure 2).

Since compounds **28a** and **28b**=**28b** provide examples of a stable benzimidazolin-2-ylidene and a dibenzotetraazafulvalene it was hoped that a variation of the steric demand of the N,N′-substituents would change the barrier for dimerization to the extent that a carbene and an entetraamine could coexist. The steric demand of the N,N′-substituents in **28a** was therefore decreased stepwise. In a first step two N-neopentyl substituted benzimidazolin-2-ylidenes were connected by a 2,2′-dimethylpropylene bridge. The bridge is flexible and the two carbene centers can avoid each other. However, introduction of the bridge leads to the formation of the entetraamine **28k** (Figure 2). In addition, removal of one methyl group from each N-substituent in **28a** leads to the *N*,*N*′-diisobutylbenzimidazolin-2-ylidene which instantly dimerizes to the dibenzotetraazafulvalene **28l**=**28l** (Figure 2). From these observations it is clear that even small changes in the steric demand of the N,N′-substituents have a dramatic influence on the dimerization behavior of benzimidazolin-2-ylidenes.[111]



	$N^1(N^3)$–C^2 [Å]	C^2–C^{2*} [Å]	sum of angles $N^1(N^3)$ [°]
28a	1.368(2)–1.397(2)	–	359.1–360.0
28b=28b	1.418(4)–1.438(3)	1.344(4)	338.2–350.5
28k	1.421(1)	1.345(2)	348.3–350.0
28l=28l	1.432(3)–1.439(3)	1.332(5)	347.0–349.9

Figure 2. Molecular structures of benzimidazolin-2-ylidene **28a** and selected dibenzotetraazafulvalenes.

Dibenzotetraazafulvalene **28l**=**28l** (Figure 2) was prepared by reductive desulfurization of *N*,*N*′-diisobutylbenzimidazolin-2-thione followed by spontaneous dimerization of the carbene formed.[111] A ^{13}C NMR spectroscopic investigation of the products of this reaction revealed that a toluene solution of **28l**=**28l** ($\delta(C^2) = 119.0$ ppm) contained also the monomeric carbene **28l** ($\delta(C^2) = 227.8$ ppm). Crystallization experiments yielded exclusively the dibenzotetraazafulvalene **28l**=**28l** presumable due to its poorer solubility. This surprising observation was the starting point for a more detailed investigation. Crystalline **28l**=**28l** was dissolved in carefully dried [D$_8$]toluene and this solution was then investigated by ^1H NMR spectroscopy. The first spectrum was recorded 0.2 h after mixing (Figure 3) and it is dominated by signals which could be assigned to the entetraamine **28l**=**28l** (bb: $\delta(NCH_2) = 3.23$ ppm; aa: δ(Ar-H) = 6.48 and 6.66 ppm). The spectrum already displays some weak resonance signals belonging to the carbene **28l** (b: $\delta(NCH_2) = 3.92$ ppm; a: δ(Ar-H) = 7.08 ppm). The presence of signals for the carbene **28l** in the first spectrum recorded, even though pure crystalline **28l**=**28l** was used, is due to the time elapsed between preparation of the sample and recording of the

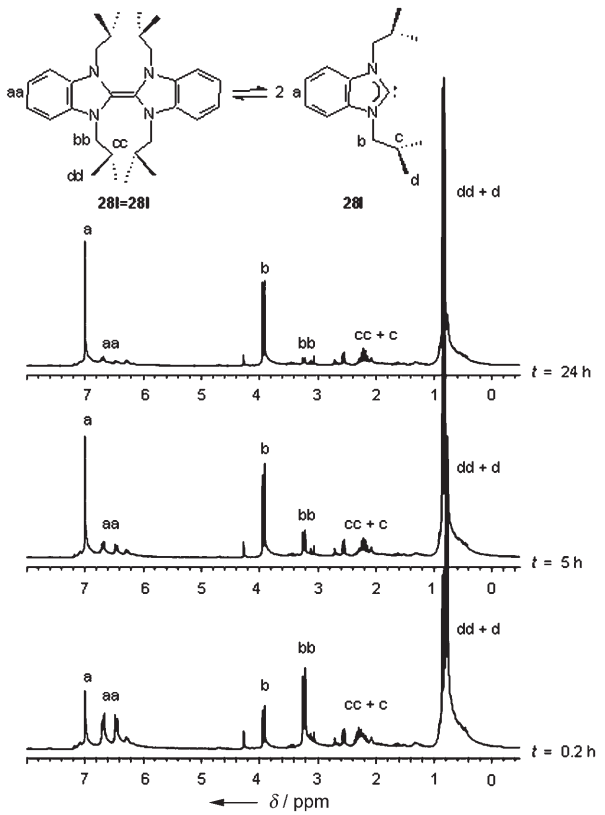


Figure 3. ^{1}H NMR spectroscopic monitoring of the cleavage of **28l**=**28l** in [D_8]toluene.

spectrum (0.2 h). Over the next hours the intensity of the signals for **28l** increases while the intensity for signals of **28l**=**28l** decreases. After 24 h the equilibrium has been established and no further change in the relative abundance of the components of the mixture (**28l**/**28l**=**28l** 90:10) was observed. An identical observation was made by ^{13}C NMR spectroscopy where the intensity of the signals for **28l**=**28l** (for example, $\delta(C^2) = 119.0$ ppm) decreases and the intensity of the signals of the free carbene **28l** ($\delta(C^2) = 227.8$ ppm) increases.[111]

The thermally induced cleavage of the dibenzotetraazafulvalene **28b**=**28b** at 110–140 °C and of the *N*,*N*′,*N*″,*N*‴-tetraethyl substituted derivative into two benzimidazolin-2-ylidenes ($\delta(C^2) = 225.3$ and 224.9 ppm) has also been reported.[112] The cleavage of **28l**=**28l** in to two benzimidazolin-2-ylidenes **28l** at ambient temperature is an exergonic reaction ($\Delta G = -12.9$ kcal mol^{-1})[113a] according to quantum chemical calculations (B3LYP/6-31G(d) + ΔZPE) while the cleavage of the *N*,*N*′,*N*″,*N*‴-tetraethyldibenzotetraazafulvalene in to two carbenes only proceeds at elevated temperatures. A value of $\Delta G \approx 5$ kcal mol^{-1} was determined experimentally from van't Hoff plots constructed from the equilibrium constants at different temperatures.[112]

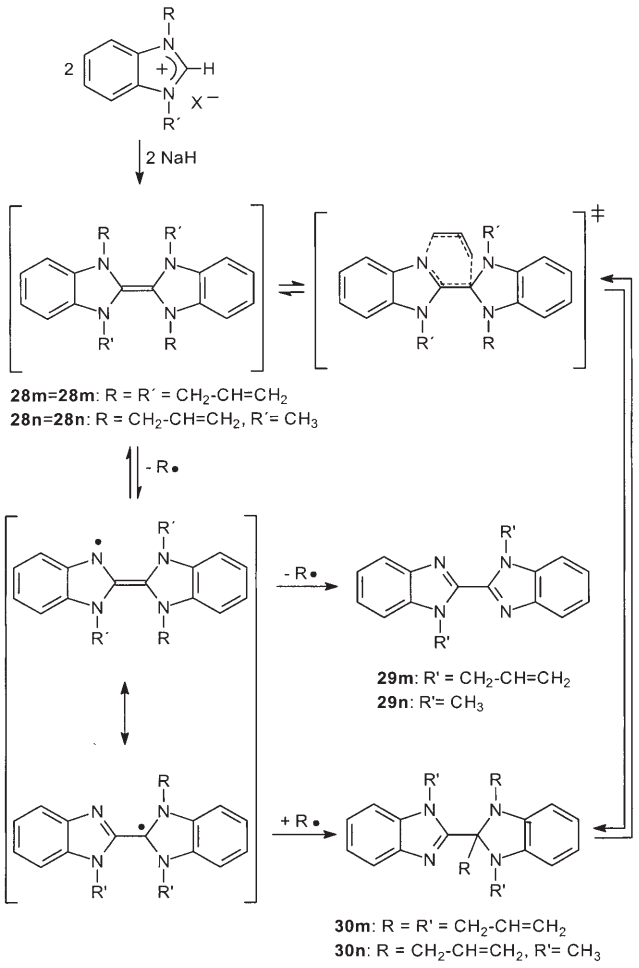
No conclusive mechanistic information about the cleavage of dibenzotetraazafulvalenes into N-heterocyclic carbenes is available at this time. Both a monomolecular cleavage as well as an electrophile-catalyzed reaction,[23a] leading to the monomer–dimer mixture are conceivable. The electrophile-catalyzed cleavage constitutes the reverse reaction of the acid-catalyzed reaction proposed by Alder et al.[43] for the dimerization of diaminocarbenes (Scheme 26). The distinction between a monomolecular and an acid-catalyzed cleavage is important from a mechanistic point of view. From the synthetic viewpoint it is only of secondary importance for the benzimidazolin-2-ylidenes discussed herein. The complete exclusion of electrophiles is impossible under the reaction conditions employed for the preparation of benzimidazolin-2-ylidenes. As well as protic impurities, the cations of the alkali-metal salts K_2S or NaX can also act as electrophiles.[43] Consequently, electrophilic catalysis cannot be ruled out completely for the cleavage of dibenzotetraazafulvalenes into monomeric carbenes. Even without exact knowledge of the reaction mechanism it can be concluded that the cleavage of **28l**=**28l** into N-heterocyclic carbenes proceeds spontaneously in an exergonic reaction using carefully dried solvents at room temperature, and that the carbene and its entetraamine can coexist in solution.[113b]

The rapid dimerization of benzimidazolin-2-ylidenes with sterically less-demanding N,N′-substituents leads to an interesting observation if the nitrogen atoms are functionalized with allyl groups (Scheme 39). After deprotonation of C^2 of the *N*,*N*′-diallylbenzimidazolium salt[94g] a dibenzotetraazafulvalene of type **28**=**28** is obtained. This entetraamine is not stable but rearranges under cleavage of one or two N–C_{allyl} bonds to give the derivatives **29m**,**n** or **30m**,**n**, respectively.[114]

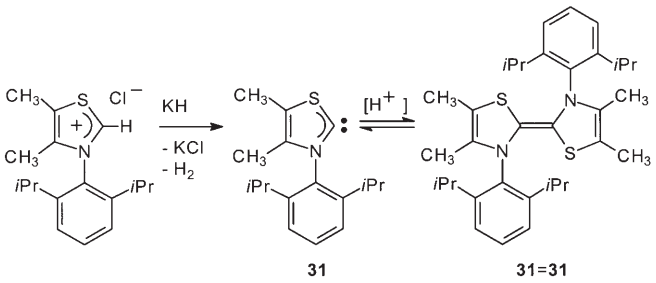
Two different reaction pathways are possible for the rearrangement. In a radical decomposition, an allyl radical is first cleaved from one nitrogen atom to give a bibenzimidazolyl radical. This species can decompose to give 2,2′-bibenzimidazole **29m**,**n** in a second radical deallylation or recombine with the allyl radical at the $C^{2'}$ position forming compounds **30m**,**n**. An alternative reaction pathway is a 3-Aza–Cope rearrangement of compounds of type **28**=**28** also leading to the reaction product **30m**,**n**. The products of the double deallylation (**29m**,**n**) have been identified together with compounds **30m**,**n** in this reaction. Quantum chemical calculations indicate that the rearrangement proceeds most likely by the radical mechanism and that kinetic factors are crucial for the product distribution. Similar rearrangement reactions have been reported for 1,3,1′,3′-tetraallyl-2,2′-biimidazolidinylidene[115] and 1,3,1′,3′-tetrabenzyl-2,2′-bibenzimidazolinylidene.[116]

2.3.5. *Thiazolin-2-ylidenes and Benzothiazolin-2-ylidenes*

The first stable thiazolin-2-ylidene **31** was obtained in 1997 by Arduengo et al. by deprotonation of the corresponding thiazolium salt with potassium hydride in THF (Scheme 40). The molecular structure of the compound was determined by an X-ray diffraction study.[117a] Dimerization of **31** to **31**=**31** occurred in the presence of protons and the molecular structure of **31**=**31** was also determined. Thiazolin-2-ylidene **31** is, to date, the only stable carbene which has been observed in equilibrium with its dimer and where both monomer and dimer have been characterized crystallographically. Thiazolin-2-ylidenes with sterically less-demanding nitrogen substituents such as mesityl or methyl, dimerize



Scheme 39. Rearrangement reactions of dibenzotetraazafulvalenes.

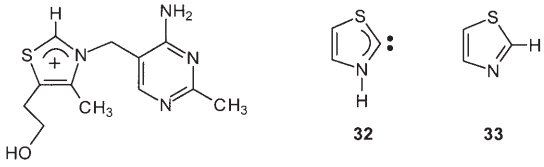


Scheme 40. Synthesis and dimerization of thiazolin-2-ylidenes.

rapidly at room temperature and can only be isolated as their dimers.[117]

Thiazolin-2-ylidenes exhibit properties similar to those of saturated imidazolidin-2-ylidenes **23** and their reaction products. Upon deprotonation of the thiazolium salts[118] to the thiazolin-2-ylidenes, the N^3-C^2-S angle becomes smaller and the endocyclic N–C^2 bond lengths increase slightly.[117a] The thiazole ring is essentially planar. The ^{13}C NMR spectrum shows a significant downfield shift for the thiazolin-2-ylidene resonances ($\delta(C^2) = 252$–254 ppm) compared to the thiazolium salt ($\delta(C^2) = 155$–160 ppm). The spectrum of the carbene dimer shows an upfield shifted resonance for the carbon atoms of the (N,S)C=C(N,S) moiety ($\delta(C^2) = 110$–120 ppm).[117]

Thiazolium cations, such as thiamin (vitamin B1, Scheme 41), play an important role in numerous enzymatic



Scheme 41. Thiamin (left) and model compounds.

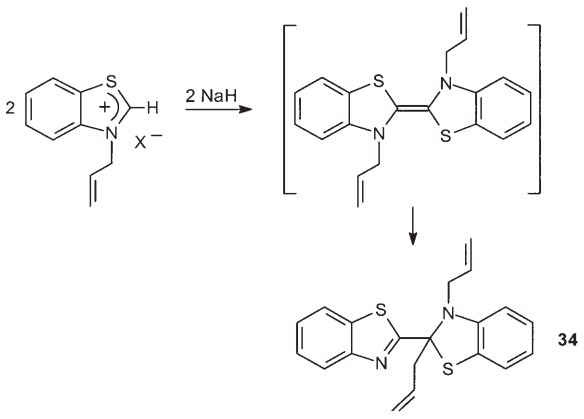
C–C coupling reactions.[119] The groups of Breslow[120a] and others[120b,c] have used model compounds to demonstrate that the enzymatic activity is caused by deprotonation of C^2 of the thiazolium cation to give the thiazolin-2-ylidene or its dimer. The parent compound of thiazolin-2-ylidenes, **32** (Scheme 41), was obtained after irradiation of thiazol-2-carboxylic acid and has been trapped in an argon matrix at 12 K.[121] IR and ^{13}C NMR labeling experiments indicate that a CO_2 adduct of **32** is formed since the liberated CO_2 remains in the same matrix cage as **32**. Further irradiation or warming to 60 K leads to tautomerization of **32** to thiazole **33**. Compound **32** was also detected by a combination of electron-ionization and neutralization–reionization mass spectrometry starting from 2-acetylthiazole.[122] Quantum chemical calculations confirm that compound **32** is less stable by 31.5 kcal mol^{-1} than **33**. Nonetheless, the existence of **32** appears possible as a result of the high energy barrier (72.4 kcal mol^{-1}) for the 1,2-hydrogen shift from nitrogen to carbon.[122] Geometric parameters calculated for **32** match equivalent parameters for **31**.

Stable benzothiazolin-2-ylidenes are not known although different benzothiazolium salts and complexes of benzothiazolin-2-ylidenes are readily accessible.[123] Upon deprotonation of C^2 of *N*-allylbenzothiazolium bromide, a rearrangement similar to that described for *N*,*N*′-diallylbenzimidazolium salts (Scheme 39) was observed. The reaction product is compound **34** (Scheme 42),[123a] which is most likely formed in a radical [1,3]-sigmatropic rearrangement.[124]

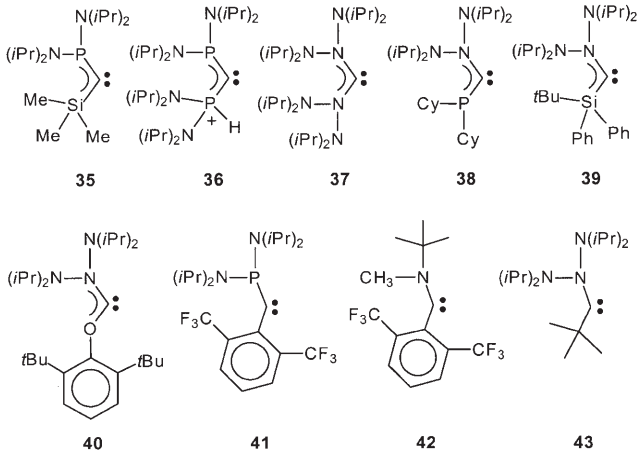
2.3.6. Cyclic Alkyl(amino)carbenes (CAACs)

Some years before the preparation of the first N-heterocyclic carbene by Arduengo et al.[30] Bertrand et al. described the stable (trimethylsilyl)[bis(diisopropylamino)phosphanyl]carbene **35**[8] and shortly thereafter the molecular structure of a crystalline phosphanyl(silyl)carbene[125] The stable noncyclic heteroatom-stabilized carbenes **36**,[9] **37**,[126] **38**,[127] **39**,[128] and **40**[129] have also been prepared (Scheme 43).[130]

The synthesis of the phosphanyl(aryl)carbene **41**[131] marked the entrance into the chemistry of stable singlet carbenes which are stabilized by only one heteroatom. Shortly thereafter, the first amino(aryl)carbene **42**[132] and the first amino(alkyl)carbene **43**[133] (Scheme 43) were prepared. The preparation of the acyclic carbenes **42** and **43** raised the



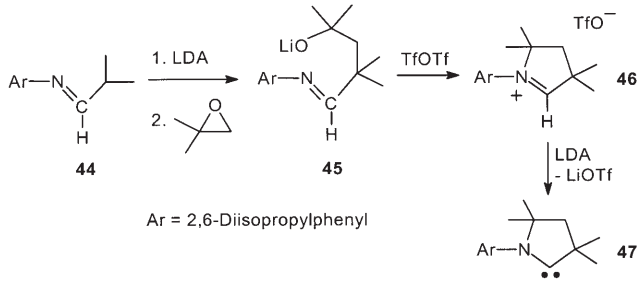
Scheme 42. Reaction products obtained after C^2 deprotonation of *N*-allylbenzothiazolium bromide.



Scheme 43. Heteroatom-stabilized, acyclic singlet carbenes.

question of the stability of N-heterocyclic carbenes containing only one nitrogen atom for the stabilization of the carbene center.

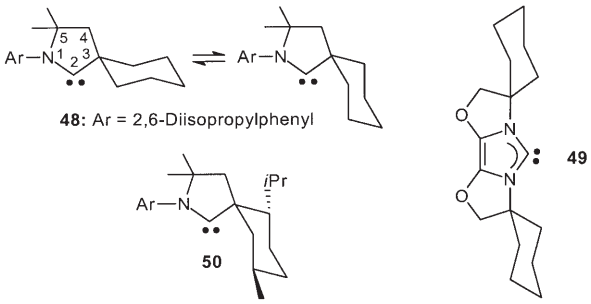
Recently, Bertrand and co-workers succeeded with the preparation of the first cyclic alkyl(amino)carbenes (CAACs).[134] CAAC **47** was obtained from imine **44** which can be synthesized from 2,6-diisopropylaniline and 2-methylpropanal (Scheme 44). Deprotonation of **44** with LDA afforded an azaallyl anion which readily induced the ring opening of 1,2-epoxy-2-methylpropane leading to **45**. The



Scheme 44. Synthesis of the cyclic alkyl(amino)carbene **47**.

cyclic aldiminium salt **46** was obtained from **45** by reaction with the anhydride of trifluoromethanesulfonic acid. Finally, deprotonation of **46** with LDA afforded CAAC **47** as a colorless solid which is stable for weeks in solution at ambient temperature.

The presence of a quaternary carbon atom in α-position to the carbene center offers the possibility of constructing ligands featuring different types of steric environments to those of the known N-heterocyclic carbenes. For example, CAAC **48** (Scheme 45) contains a spiro carbon atom next to



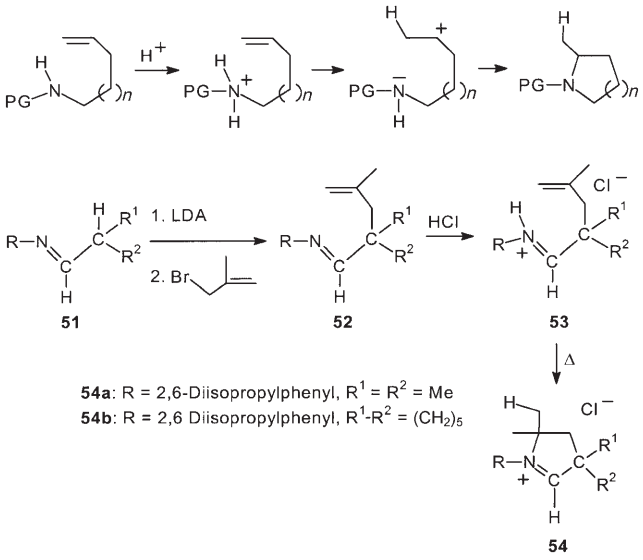
Scheme 45. Carbene ligands with flexible steric demand.

the carbene center. This CAAC was readily prepared in analogy to **47** from cyclohexyl carbaldehyde and 2,6-diisopropylaniline. It exhibits, similarly to the carbene ligand **49**[60] derived from bisoxazoline (Scheme 45), a flexible steric demand based on conformational changes of the cyclohexyl ring. The influence of the "flexible wing" is amplified in carbene **48** compared to **49** because it is located directly next to the carbene center.[135]

The most remarkable compound in this series is CAAC **50**.[134] In this case, by intelligent substitution, the "flexible wing" has been fixed in one conformation which excludes conformational changes and results in a maximal protection of the carbene center and the metal center to which it is bound.

The steric environment of CAACs such as **48** or **50** differs significantly from that of tertiary phosphines or "normal" NHCs. The exchange of an electronegative amine substituent in normal NHCs by the strong σ-donor carbon makes CAACs particularly electron-rich. Consequently, CAACs function as excellent donor ligands with a donor strength which is often superior to that of phosphines or "normal" NHCs. The N^1–C^2 bond length (1.315(3) Å) is comparable to the value found for imidazolidin-2-ylidenes of type **23** (Scheme 31) while the C^2–C^3 bond length is typical for a C–C single bond. The N^1-C^2-C^3 bond angle of 106.5(2)° is significantly larger than the equivalent value in imidazolin-2-ylidenes and corresponds to the values found for imidazolidin-2-ylidenes. A significant downfield shift of the resonance signal for the carbene carbon atom (**47**: $\delta = 304.2$ ppm, **48**: $\delta = 309.4$ ppm, **50**: $\delta = 319.0$ ppm, measured in [D_8]THF) was observed. The rigid CAAC **50** forms remarkable complexes in which the conformational-fixed cyclohexyl ring protects the metal center like a wall.[135]

During the synthesis of CAACs, the deprotonation of aldiminium salts **46** proceeds readily whereas the synthesis of the nitrogen-containing heterocycles is tedious and time consuming (Scheme 44). Nitrogen-containing heterocycles are often obtained by intramolecular hydroamination. Hartwig and co-workers developed an acid-catalyzed intramolecular hydroamination for aminoalkenes in which the amine function has to be substituted with an electron-withdrawing substituent (Scheme 46, top).[136] Mechanistic studies on this



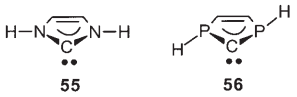
Scheme 46. Proton-catalyzed hydroamination (top) and "hydroiminiumation" (bottom).

reaction indicate that the amine function is initially protonated and that this proton is then transferred to the double bond in the rate-determining step. The resulting carbocation then reacts with the amine in a ring-closing reaction. The cyclization sequence was not observed in the absence of an electron-withdrawing substituent at the nitrogen atom because the enhanced basicity of the amine prevents the transfer of the proton to the double bond.

Bertrand and co-workers adapted this proton-catalyzed cyclization to the less-basic imines and developed the "hydroiminiumation" reaction for the preparation of the C^2 protonated precursors **54** of CAACs (Scheme 46, bottom).[137] First an aldimine **51** was prepared in analogy to **44** in Scheme 44. After deprotonation of **51** with LDA, the formed azaallyl anion was treated with 3-bromo-2-methylpropene to give the alkenyl aldimine **52**. Compound **52** reacts with HCl/Et_2O to afford **53** which has been characterized crystallographically. Heating of various derivatives of **53** results in cyclization to give the salts **54a** and **54b** which are easily deprotonated to the free CAACs with LDA. This reaction sequence allows the preparation of iminium salts in which the quaternary carbon atom C^3 is part of a cyclohexyl ring. In addition, larger heterocycles (six-membered rings) are accessible. An asymmetric version of the reaction is also possible generating a stereocenter at atom C^5 (for ring nomenclature see Scheme 45).[138]

2.3.7. *P-Heterocyclic Carbenes (PHCs)*

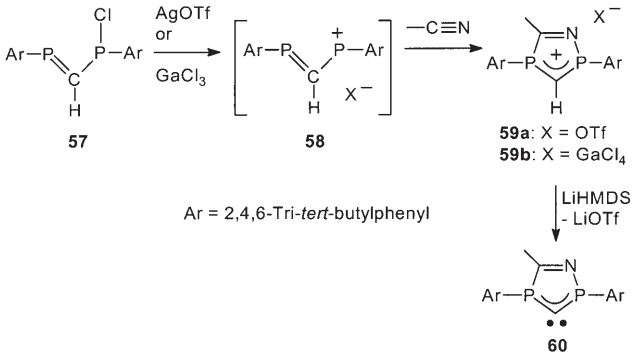
The unusual stability of N-heterocyclic carbenes derives from the ability of the nitrogen atoms within the heterocycle to act as π donors thereby reducing the electron deficiency at the neighboring carbene center. In this context, it is surprising that the heavier analogues of nitrogen, such as phosphorus, were initially disregarded for the stabilization of cyclic carbenes particularly since acyclic phosphorus-stabilized carbenes have been known since 1988 (see Scheme 43). Experimental observations, as well as ab initio calculations, demonstrated[139] that the π-donor capability of the third-row elements is as large as or even larger than those of their second-row counterparts. However, these calculations also showed that the nitrogen atoms in a hypothetical N-heterocyclic carbene **55** are planar,[14] whereas the phosphorus atoms in a hypothetical P-heterocyclic carbene (PHC) **56** are expected to be pyramidalized[140] which impedes an efficient stabilization of the carbene center (Scheme 47).



Scheme 47. Geometry at the heteroatoms in the hypothetical NHC **55** and the hypothetical PHC **56**.

In 2004, Le Floch et al. described the first complex with a P-heterocyclic carbene[141] that is the analogue of the imidazolin-2-ylidene **7** (Scheme 6).[141] Previously other groups had reported some metal complexes with phosphorus-stabilized carbene centers.[142] The free P-heterocyclic carbene could, however, not be isolated. It was Bertrand et al. who recently prepared the first stable PHC **60**,[143] where a pyramidalization of the phosphorus atoms[144] was prevented by the use of sterically demanding substituents. NHCs are normally obtained by deprotonation of azolium salts. The phosphorus analogues of these salts are unknown and the preparative methodology employed for the preparation of substituted imidazoles and imidazolium salts cannot be transferred to phosphorus heterocycles. Consequently Bertrand and coworkers developed a new method for the preparation of the salts **59a** and **59b** (Scheme 48). Phosphaalkene **57** was initially dehalogenated with AgOTf or $GaCl_3$ and the resulting intermediate, the diphosphaallylic cation **58**, reacts in a formal [3+2]-cycloaddition with the dipolarophile acetonitrile. The cations in **59a** and **59b** were then deprotonated with LiHMDS to give the free stable PHC **60** (m.p. 123–127 °C).

The molecular structures of **59b** and **60** provide proof that the use of the sterically demanding 2,4,6-tri-*tert*-butylphenyl substituents had the desired effect. The phosphorus atoms in both compounds are surrounded in an essentially planar fashion (sum of angles at the phosphorus atoms: 354° and 348° for **59b**; 353° and 348° for **60**). The slight deviation from planarity together with the *trans*-arrangement of the aryl substituents at the phosphorus atoms leads to chiral compounds in the solid state. The solution ^1H and ^{13}C NMR



Scheme 48. Synthesis of the P-heterocyclic carbene **60**.

spectra, however, each show only one resonance signal for the diastereotopic groups, even at low temperature (−100 °C). This result was taken as evidence for a rapid interconversion of the enantiomers in solution and a low inversion barrier at the phosphorus atoms. The donor character of the phosphorus atoms is demonstrated by the short $P-C_{carbene}$ distances which are significantly shorter than P–C single bonds. Deprotonation of **59b** to the P-heterocyclic carbene **60** causes the P-C-P angle to become more acute from 106.2(5)° in **59b** to 98.2(3)° in **60**. This behavior is analogous to the azolium salts and the NHCs obtained from these by deprotonation. The ^{13}C NMR resonance signal for the carbene carbon atom in PHC **60** ($\delta =$ 184 ppm) appears strongly deshielded relative to **59a** ($\delta =$ 119 ppm) but is shifted upfield in comparison to NHCs. Ab initio calculations show that a decrease in the steric bulk of the phosphorus substituents in **60** leads to a pyramidalization of the phosphorus atoms (sum of angles 328° and 342° in **56**) and to a decrease of the singlet–triplet energy gap thereby destabilizing the P-heterocyclic carbene.[144]

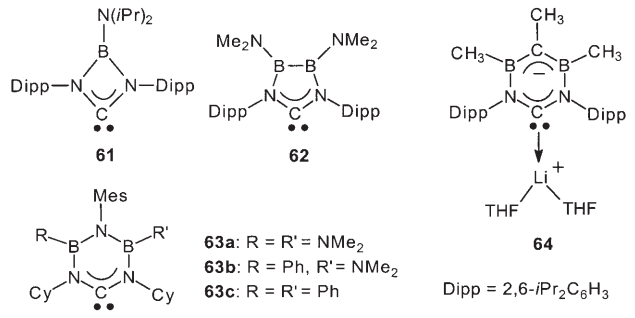
2.3.8. *N-Heterocyclic Carbenes with Boron Atoms within the Carbene Ring*

A series of N-heterocyclic carbenes containing Lewis acidic boron atoms within the carbene ring has recently been described. Carbene **61** with a four-membered heterocycle (Scheme 49) shows similarities with the previously discussed carbene **14b** (Scheme 12).[145] Substitution of the phosphorus atom in **14b** with a boron atom in **61** resulted in a shift of the ^{13}C NMR resonance for the carbene carbon atom down to the lowest value observed to date for cyclic diaminocarbenes ($\delta =$ 312.6 ppm in C_6D_6). The four-membered carbene ring is planar and the exocyclic nitrogen atom is also surrounded in a planer fashion. The lengths of the endocyclic C–N and B–N bonds indicates an efficient donation of the π electrons from the nitrogen atoms to the electron-poor carbon and boron atoms. The endocyclic N-C-N angle in **61** (94.0(2)°) represents the smallest value observed to date for N-heterocyclic carbenes.

The five-membered carbene ring in **62** (Scheme 49) is derived from an inorganic framework.[146] The carbene is stable for several weeks under an inert-gas atmosphere. However, the B–N bonds are rapidly hydrolyzed in air. The resonance signal for the carbene carbon atom appears downfield at $\delta = 304$ ppm in the ^{13}C NMR spectrum. A comparison of the geometrical parameters of **62** with carbenes of the imidazolin-2-ylidene (**17**) or imidazolidin-2-ylidene (**23**) type reveals a relatively long B–B separation (1.731(2) Å) in **62** in addition to an enlarged N-C-N angle (108.45(8)°). The carbene ring in **62** is nearly planar. The endocyclic B–N bonds are about 0.1 Å longer than the exocyclic ones, indicating that N→B π delocalization is weak within the heterocycle and stronger involving the exocyclic amine substituents. A significant N→B π interaction from the exocyclic amine groups is also confirmed by the observation of a hindered rotation around the $B-NMe_2$ bond that can be seen by the signals for non-equivalent methyl groups in both the ^1H and ^{13}C NMR spectrum at room temperature. First experiments show that carbene **62** is most likely a better σ donor than its analogues **17** and **23** with a carbon backbone.[146]

Heterocycles of type **63** are derived from and are isoelectronic with the stable borazine. The carbene ring in **63c** is nearly planar and the cyclohexyl groups are oriented to achieve a maximal steric protection of the carbene center.[147] The N-C-N angle is enlarged to 114.5(1)° in accordance with expectations for a six-membered ring. The resonances for the carbene carbon atoms fall in the narrow range of $\delta = 281.5$–282.9 ppm in the ^{13}C NMR spectra of **63a–c**. The IR spectra of complexes [RhCl(CO)$_2$(**63**)] were used to demonstrate that the σ donor strength of the carbenes **63a–c** can be modulated by the exocyclic substituents at the boron atoms. The σ-donor strength of the carbene ligand decreases together with the donor strength of the exocyclic substituents at the boron atoms in the order **63a** > **63b** > **63c**.[147]

The anionic carbene **64** was isolated and characterized as the lithium adduct.[148] The crystallographically determined molecular parameters of **64** are very similar to those found for the isoelectronic lithium terphenyl derivatives.[149] DFT calculations suggest that **64** exhibits a σ-donor strength between that of imidazolin-2-ylidenes and terphenyl anions.[148]



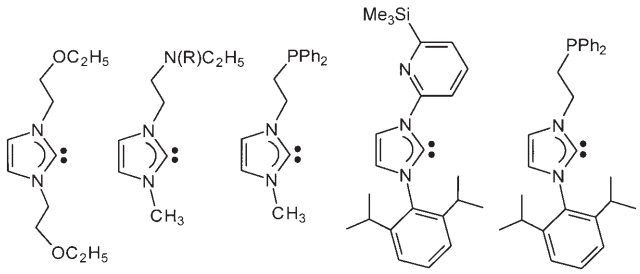
Scheme 49. N-Heterocyclic carbenes with boron atoms in the carbene ring.

2.3.9. *Donor-Functionalized, Chiral-Modified, and Polydentate Carbene Ligands*

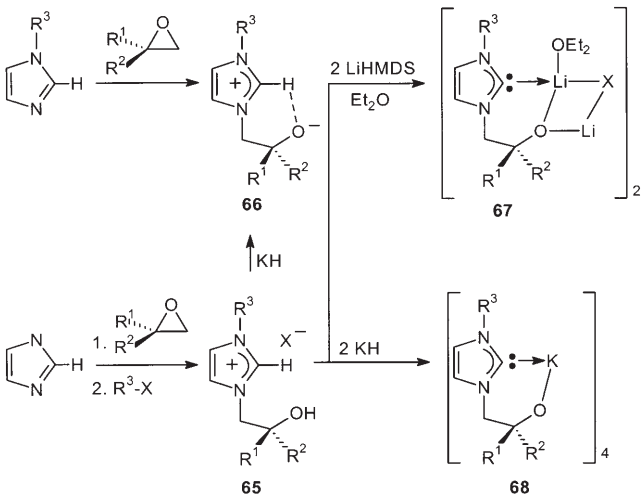
Reports on N,N′-donor-functionalized, chiral, and polydentate N-heterocyclic carbenes appeared almost immediately after the preparation of the first stable N-heterocyclic

carbenes. Since then, the number of such derivatives has grown dramatically. Therefore only a selection of the most important ligand types or their protonated precursors, respectively, is presented herein.

Herrmann et al. described the first donor-functionalized N-heterocyclic carbenes (Scheme 50) as early as 1996.[56a] N-



Scheme 50. Donor-functionalized N-heterocyclic carbenes.

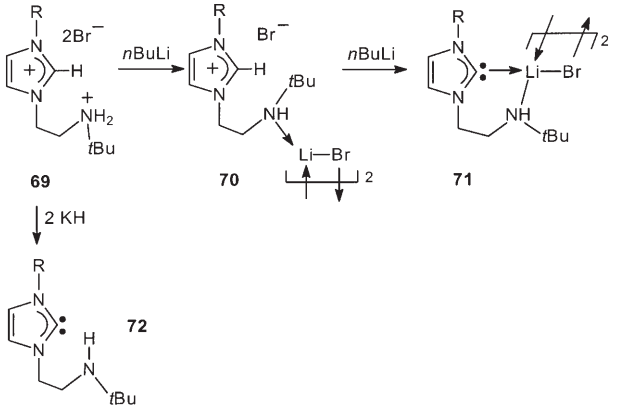


Scheme 51. Alkali-metal adducts of N-alcoholato functionalized imidazolin-2-ylidenes.

functionalized carbenes with amine, phosphine, or alkoxy groups were synthesized in liquid ammonia. Additionally, imidazolium salts with carbonyl,[55a,150] pyridyl,[150] pyrazolyl,[151] and phosphine substituents[152] at the nitrogen atoms have been described. They can be deprotonated in situ and thus are suitable for the preparation of metal complexes, although the free carbene ligands have not been isolated. The same is true for N-allyl substituted imidazolium,[55b,c,153] benzimidazolium,[94e] and benzothiazolium salts[123a] as well as for N-benzyl-functionalized imidazolidinium salts[55d,e] with olefin or aryl donor groups. The N-aryl-N′-phosphine and the N-pyridyl-functionalized ligands depicted in Scheme 50 have been prepared by Danopoulos et al. and were fully characterized including single-crystal X-ray diffraction. In the solid state these derivatives adopt a conformation which puts the free electron pairs of the donor groups in *anti*-positions.[154]

The preparation of N-heterocyclic carbenes bearing acidic substituents, such as alcohols or secondary amines, at the N centers constitutes a special challenge. Ground-breaking studies by Arnold et al.[155] demonstrated that alcohol-functionalized imidazolium salts **65** are readily accessible by nucleophilic opening of epoxides (Scheme 51). The single deprotonation, however, leads to the zwitterionic alcoholato imidazolium derivative **66**. The alcohol function is probably more acidic than the heterocycle. The reaction with two equivalents of a base yields the alkali-metal carbene adducts **67**[82e] and **68**[83b] which have been shown to be superb carbene transfer agents. The silver complexes of these ligands are also readily accessible (see also Section 3.1).[155]

Imidazolin-2-ylidenes with secondary amine substituents at the nitrogen centers can be isolated without intramolecular N→C^2 hydrogen transfer (Scheme 52). The imidazolium ammonium cation **69** reacts stepwise with *n*BuLi. The first deprotonation is of the ammonium function to yield compound **70**, this is followed by deprotonation of the azolium ring to give **71**. It proved difficult to remove the lithium bromide from **71**. The free carbene **72** was therefore obtained by deprotonation of **69** with two equivalents of KH.[82d]

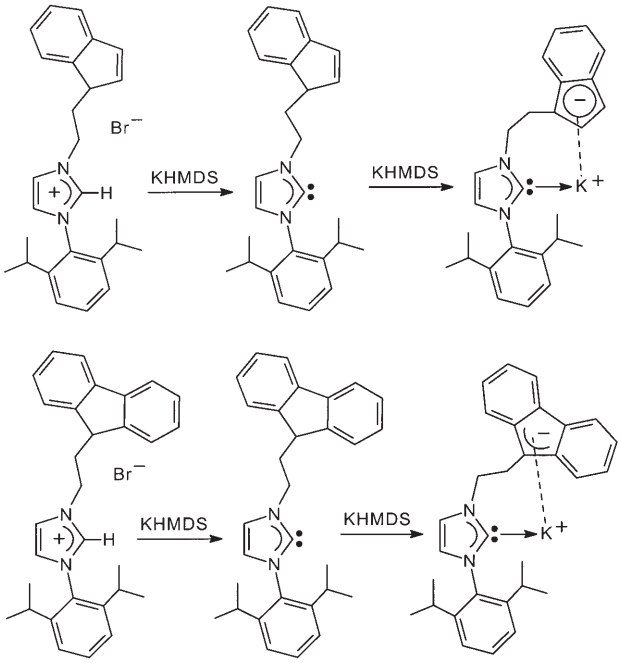


Scheme 52. Synthesis of secondary amine N-functionalized imidazolin-2-ylidenes.

Recently, Fryzuk et al. succeeded with the preparation of an imidazolin-2-ylidene with two secondary amine substituents by the deprotonation of the imidazolium salt with the bulky base KHMDS.[156]

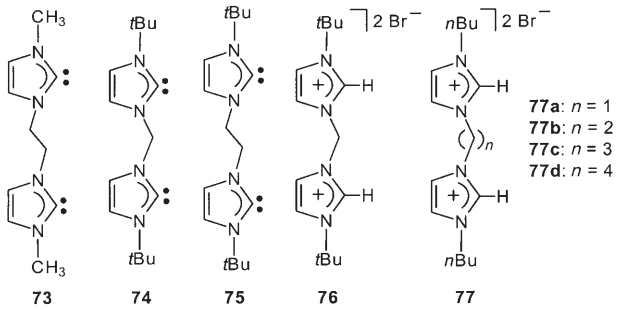
Indenyl and fluorenyl substituted imidazolin-2-ylidenes have been described by Danopoulos et al.[157a,b] and Cui et al. (Scheme 53).[157c] The deprotonation of the azolium salts proceeds in a stepwise manner. The N-heterocyclic ring is deprotonated first followed by the unsaturated cyclic hydrocarbon. This sequence does not correspond to the sequence of basicities of imidazolin-2-ylidenes and indenylato or fluorenylato anions. The molecular structure of the potassium adduct of the NHC-fluorenylato ligand and the molecular structures of some transition metal complexes bearing fluorenylato or indenylato substituted carbene ligands have been determined crystallographically.[157]

Some bidentate bis(imidazolin-2-ylidenes) have been prepared in addition to a sizable number of differently bridged diazolium salts. Herrmann et al. prepared, for example, the ethylene-bridged dicarbene **73**.[56a] The synthesis



Scheme 53. Synthesis of indenylato and fluorenylato substituted imidazolin-2-ylidenes.

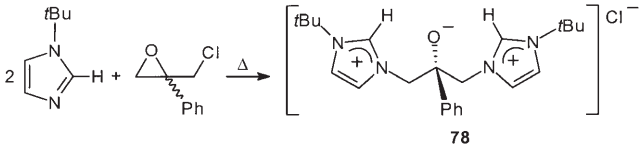
and spectroscopic properties of the methylene- and ethylene-bridged bis(imidazolin-2-ylidenes) **74** and **75** have also been reported (Scheme 54).[158]



Scheme 54. Bis(imidazolin-2-ylidenes) and diimidazolium salts.

There are a large number of reports about diimidazolium salts.[159] Herrmann et al. prepared the methylene-bridged salt **76**[159a] while Crabtree et al. described the C_1- to C_4-bridged diimidazolium salts **77a–d**[159b] (Scheme 54). All of these diimidazolium salts are readily deprotonated in situ to the bis(imidazolin-2-ylidenes) during the synthesis of metal complexes (see Section 3).

The precursor for an interesting dicarbene containing three donor functions has been presented by Arnold et al.[160] The diimidazolium alcoholato compound **78** is obtained when two equivalents of an *N*-alkylimidazole react with functionalized epichlorhydrin (Scheme 55). Deprotonation of the two imidazolium rings yields a tridentate ligand containing two soft carbene and one hard alcoholato donor functions.



Scheme 55. Synthesis of the ligand precursor **78**.

Dibenzimidazolium salts[161] and bis(benzimidazolin-2-ylidene) ligands[111] are also known. In contrast to the bis(imidazolin-2-ylidenes), which are stable carbenes, the formation of C=C double bonds is normally observed during the preparation of bis(benzimidazolin-2-ylidenes) (see Section 2.3.4). Hahn et al. described the synthesis of the 2,2′-dimethylpropylene-bridged dibenzotetraazafulvalene **28k** (Figure 2).[111] Subsequently, additional bis(benzimidazolin-2-ylidenes) (Figure 4) have been were prepared by deprotonation of bridged dibenzimidazolium salts[162] or by reductive desulfurization of bis(benzimidazolin-2-thiones).[163] As expected, the C_3- to C_5-bridged derivatives **28m–28o** were obtained as dibenzotetraazafulvalenes with nonplanar intramolecular C=C double bonds.

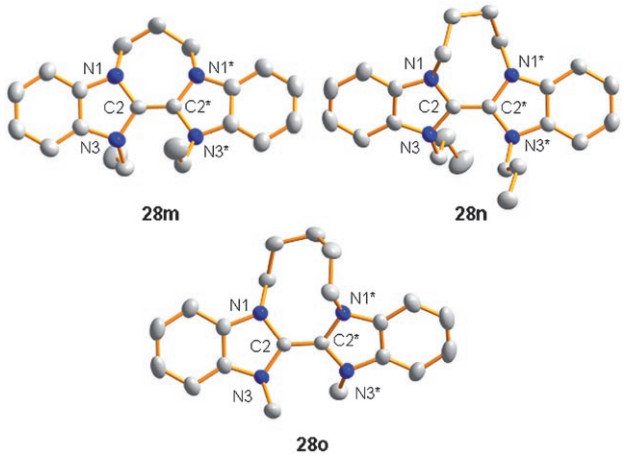
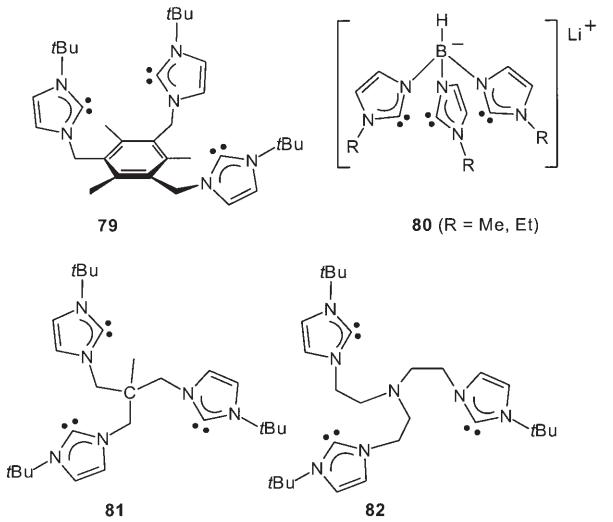


Figure 4. Molecular structures of C_3- to C_5-bridged dibenzotetraazafulvalenes.

The tridentate tris(imidazolin-2-ylidene) **79** (Scheme 56) was first described by Rasika Dias and Jin.[164] Evidence for the formation of a tricarbene came from NMR spectroscopy. The preparation and crystal structure of the anionic tricarbene **80**,[82c,165] which can be considered as an isomer of tris(pyrazolyl)borate, appeared shortly thereafter. Later Meyer et al. prepared the tricarbenes **81**[166] and **82**.[167] This group also succeeded in establishing the molecular structure of **79** by single-crystal X-ray diffraction.[168] Important aspects of the synthesis, properties, and coordination chemistry of tripodal tris(imidazolin-2-ylidenes) were recently summarized in a review by Hu and Meyer.[169]

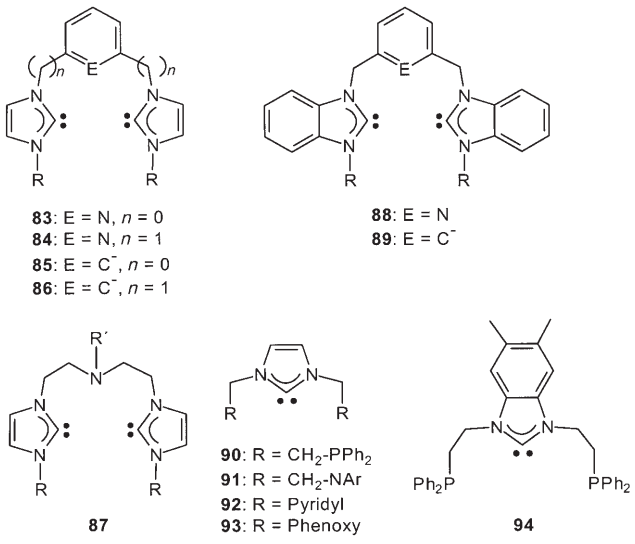
The development of "pincer" ligands containing phosphine or amine donor groups by Milstein et al.[170a] and van Koten et al.[170b] inspired some research groups to transfer this useful rigid-ligand topology to tridentate ligands with NHC



Scheme 56. Tripodal tricarbenes.

donor groups. Today pyridine- (**83**),[171] lutidine- (**84**),[172] and phenylene-bridged (**85**[173] and **86**[172a,c,d]) bis(imidazolin-2-ylidenes) are known in addition to the diethyl amine bridged ligand **87**.[174] Often, the free ligands were not isolated but generated in situ by deprotonation of the diimidazolium salts. The molecular structure of a pincer ligand of type **83** (R = 2,6-diisopropylphenyl) was reported by Danopoulos et al.[175] The lutidine- and phenylene-bridged diazolium precursors of the bis(benzimidazolin-2-ylidenes) **88**[176] and **89**[177] and their metal complexes have also been described without the isolation of the free dicarbene ligands (Scheme 57).

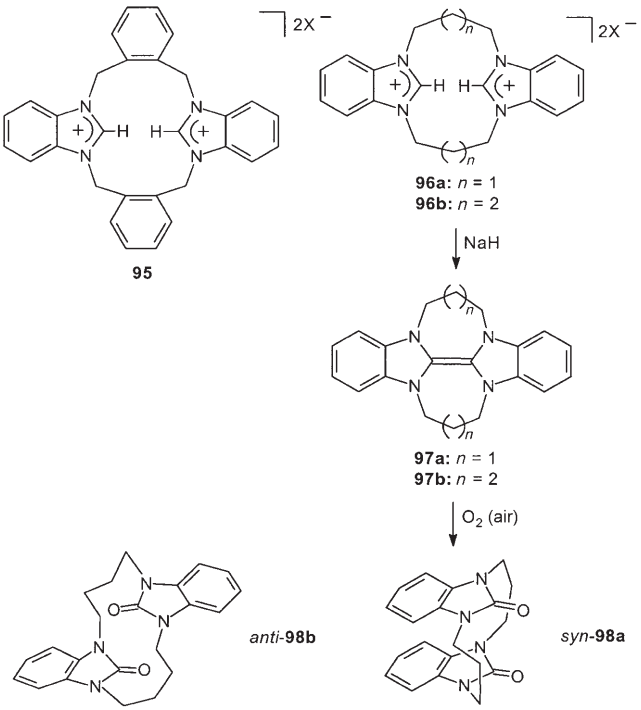
Pincer ligands containing one NHC and two additional donor groups are also known. Phosphines (**90**),[178] secondary amines,[156] pyridyl (**92**),[179] or phenoxylato groups (**93**)[180] can function as additional donors. Again, the free ligands were not usually isolated but generated in situ. A double-phosphine-substituted benzimidazolin-2-ylidene **94**[181] has also been reported in addition to the unstable diallyl-substituted



Scheme 57. "Pincer" ligands with NHC donor groups.

derivatives (Scheme 39). NHC ligands with chiral N,N′-donor groups will be presented below. A detailed account of the chemistry of carbene-containing pincer ligands has been presented by Pugh and Danopoulos.[182] Catalytic applications for complexes with carbene pincer ligands are discussed in a review by Peris and Crabtree.[183]

Among the polydentate carbene ligands, particular interest has recently been placed on cyclic polycarbenes, which can be considered as isomers of porphyrins (N-confused porphyrins),[184] phthalocyanins, or crown-ethers with carbon donor groups. The synthesis of such ligands requires the prior preparation of suitable cyclic polyazolium salts. Shi and Thummel prepared compounds **95** and **96** in 1995, which at the time were the first derivatives of this type (Scheme 58).[185]



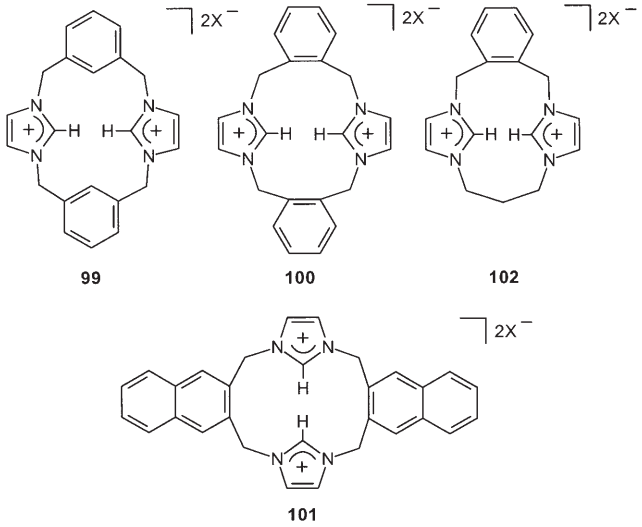
Scheme 58. Cyclic dibenzimidazolium salts and their reactions.

The cation in **96a** can be double deprotonated and the resulting bis(benzimidazolin-2-ylidene) reacts, as was observed for the singly bridged derivatives (Figure 4), immediately under formation of the dibenzotetraazafulvalene **97a**. Reaction of **97a** with oxygen yields the bisurea derivative *syn*-**98a**.[185c]

An expansion of the alkyl bridges by just one methylene group leads under similar reaction conditions to the isolation of *anti*-**98b** (Scheme 58).[185c] A similar reactivity regarding deprotonation and oxidation was observed for **95**.

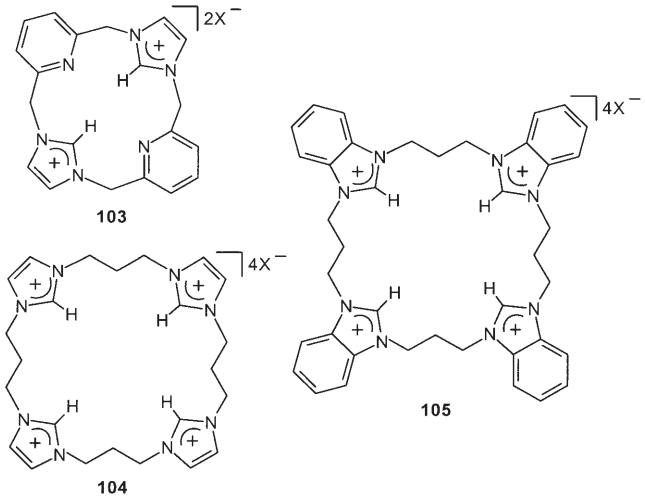
The molecular structures of *syn*-**98a** and *anti*-**98b**[185a,c] and in particular the molecular structure of the rhodium(I) complex with the dicarbene ligand derived from **97a**[185b] clearly demonstrate that dibenzimidazolium salts such as **95** and **96** are not capable of forming macrocyclic carbene complexes. The carbene donors obtained after deprotonation at C^2, for example, occupy *cis*-positions in a square-planar

metal complex and therefore the metal is not bound in the center of the cycle. Similar results were obtained with the dicarbene ligands obtained after deprotonation of **99**,[186,187] **100**,[188] **101**,[189] and **102**[190] (Scheme 59). The ligands are readily deprotonated, but they do not form macrocyclic complexes with coplanar oriented carbene donor groups.



Scheme 59. Cyclic diimidazolium salts.

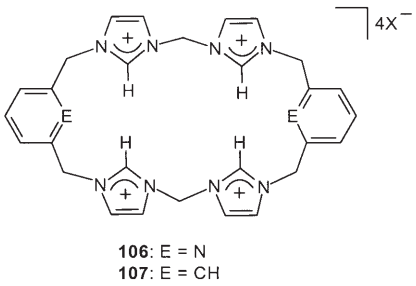
The potentially tetradentate macrocycle derived from **103** (Scheme 60), described by Baker et al.,[191] does after deprotonation of the imidazolium groups bind a metal in the center



Scheme 60. Macrocyclic di- and tetraazolium salts.

of the ring. Cyclic tetraimidazolium[192] and tetrabenzimidazolium salts,[185a,192] such as **104** and **105**, were synthesized during the search for anion receptors. The azolium salts **103**–**105** are in principle suitable for the preparation of complexes with macrocyclic di- and tetracarbene ligands. The orientation of the carbene donor groups in complexes with flexibly bridged carbene ligands derived from **104** and **105** remains, however, a point of interest (see Scheme 110).

The tetraimidazolium salt **106** with two additional pyridyl donors has been prepared recently (Scheme 61).[193] The X-ray structure analysis (Figure 5) shows that the C^2–H groups of the imidazolium rings are directed towards the center of the macrocycle.[193] This orientation leads to C^2–H···X hydrogen bonds to the halogen anions located in the center of the macrocycle where they remain after functioning as inorganic templates in its formation. Quadruple deprotonation yields a tetracarbene ligand which contains a total of six donor groups arranged in two connected endocyclic "pincer" units (compare with **84**, Scheme 57). The coordination chemistry of **106** is discussed in Section 3.6.



Scheme 61. Macrocyclic tetraimidazolium salts.

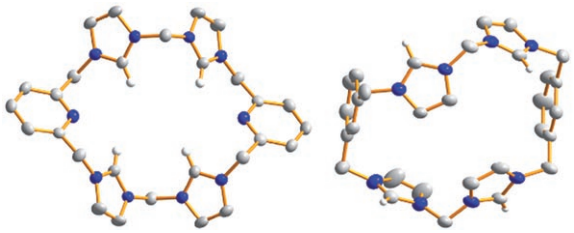


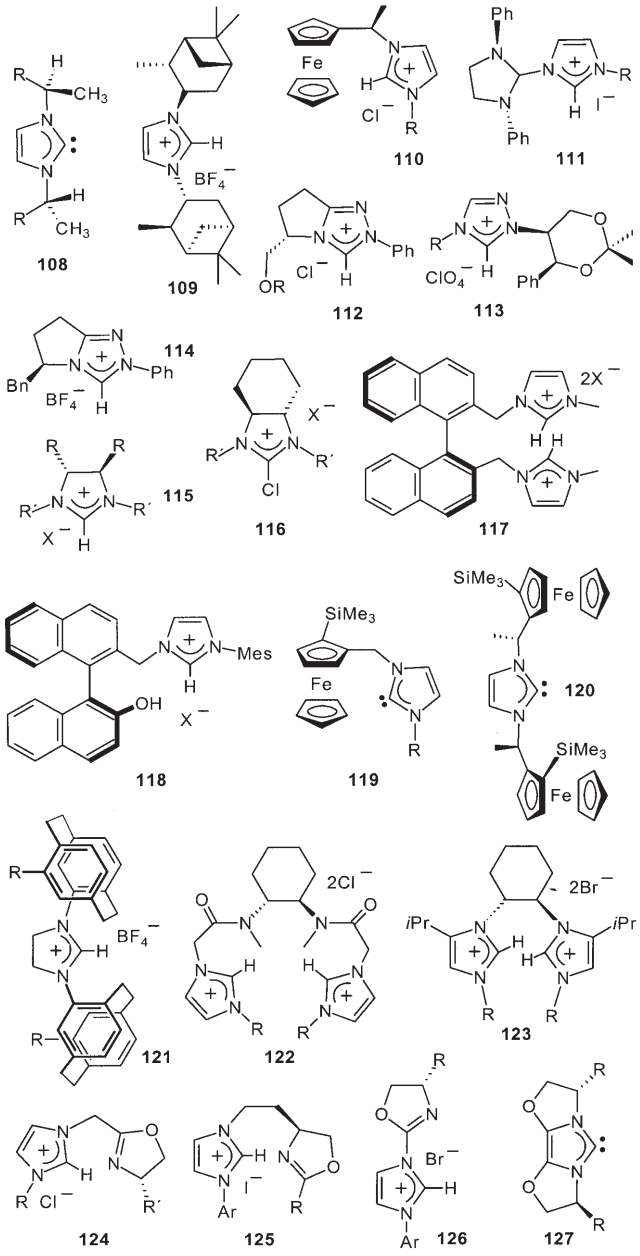
Figure 5. Molecular structures of the tetraimidazolium cations in **106** (left) and **107** (right).

The macrocyclic tetraimidazolium salt **107**[194] has been prepared by Hahn and co-workers. The structure analysis (Figure 5) shows a different conformation of the tetracation in **107** compared to the tetracation of **106**. The potential donor groups in the tetracation of **107** are not oriented towards the center of the macrocycle. It can be expected, however, that, as found for **106**, a dinuclear complex with two endocyclic $C_{carbene}$-$C_{phenylene}$-$C_{carbene}$ pincer units is obtained after deprotonation of the imidazolium groups and metalation of the carbene and phenylene groups.

Substituted heterocyclic carbenes form an important group of chiral ligands. Complexes of such ligands have found applications in asymmetric catalysis. Whereas the chirality of the carbene is of paramount importance for asymmetric catalysis it is normally of no significance regarding the stability of the carbene ligand or its bond to a metal center. In principle, chirally modified carbene ligands behave

like their achiral imidazolin-2-ylidene **17**, imidazolidin-2-ylidene **23**, triazolin-5-ylidene **26**, and benzimidazolin-2-ylidene **28** analogues. Since asymmetric catalysis is not the subject of this review, the reader interested in this topic is referred to the recent reviews by Gade et al,[42,195] an older review by Herrmann,[33a] and additional accounts.[196] The following is a brief summary about selected chiral NHC ligands.

Following the classification of Gade et al.[42] chiral N-heterocyclic carbenes (Scheme 62) can be subdivided into six groups. Carbenes such as **108**, which contain a chiral center at one of the N-substituents were first prepared by Herrmann et al. according to the method depicted in Scheme 15. They were the first chiral NHC ligands.[197] Additional imidazolium salts with chiral N,N′-substituents, such as **109**,[198] **110**[199] and **111**,[200] were subsequently synthesized. The triazolium salts **112**,[201] **113**,[202] and **114**[203] containing chiral N-substituents have also been described. The second group of chiral carbenes or their azolium precursors contain a chiral center within the N-heterocyclic ring. Such carbenes or imidazolidinium salts normally have substituents at the C^4 and C^5 positions of the heterocycle and are in general derived from compound **115**.[204] The substituents R′ at the nitrogen atoms can also contain a chiral carbon atom. This group also includes the salt **116** derived from *trans*-1,2-diaminocyclohexane[205] which was first presented by Fürstner et al. Additional examples for carbenes with chirally modified heterocycles are presented in Schemes 23 and 24. Bridging of two carbene donor groups with the 1,1′-binaphthyl moiety leads to ligands with axial chirality. The diimidazolium salt **117**[206] and the analogous benzimidazolium derivative[207] belong to these ligand precursors as well as the hydroxy-substituted imidazolium derivative **118**.[208] The fourth group of chiral N-heterocyclic carbenes or imidazolium precursors are the planar-chiral derivatives. The first representative of this group **119** was presented by Bolm et al.[209] Shortly thereafter, Togni et al. described the C_2-symmetrical ferrocenyl carbene **120**.[210] Similar compounds[211] or derivatives with phosphine substituents[212] at the ferrocenyl moiety are also known. Novel NHC ligands with N-paracyclophane substituents (**121**) were first reported in 2003.[213] It was again the group of Bolm who in 2004 prepared an N-paracyclophane-N′-phosphine substituted planar-chiral imidazolium salt.[214] The enantiomerically pure *trans*-1,2-diaminocyclohexane has been a useful starting material for the generation of chiral ligands. Burgess et al. synthesized the first diimidazolium salt **122** with this backbone.[215] Douthwaite et al. also used this chiral building block for the synthesis of a bidentate ligand containing an imidazolidin-2-ylidene and an imine donor.[216] Subsequently the chiral diimidazolium-ligand precursor **123**[217] was prepared. The last group of chiral NHC ligands or ligand precursors contains oxazoline groups. The first ligand of this type, **124**, was reported by Herrmann et al. in 1998.[218] Burgess et al. slightly modified the ligand backbone and used the oxazoline C^4 atoms for bridging to obtain the imidazolium salt **125**.[219] Gade et al. described the synthesis of **126** in which the two heterocycles are directly connected.[195,220] Monodentate carbenes, substituted with two oxazoline heterocycles such as **127**, have been prepared by Glorius et al.,[221] while Bolm et al. presented a mixed oxazoline-(imidazolidin-2-ylidene) ligand containing a chiral paracyclophane unit as bridge between the donor groups.[222] In addition, a planar-chiral imidazolium salt containing both an oxazoline and an imidazolium group as substituents of a cyclopentadienyl ligand in ferrocene is also known.[223] The preparation and coordination chemistry of oxazoline-substituted NHC ligands has recently been reviewed by Gade et al.[195]

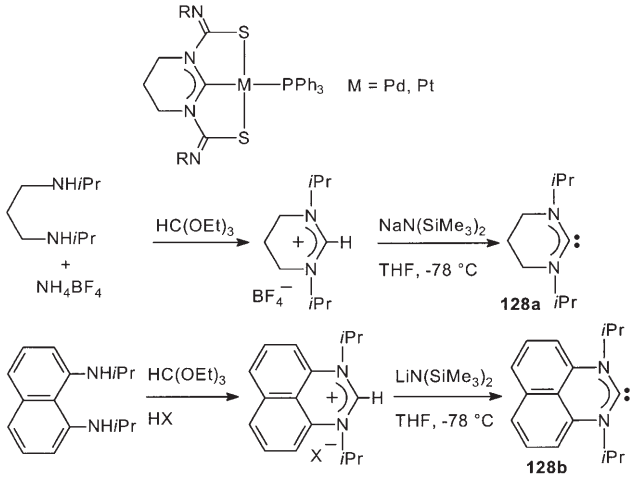


Scheme 62. Chiral azolium salts and NHC ligands.

2.4. N-Heterocyclic Carbenes Derived from Six- or Seven-Membered Heterocycles

Complexes with cyclic diaminocarbenes derived from a six-membered heterocycle have been known since 1996

(Scheme 63).[224] The first stable carbene with a six-membered heterocycle **128a** was prepared by Alder et al. according to Scheme 63.[83a] Richeson et al. described a similar carbene with a six-membered heterocycle **128b**,[225] which is derived



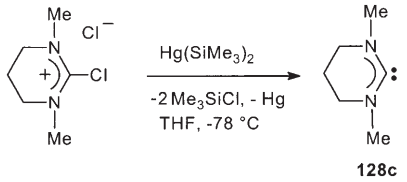
Scheme 63. N-Heterocyclic carbenes with a six-membered heterocycle.

from diaminonaphthalene. The carbenes **128a** and **128b** do not dimerize to the entetraamines under standard conditions. However, the formation of *syn*- and *anti*-entetraamines has recently been described for N,N′-diaryl and unsymmetrically N,N′-substituted derivatives of **128b**.[225b] The resonance signals for the C^2 carbon atoms have been recorded downfield in the ^{13}C NMR spectra at $\delta = 236$ ppm (**128a**)[83a] and $\delta =$ 241.7 ppm (**128b**)[225] as expected for saturated N-heterocyclic carbenes. These values fall in the range normally observed for the C^2 carbon atom of saturated imidazolidin-2-ylidenes of type **23** (Scheme 31).

X-ray structure analyses (for **128a**, only the molecular structure of the potassium adduct was determined) show short endocyclic C–N bonds (1.359(6) Å for **128b**) and longer exocyclic (1.414(6) Å for **128b**) C–N bonds which are typical for N-heterocyclic carbenes. In contrast to their analogues with a five-membered heterocycle, carbenes of type **128** exhibit a larger N^1-C^2-N^3 angle of 116.3(2)° (potassium adduct of **128a**) and 115.3° (**128b**).

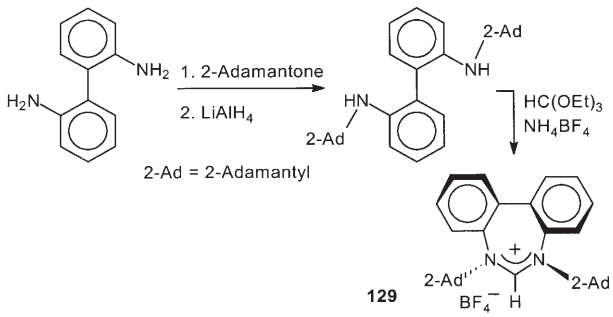
The synthetic method for **128a** depicted in Scheme 63 also allows the preparation of chirally modified carbenes with a six-membered ring or the preparation of their formamidinium precursors starting from chiral-substituted 1,3-diaminopropane.[226] An alternative method for the generation of cyclic six- or seven-membered formamidinium cations has been described by Bertrand et al.[227] Reaction of the lithium salt of dimesitylformamidine with dielectrophiles such as 1,3-dibromopropane or α,α′-dibromo-*o*-xylene, results in the formation of cyclic six- or seven-membered formamidinium salts in good yield relative to the classic method for the preparation of such derivatives.[228]

It is generally accepted that the saturated carbenes possessing a six-membered heterocycle as well as the acyclic diaminocarbenes such as **37** (Scheme 43) are stronger bases than the carbenes derived from a five-membered heterocycle of types **17** and **23**. The six-membered cyclic formamidinium ions are also attacked by nucleophiles much faster than the imidazolium and imidazolidinium cations. To prevent a nucleophilic attack, sterically demanding bases are therefore used for the generation of carbenes of type **128** from formamidinium salts (Scheme 63). If, for example, the formamidinium precursor of **128b** is deprotonated with the less-bulky base NaO*t*Bu, no N-heterocyclic carbene can be isolated but addition of the O*t*Bu$^-$ ion at the C^2 carbon atom is observed. In addition, the deprotonation of cyclic six-membered formamidinium salts often leads to the isolation of alkali-metal adducts of the carbene as observed in the synthesis of **128a**. Bertrand et al. developed a method for the preparation metal-free diaminocarbenes which is also suitable for the synthesis of cyclic diaminocarbenes of type **128**.[229] In this synthesis 2-chloro-1,3-dimethyltetrahydropyrimidin-2-ium chloride is treated with bis(trimethylsilyl)mercury[230] resulting in dehalogenation of the N-heterocyclic ring to give the carbene **128c** (Scheme 64). In spite of the sterically less-demanding N-methyl substituents, carbene **128c** shows no tendency to dimerize.



Scheme 64. Synthesis of NHCs by dehalogenation with $Hg(SiMe_3)_2$.

The heterocycles of the cyclic carbenes with three to six ring atoms are more or less planar. Condensation of 2,2′-diaminobiphenyl with 2-adamantone followed by reduction of the imine and cyclization with triethyl orthoformiate yields the nonplanar cyclic C_2-symmetrical amidinium salt **129** (Scheme 65).[231] The amidinium salt **129** can be deprotonated in situ and has been used for the preparation of a number of metal carbene complexes.[231] The free carbene with a seven-membered ring has not yet been isolated.



Scheme 65. Synthesis of the amidinium salt **129**.

3. Synthesis and Reactivity of Complexes with Heterocyclic Carbene Ligands

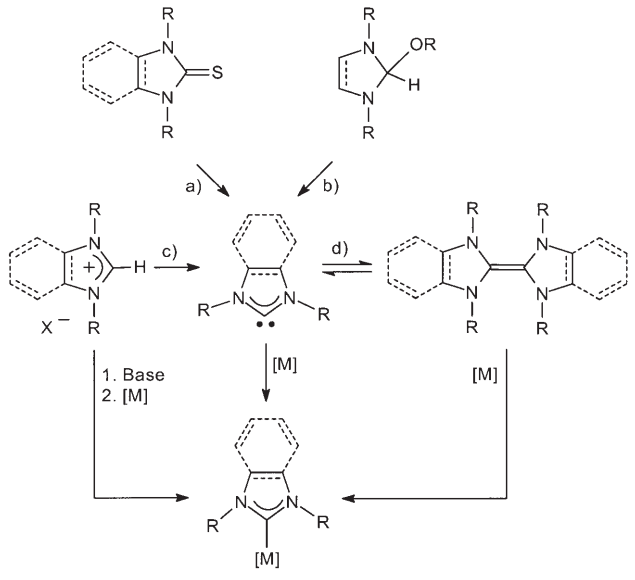
Over the last few years the number of complexes bearing heterocyclic carbene ligands has increased rapidly. In addition to complexes of all the transition-metals[31,33,34] and adducts with a large number of main-group elements,[41] carbene complexes of the lanthanides,[232] uranium,[233] and of the radioactive technetium isotope ^{99}Tc are known.[234] A large number of these complexes have found application in catalytic reactions[33,34] such as the C-C cross-coupling[35] or the olefin metathesis.[36,37] Recent studies deal with complexes containing N-heterocyclic carbenes substituted at the nitrogen atoms with carbohydrate[235] or dendritic groups.[236] In addition, complexes with carbene ligands derived from caffeine[237] are known as well as the potentially hexanuclear complex of a hexaimidazolium salt.[238]

The vast majority of the complexes bearing heterocyclic carbene ligands have been obtained by ligand substitution at the metal center. To apply this method, the carbene to be introduced must be available as a stable species, or at least, as a reactive intermediate. This explains the dominance of the stable N-heterocyclic carbenes with five-membered heterocycles in the organometallic NHC coordination chemistry, although meanwhile some stable P-heterocyclic carbenes, cyclic alkyl(amino)carbenes, and thiazolin-2-ylidenes derived from five-membered heterocycles, as well as some diaminocarbenes exhibiting larger or smaller heterocycles are known (see Section 2). The two most important methods for the synthesis of complexes with cyclic heterocarbene ligands are shown in Scheme 66 for diaminocarbenes with five-membered heterocycles.

The simplest method for the preparation of an NHC complex is the reaction of the free carbene with a suitable metal complex. The preparation of the generally air-sensitive carbenes according to Scheme 66 a–d has been discussed in Section 2. However, metal complexes with N-heterocyclic diaminocarbenes were known long before the first stable NHCs were isolated. Wanzlick and Öfele demonstrated as early as 1968 that NHC complexes can be obtained by in situ deprotonation of azolium salts in the presence of a suitable metal complex, without isolation of the free carbene ligand. Wanzlick and Schönherr treated an imidazolium salt with mercury(II) acetate and generated the carbene complex and acetic acid,[27] while Öfele simply heated dimethylimidazolium hydridopentacarbonylchromate(−II) resulting in formation of the carbene complex and molecular hydrogen (Scheme 7).[28] A ligand of the metal precursor (acetate or hydride) acted in both cases as the base for the deprotonation of the imidazolium cation. This method can be adapted to other metal precursors containing basic ligands such as $Pd(OAc)_2$[161,239] and [(cod)Ir(μ-OR)$_2$Ir(cod)] (cod = cyclooctadiene).[94e,240] or modified by addition of an external base, such as NaOAc, NaH, KO*t*Bu, or MHMDS (M = Li, Na, K). Many NHC complexes have been prepared by the in situ deprotonation of azolium salts including complexes bearing carbenes based on three-,[48,49] four-,[241] six-,[83a] or seven-membered[231] cycles. The in situ deprotonation is also suitable for the preparation of complexes with thiazolin-2-ylidene-[242] and benzothiazolin-2-ylidene ligands.[123,243]

An alternative, also very general method for the preparation of complexes with heterocarbene ligands, has been developed by Lappert et al. This group demonstrated that electron-rich entetraamines can be cleaved into the carbene monomers in the presence of coordinatively unsaturated electrophilic metal complexes. The heterocyclic carbene ligands are then stabilized by coordination to the metal center (Scheme 66).[29,244] The empty p orbital of an N-heterocyclic diaminostannylene is sufficiently electrophilic to cleave the tetramethyldibenzotetraazafulvalene **28b**=**28b** (Figure 2).[245a] Other dibenzotetraazafulvalenes have been cleaved by [{RhCl(cod)}$_2$],[246] PdI_2[163,247] or [Mo(nor)(CO)$_4$][111] (nor = norbornadiene) to give complexes with benzimidazolin-2-ylidene ligands.

The preparation of NHC complexes according to the methods shown in Scheme 66 and the properties of such complexes have been the subject of a number of reviews.[31–34] Selected new methods for the preparation of NHC complexes will be presented in the following sections.

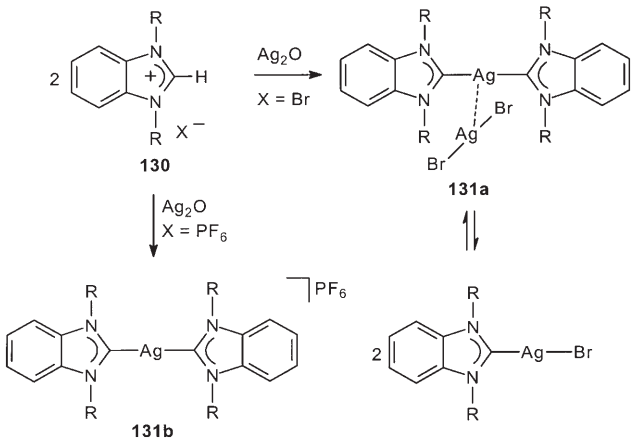


Scheme 66. Standard methods for the preparation of NHC complexes.

3.1. Carbene Transfer Reactions with Silver NHC Complexes

One method for the in situ deprotonation of azolium salts under formation of NHC complexes deserves special attention. Arduengo et al.[248] and Bertrand et al.[92a,b] have prepared silver(I) NHC complexes using the methods shown in Scheme 66. An alternative, versatile procedure leading to such complexes was introduced by Lin et al. in 1998. They treated the *N*,*N*′-diethylbenzimidazolium salt **130** with Ag_2O, which serves as a particularly mild base (Scheme 67).[249] Depending on the counterions present in the benzimidazolium salt they obtained the complexes **131a** or **131b**.

NMR spectroscopy shows that in solution, complex **131a** dissociates into two mononuclear silver NHC complexes, thus indicating the lability of the Ag–C^2 bond. In fact, silver NHC



Scheme 67. Synthesis of silver NHC complexes by the Ag_2O method.

complexes have been shown to be excellent agents for the transfer of a carbene ligand to another metal center. In the meantime, a series of silver NHC complexes has been obtained by the reaction of azolium salts with Ag_2O in dichloromethane at ambient temperature. Depending on the N,N′-substituents and the counterions they were isolated as salts [NHC-Ag-NHC][AgX_2] (analogous to **131a**) or as neutral complexes [NHC-Ag-X] or [NHC-Ag(μ-X)$_2$Ag-NHC]. The transfer of the NHC ligands from such complexes to a number of transition metals has been described (Ag_2O method). The Ag_2O method offers a number of advantages. The silver NHC complexes can be prepared in air. Specially purified solvents or an additional base are not necessary. Deprotonation of the azolium salts normally occurs at the C^2 position and other acidic protons in the azolium salts generally do not react. The preparation of silver NHC complexes using the Ag_2O method and the transfer of the NHC ligand to other transition metals has become a standard procedure in spite of a few reported cases where the method failed.[87] The Ag_2O method often gives access to NHC complexes where alternative syntheses are tedious or unsuccessful.

Alternative NHC-transfer procedures, such as the carbene transfer from triethylborane-carbene adducts[250] or from complexes of type [M(NHC)(CO)$_5$] (M = Cr, Mo, W),[251] have not reached anything like the general applicability of the Ag_2O method. The reported carbene transfer of the *N*,*N*′-diallylimidazolidin-2-ylidene ligands from palladium to rhodium[252a] or of pyrazolin-3-ylidenes from chromium to other transition metals[252b] are also interesting but rather exotic examples. The diverse molecular structures and the properties of silver NHC complexes have been reviewed in a comprehensive manner by Garrison and Youngs.[253] Lin and Vasam have recently summarized the advantages and applications of the Ag_2O method.[254] Silver NHC complexes have been shown to possess antibiotic properties. This interesting aspect of NHC coordination chemistry has been reviewed recently by Youngs et al.[255]

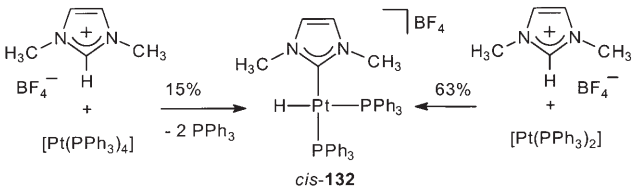
3.2. Synthesis of NHC Complexes by Oxidative Addition of the C^2–X Bond and Reductive Elimination Reactions

More than 30 years ago Roper et al. reported on the oxidative addition of 2-chloro derivatives of 5-methylthiazole, benzothiazole, benzoxazole, and of the *N*-methyl-2-chloro-5-methylthiazolium cation to d^8 or d^{10} complexes of iridium, palladium, platinum, and nickel.[256] This account of a potential synthetic method for the preparation of NHC complexes of the late transition metals went largely unnoticed. Cavell and Yates showed in 2001 experimentally and by DFT calculations that the oxidative addition of the C^2–X bond of imidazolium cations to electron-rich d^{10} metals is energetically feasible.[257] The results of the DFT calculations indicate that

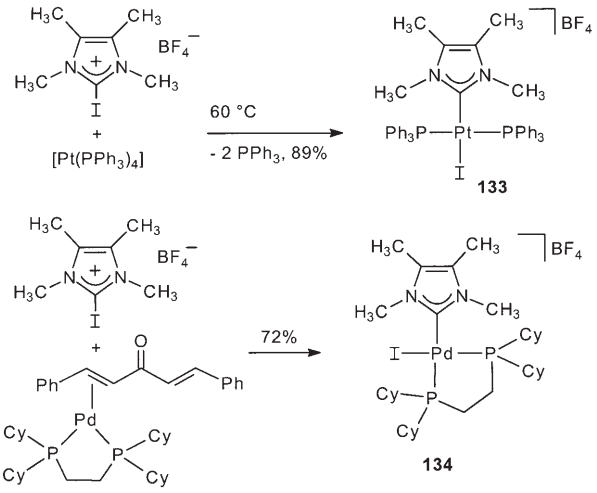
1. the oxidative addition of the 1,2,3-trimethylimidazolium cation (C^2–X; X = CH_3) to [H_3P-M-PH_3] is an exothermic reaction for M = Pt^0 and Ni^0, whereas it is slightly endothermic for M = Pd^0 (3.7 kcal mol^{-1}), and the activation enthalpy is lowest for Ni^0 (7.1 kcal mol^{-1});
2. *cis*-coordinated basic chelate ligands at Pd^0 lower the activation barrier for the oxidative addition of imidazolium cations (C^2–X; X = CH_3, H, halogen) compared to monodentate phosphines and make the oxidative addition more exothermic;
3. the exothermic character of the oxidative addition to Pd^0 increases in the order X = alkyl < H < halogen and the activation barrier decreases in the same order.

These predictions were experimentally confirmed by oxidative additions of C^2–H and C^2–I bonds to Pt^0 complexes, whereas the oxidative addition of the 1,2,3-trimethylimidazolium cation was not observed. The reaction of the 1,3-dimethylimidazolium cation with complex [$Pt(PPh_3)_4$] leads in low yield (15%) to the *cis*-hydrido complex **132** (Scheme 68). The yield did not increase at elevated temperatures but isomerization to the *trans*-complex was observed instead. Based on this observation an equilibrium between the reaction products of the oxidative addition and the reductive elimination was postulated (see below). Use of the coordinatively unsaturated 14-electron complex [$Pt(PPh_3)_2$] increases the yield of the hydrido complex **132** to 63% (Scheme 68).

As indicated by the DFT calculation, the oxidative addition of the C^2–halogen bonds to Pt^0 and Pd^0 proceeds readily. The 2-iodotetramethylimidazolium cation can be added to both Pt^0 and Pd^0 giving complexes **133** and **134** in good yields (Scheme 69).[257]

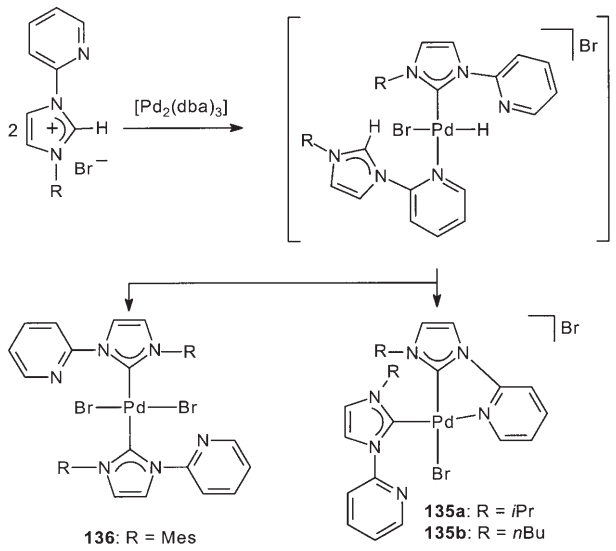


Scheme 68. Oxidative addition of the C^2–H bond of an imidazolium cation to Pt^0.



Scheme 69. Oxidative addition of C^2–I bonds to Pt^0 and Pd^0.

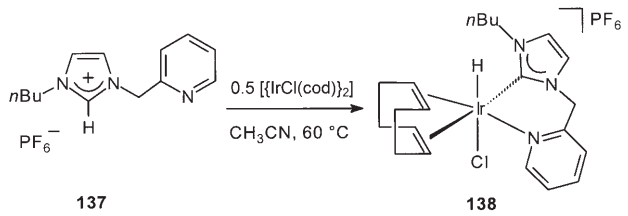
Crabtree and Faller tried to use the chelate effect of *N*-(2-pyridyl)imidazolium cations to prepare Pd^0 hydrido complexes by oxidative addition.[258] They could, however, only isolate the dicarbene complexes (Scheme 70). The formation



Scheme 70. Oxidative addition of *N*-(2-pyridyl)imidazolium cations to Pd^0. dba = dibenzylideneacetone.

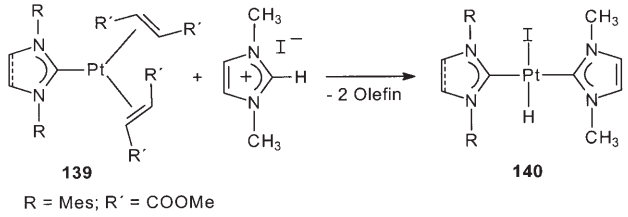
of the cationic complex *cis*-**135** and of the neutral *trans*-dicarbene complex **136** is based on the steric demand of the *N*′-substituents with the more demanding mesityl substituent enforcing the formation of *trans*-**136**. A monocarbene hydrido complex was proposed as primary reaction product of the oxidative addition. However, this complex could not be isolated. Coordination of the pyridyl group proved essential for the oxidative addition reaction. No oxidative addition was observed for imidazolium salts without an additional donor group.

Peris et al. had more success when they studied the oxidative addition of *N*-(2-pyridylmethyl)imidazolium cations to iridium(I). Reaction of *N*-*n*-butyl-*N*′-(2-pyridylmethyl)imidazolium hexafluorophosphate **137** with [{IrCl(cod)}$_2$] in acetonitrile yields, at 60 °C within 2 h, the hydrido chelate complex **138** in a yield of 70 % (Scheme 71).[259] The reaction proceeds most likely by initial coordination of the nitrogen donor which brings the imidazolium C^2–H bond in close proximity to the metal center. No reaction was observed with rhodium(I) under the conditions described above.



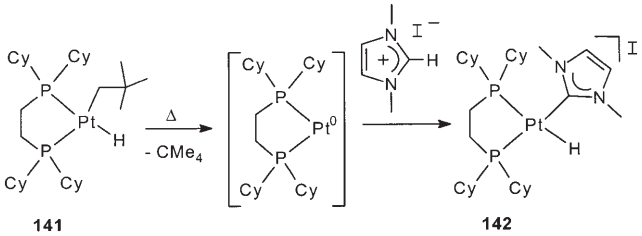
Scheme 71. Oxidative addition of the *N*-*n*-butyl-*N*′-(2-pyridylmethyl) imidazolium cation to an Ir^I center.

Cavell and Elsevier used NHC complexes of type **139** for the oxidative addition of imidazolium salts. Monocarbene complexes of Pt^0 bearing saturated or unsaturated NHC ligands activate the C^2–H bond of imidazolium salts at ambient temperature forming the thermally stable hydrido platinum complex **140** bearing two NHC ligands in *trans*-positions (Scheme 72).[260] The good σ-donor properties of the first carbene ligand most likely support the subsequent oxidative addition of the imidazolium cation.



Scheme 72. Oxidative addition of an imidazolium salt to the monocarbene Pt^0 complex **139**.

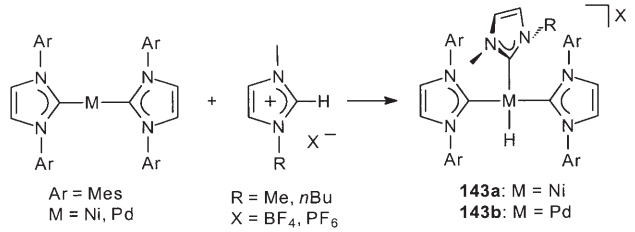
Particularly electron-rich platinum complexes are obtained with phosphine ligands. The reductive elimination of neopentane from **141**[261] yields a highly reactive Pt^0 compound as an intermediate, which at 80 °C oxidatively adds dimethylimidazolium iodide to give the hydrido complex **142** (Scheme 73).[260] This method is only applicable for sterically less-demanding N,N′-substituted imidazolium salts



Scheme 73. Oxidative addition to a Pt^0 diphosphine complex.

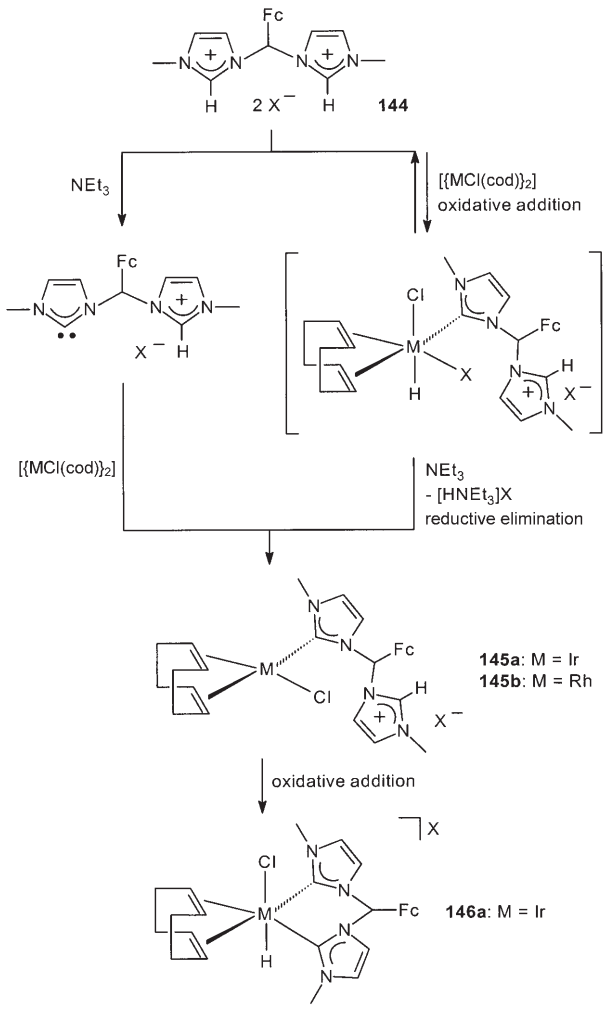
because the sterically demanding cyclohexyl substituents at the phosphorus atoms prevent the addition of imidazolium cations with bulky substituents.

Cavell et al. have prepared the tris(NHC) hydrido complexes of nickel(II) (**143a**) and palladium(II) (**143b**) by oxidative addition of dialkylimidazolium cations (Scheme 74)[262] to electron-rich and coordinatively unsaturated complexes of the type $[M^0(NHC)_2]$ (M = Ni, Pd) which were generated in situ.[263] The oxidative addition to nickel(0) proceeds at ambient temperature, whereas the palladium complex **143b** forms at 55 °C. The tris(NHC) hydrido complexes are surprisingly stable. Complex **143a** does not decompose after heating in boiling THF for 16 h. The remarkable stability is caused by the electronic situation at the metal center in addition to the steric protection granted by the three carbene ligands. The reductive elimination of an imidazolium cation is prevented by the lack of orbital overlap between the hydrido ligand and the carbene carbon atom.



Scheme 74. Oxidative addition of dialkylimidazolium cations to M^0 dicarbene complexes. M = Ni, Pd.

Peris et al. have studied the oxidative addition of bridged diimidazolium salts to $[\{RhCl(cod)\}_2]$ and $[\{IrCl(cod)\}_2]$ in the presence of the base triethylamine (Scheme 75).[264] The square-planar rhodium complex **145b** was obtained with the Fc-CH-bridged diimidazolium salt **144** (Fc = ferrocenyl). The analogous iridium complex **145a** could not be isolated in a pure form. It reacted spontaneously under oxidative addition of the second imidazolium moiety to give the octahedral iridium(III) hydrido complex **146a**. The iridium(III) complex **146a** is stable in solution. The rhodium complex **145b**, on the other hand, does not react in a second oxidative addition to give the rhodium(III) dicarbene hydrido complex. The reaction **145a**→**146a** is clearly an oxidative addition. Two different reaction pathways were proposed for the first metalation to give **145a** and **145b**.[264b] The presence of the base triethylamine is required for the formation of **145a** and **145b**. No metalation was observed without the base. The deprotonation of the diimidazolium salt by the weak base triethylamine is, however, not very likely. Alternatively, the operation of an addition–elimination equilibrium is conceivable (Scheme 75). Initially one imidazolium cation adds oxidatively to Rh^I or Ir^I. This initial reaction product can decompose by reductive elimination of the imidazolium cation to the starting materials. In the presence of the base triethylamine the intermediate M^{III} complex is capable of undergoing a different reductive elimination, this time of HX, to give the M^I complexes of type **145**. Both reaction pathways depicted in Scheme 75 (the deprotonation of the imidazolium cation followed by coordination or the oxidative addition of the imidazolium cation followed by the NEt_3-promoted reductive elimination of HX) yield identical reaction products, namely the complexes of type **145**. The actual type of reaction pathway might be of significance for the preparation of NHC complexes.

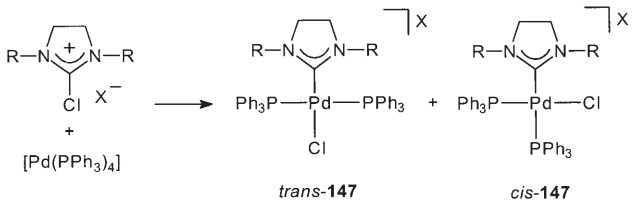


Scheme 75. Oxidative addition of diimidazolium salts to Rh^I and Ir^I. Fc = ferrocenyl.

The type of bridge between the imidazolin-2-ylidene groups in **146** is of importance for the stability of the complexes. Complexes with longer alkyl chains between the imidazolin-2-ylidene donors are not stable but decompose by reductive elimination of HCl to give square-planar bis(imidazolin-2-ylidene) complexes.[264b]

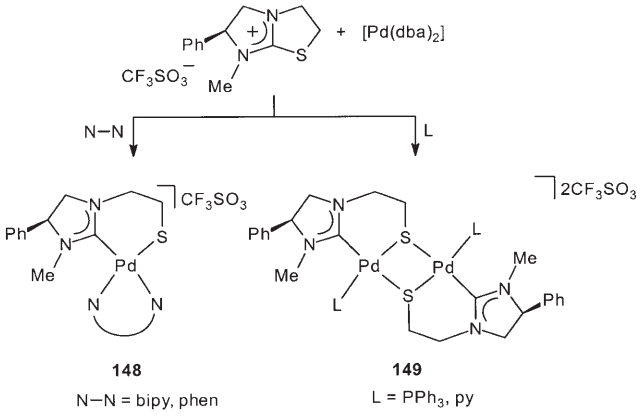
The first calculations of Cavell et al.[257] already demonstrated that the oxidative addition of C^2–X functionalized imidazolium cations (X = halogen) to d^{10} metal centers (Scheme 69) proceeds faster and with a more favorable reaction enthalpy than the oxidative addition of the C^2–H and C^2–C bonds. The oxidative addition of C^2–X functionalized azolium cations to different transition metal was therefore studied in detail. Fürstner et al. demonstrated that the oxidative addition of 2-chloroimidazolidinium cations to $[Pd(PPh_3)_4]$ provides an easy access to palladium complexes

of saturated N-heterocyclic carbenes (main product: *trans*-**147**, side-product: *cis*-**147**; Scheme 76).[205,265] A large number of 2-chloroazolium salts are commercially available and a simple synthetic procedure was developed for additional derivatives.[265] This procedure involves the cyclization of a suitable diamine with thiophosgene followed by chlorination to the 2-chloroazolium salt by phosgene or oxalyl chloride. Starting with chiral diamines this method also allows the preparation of chiral 2-chloroazolium salts, such as **116** (Scheme 62). Access to derivatives with a six-membered heterocycle, such as 2-chloro-1,3-dimethyltetrahydropyrimidin-2-ium chloride (see Scheme 64), is also possible. Bertrand et al.[229] have shown that the dehalogenation of this compound leads to the free carbene with a six-membered heterocycle (Scheme 64) which can coordinate to a metal center. The oxidative addition of the 2-chloro-1,3-dimethyltetrahydropyrimidin-2-ium chloride to Pd^0 yields directly the palladium complex.[265] The oxidative addition of the C^2–Cl bond can be applied for the synthesis of various palladium complexes including those with acyclic mono and diaminocarbene ligands.



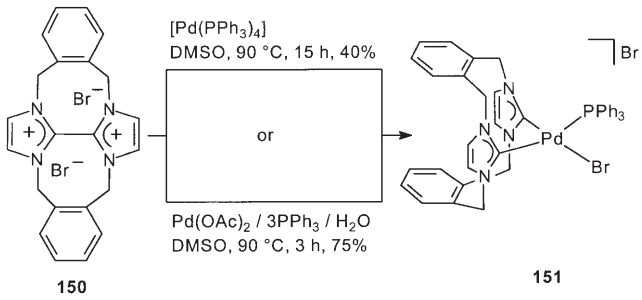
Scheme 76. Oxidative addition of C^2–Cl bonds to Pd^0 centers.

An example for the oxidative addition of a C^2–S bond to Pd^0 was recently described. Cabeza et al. demonstrated that methyl levamisolium triflate reacts with $[Pd(dba)_2]$ (dba = dibenzylideneacetone) to give the cationic palladium complex bearing a chiral bidentate imidazolidin-2-ylidene ligand.[266a] Mono (**148**) or dinuclear (**149**) palladium complexes were obtained in this reaction (Scheme 77) depending on the coligands at the metal center. The reaction of the levamisolium cation with triruthenium or triosmium carbonyl compounds also yields carbene complexes.[266b]



Scheme 77. Oxidative addition of the methyl levamisolium cation to Pd^0 centers. bipy = 2,2′-bipyridyl; phen = 1,10-phenathroline.

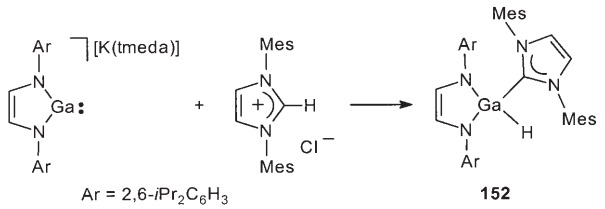
Baker et al. described the reaction of the diimidazolium bromide **150**[267] with a palladium(0) complex which yields the cyclophane carbene complex **151** (Scheme 78).[268] This reaction can, at least formally, be classified as an oxidative addition. Similar complexes with cyclophane carbene ligands have been obtained by in situ deprotonation of the diimidazolium salt **100** (Scheme 59) and coordination of the resulting dicarbene to Pd^{II}.[189] The reactivity of the diimidazolium salt with $[Pd(PPh_3)_4]$ is influenced by the counterion. A 40% conversion was found for the reaction of **150** after 15 h whereas the hexafluorophosphate analogous to **150** did not react. This oxidative addition could however, be initiated by addition of NBu_4Br. A number of reactive Pd^0 species, including $[Pd^0(PPh_3)_2]$ and compounds of type $[Pd^0X(PPh_3)_2]^-$ (X = Br) are plausible reaction intermediates.[269] Similar observations were made for the reaction of **150** with the mixture $[Pd(OAc)_2]/3\,PPh_3/H_2O$ which most likely contains $[Pd^0(PPh_3)_2Br]^-$ as the active metal species.[270] The reduction by Pd^0 of the diimidazolium cation to give the bis(imidazolin-2-ylidene) or, possibly, to the carbene dimer (Scheme 21), and the subsequent addition to Pd^{II} cannot be ruled out. Bridging of the diimidazolium cation proved essential for the formation of carbene complexes since the unbridged tetramethyl-substituted diimidazolium dication does not react with $[Pd(PPh_3)_4]$ or $[Pd(OAc)_2]/3\,PPh_3/H_2O$.[268]



Scheme 78. Postulated oxidative addition of **150** to Pd^0 centers.

Jones et al. studied the reaction of 1,3-dimesitylimidazolin-2-ylidene and of the parent imidazolium salt with an anionic gallium(I) heterocycle which is isoelectronic to the imidazolin-2-ylidenes.[271] The free carbene does not react with the gallium heterocycle. The imidazolium salt reacts by oxidative addition to gallium(I) to form the gallium(III) hydrido complex **152** (Scheme 79).

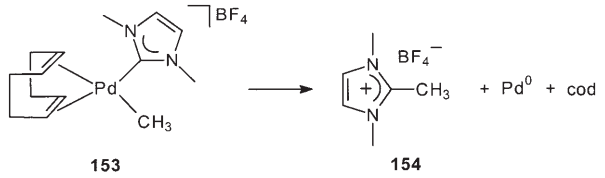
The stability of metal complexes with NHC ligands is limited despite of the superb properties of the NHC ligand. An important decomposition route, which is also of significance for catalytic applications of NHC complexes, is the reductive elimination of 2-alkyl- or 2-aryl-substituted azolium salts from NHC complexes. This type of decomposition can be considered the reverse reaction of the oxidative addition of C^2–C bonds to transition metals (discussed above). The reductive elimination produces an azolium cation from a coordinated NHC ligand and an alkyl or aryl ligand in *cis*



Scheme 79. Oxidative addition of an imidazolium cation to a Ga^{I} center.

position. The reductive elimination of azolium salts from NHC complexes has been the subject of two review articles.[34a,272]

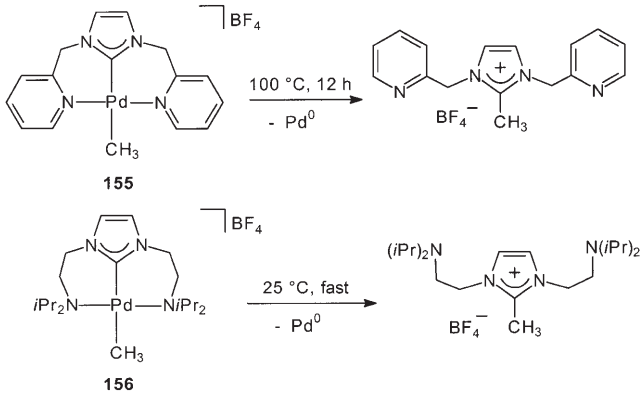
In 1998, Cavell et al. prepared and studied palladium complexes with an imidazolin-2-ylidene and a methyl ligand in *cis* position to the NHC.[150,273] Complex **153** prepared in the course of these studies not only features three different Pd–C bonds but it also decomposes upon heating to Pd^0, cod, and the 1,2,3-trimethylimidazolium salt **154** (Scheme 80).[273b]



Scheme 80. Reductive elimination of 1,2,3-trimethylimidazolium tetrafluoroborate from **153**.

Since then, a number of examples for the reductive elimination of 2-alkyl- and 2-aryl-substituted azolium salts from palladium or nickel NHC complexes have been reported.[274] Particularly, the reductive elimination of 2-aryl-substituted azolium salts from Pd^{II} provides important information regarding the catalytic cycle of the Heck C–C coupling reaction.[272,274a] Today, the reductive elimination is established as one of the important reaction pathways for the deactivation of catalytically active NHC complexes.[274,275]

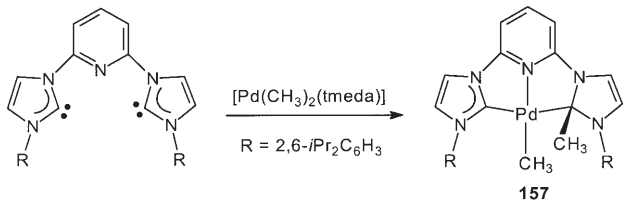
Based on theoretical and experimental studies, Cavell et al. established which features favor the reductive elimination.[276] Although different mechanisms are conceivable for the degradation of **153**, a combination of kinetic studies and quantum chemical calculations points to a reductive elimination with direct formation of Pd^0.[276a] The reductive elimination **153**→**154** is an exothermic reaction with a low activation barrier. The additional ligands at the palladium atom play an important role for the reductive elimination. Palladium complexes of the type [Pd(Me)(NHC)(P-P)] with a chelating diphosphine ligand P-P, are significantly more stable against reductive elimination than their analogues bearing two monodentate phosphine ligands. Quantum chemical calculations show that the C(Me)-Pd-C(NHC) angle becomes more acute during the reductive elimination to allow an optimal orbital overlap for the groups to be eliminated. At the same time the P-Pd-P angle becomes larger. These geometry changes, which are required for a fast reductive elimination, are best accommodated by two monodentate phosphine ligands whereas a rigid bidentate diphosphine prevents the necessary geometry change and thus slows down the reaction.[276a] Similar observations have been made for complexes with bidentate carbene ligands (donor functionalized NHCs or bis(NHC) ligands). Consequently, methyl palladium complexes bearing a chelate ligand composed of one NHC and another donor group are relatively stable[150,172b,277] because the rigid chelate ligand obstructs the mutual approach of the carbene and the methyl group during the reductive elimination. Similar conditions exist in pincer complexes where the position *cis* to the carbene ligand is not available for an alkyl group to be eliminated. Complex **155** is one of the most stable cationic methyl palladium complexes whereas complex **156** with the weaker amine donors decomposes even at ambient temperature by reductive elimination of the 2-methylimidazolium salt (Scheme 81).[187]



Scheme 81. Reductive elimination of imidazolium salts from the methyl palladium carbene complexes **155** and **156**.

Danopoulos et al. could show that the reductive elimination does not happen under certain conditions. For example, no reductive elimination, but a methyl migration was observed during the synthesis of the pincer complex **157**, which conatins particularly stable five-membered chelate rings (Scheme 82).[278]

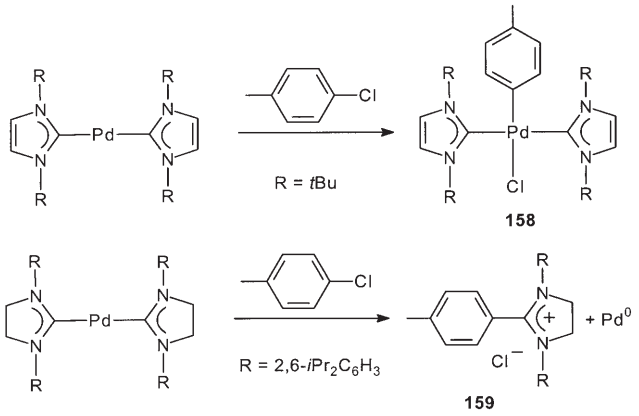
Additional factors, which determine the stability of carbene complexes towards reductive elimination, are the orientation of the NHC ligands relative to the coordination plane of the metal center, the type of NHC ligand and its N,N′-substituents. A perpendicular orientation of the carbene plane relative to the coordination plane of the metal center



Scheme 82. Synthesis of **157** by methyl migration. tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

allows for a particularly good overlap of the p_π orbital at the carbene ligand with orbitals of a methyl ligand in *cis*-position enabling a fast reductive elimination. A coplanar orientation of the carbene ligand with the coordination plane, which can be achieved by incorporation of the carbene donor into a chelate ligand,[159b,161] leads to a stabilization of the complex against reductive elimination.

Cloke and co-workers studied the oxidative addition of *p*-tolyl chloride to Pd^0 complexes with two unsaturated imidazolin-2-ylidene or two saturated imidazolidin-2-ylidene ligand. They found that in both cases the oxidative addition proceeds readily. The product of the oxidative addition in the first case (**158**) is stable whereas the Pd^{II} complex obtained in the second reaction reacts rapidly by reductive elimination of the imidazolidinium salt **159** (Scheme 83). Apparently small modifications in the electronic situation at the carbene center are sufficient to determine the course of the subsequent reactions.[279]

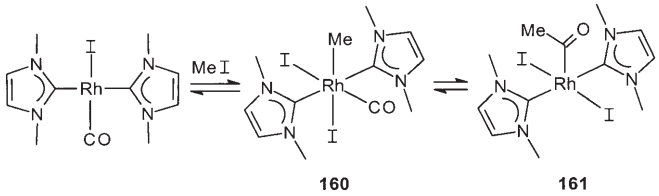


Scheme 83. Reactions of $[Pd(NHC)_2]$ complexes with *p*-tolyl chloride.

The influence of the N-substituents at the carbene ligands on the course of the reductive elimination is based on electronic effects rather than on steric effects, if their influence on the orientation of the carbene ligand relative to the metal coordination plane in square-planar metal complexes is neglected. N-substituents with a strong (+I)-effect, such as neopentyl or *tert*-butyl, lead to electron-rich NHC ligands which reduce the positive charge at the metal center and thus stabilize the complex against reductive elimination. Aromatic N-substituents oriented coplanar to the carbene ring can interact with the π system of the heterocycle. This interaction decreases the electron density at the carbene carbon atom and thus at the metal center, facilitating the reductive elimination.[272]

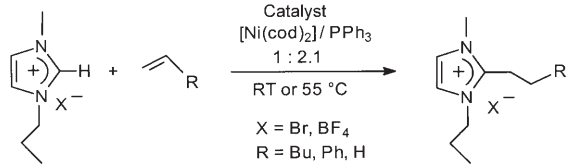
In contrast to palladium and nickel NHC complexes, no reductive elimination of azolium salts was observed for rhodium(I) NHC complexes after oxidative addition of methyl iodide.[280] Instead, an equilibrium involving two compounds is established. Slow oxidative addition of methyl iodide leads to the octahedral rhodium(III) complex **160** which then reacts by methyl migration to give the square-pyramidal complex **161** containing an acyl ligand (Scheme 84). The reductive elimination of 2-methylimidazolium salts has not been detected.

An interesting example for the combination of oxidative addition and reductive elimination has been described by



Scheme 84. Oxidative addition to a Rh^I center followed by methyl migration to yield **161**.

Cavell et al.[281] The nickel catalyst $[Ni(PPh_3)_2]$, generated in situ, oxidatively added the C^2–H bond of an imidazolium salt to form a nickel(II) hydrido complex. This complex reacts by alkene insertion into the Ni–H bond followed by reductive elimination of the 2-alkylimidazolium salt (Scheme 85). A

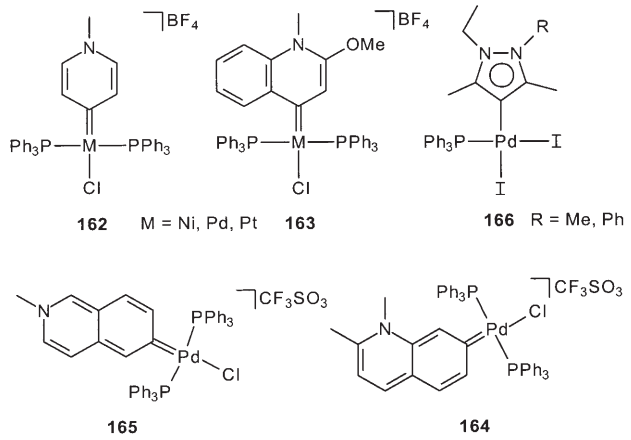


Scheme 85. Nickel-catalyzed imidazolium–alkene coupling.

similar catalytic transformation of benzimidazoles, thiazoles, and oxazoles into the 2-alkylated azoles using a rhodium NHC complex has been reported by Bergman and Ellman.[282] However, for this transformation, a different mechanism has been proposed starting from *N*-methylbenzimidazole (see Section 3.5).

3.3. Remote N-Heterocyclic Carbenes (rNHCs)

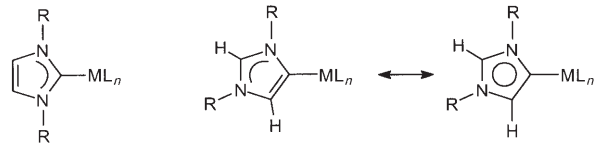
A new and interesting type of metal coordinated N-heterocyclic carbenes has recently been found. In contrast to "normal" NHCs, remote N-heterocyclic carbenes (*r*NHCs) have no heteroatom directly adjacent to the carbene carbon atom. To date no free *r*NHC ligand could be isolated. The *r*NHC complexes **162** and **163** have been prepared by Raubenheimer et al. by the oxidative addition of chloropyridinium or chloroquinolinium cations to d^{10} metal complexes (Scheme 86).[283] Calculations have shown that the metal–carbon bond in such complexes is stronger than in comparable complexes of "normal" cyclic diaminocarbenes. The complexes **164** and **165** with *r*NHC ligands which contain no heteroatom in the carbene ring have also been prepared.[284] Han and Huynh synthesized *r*NHC complexes of type **166** by oxidative addition of iodopyrazolium iodide to Pd^0 (Scheme 86).[285]



Scheme 86. Complexes bearing *r*NHC ligands.

3.4. Abnormal Carbenes

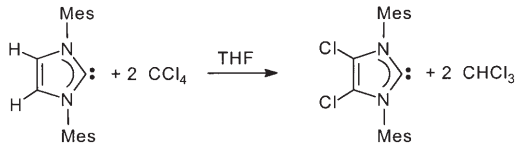
In Section 3, complexes were discussed which contain diaminocarbene ligands metalated at the C^2 carbon atom of the heterocycle. The preparation of the CAACs by Bertrand et al. demonstrated that just one nitrogen atom within the heterocycle is sufficient for the stabilization of the carbene center. (see Section 2.3.6, Scheme 44).[134,135] A similar situation was found for the recently described complexes with abnormal carbene ligands where an NHC ligand derived from an imidazolium cation is bound to the metal through the C^4 or C^5 carbon atom of the heterocycle (Scheme 87).[286]



Scheme 87. Metal complexes with normal and abnormal NHC ligands.

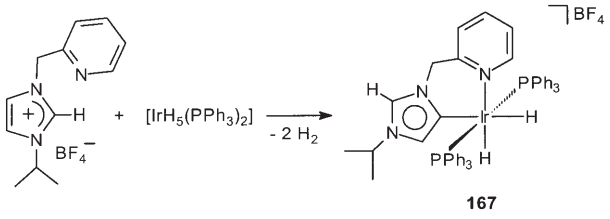
First indications concerning the reactivity of the C^4–H and C^5–H groups of imidazolin-2-ylidenes were furnished by Herrmann et al. with the osmylation of the C^4–C^5 bond of a coordinated *N*,*N*′-dimethylimidazolin-2-ylidene[287] and by Arduengo et al. with the chlorination of 1,3-dimesitylimidazolin-2-ylidene at C^4 and C^5 (Scheme 88).[70]

The formation of complexes with abnormal bound carbene ligands is controlled by the interplay of steric, electronic, and kinetic factors. In selected cases, the counterion of the imidazolium salt and the base used for deprotonation also play a significant role. Some representative examples of complexes with abnormal carbene ligand and the reasons for their formation will be discussed below.



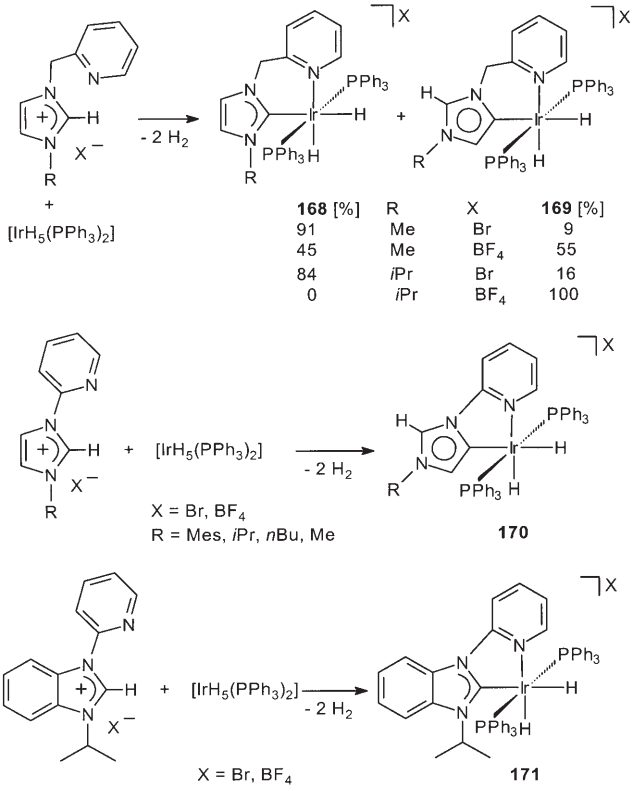
Scheme 88. Chlorination of 1,3-dimesitylimidazolin-2-ylidene at C^4 and C^5.

The first complex containing an abnormal bound NHC ligand, **167**, was isolated by Crabtree et al. from the reaction of an N-(2-pyridylmethyl)-substituted imidazolium salt with $[IrH_5(PPh_3)_2]$ (Scheme 89).[288] The formation of a complex with a C^5-metalated NHC ligand was initially surprising since DFT calculations on similar complexes had previously shown that the derivative with the C^2-metalated NHC ligand is about 20 kcal mol^{-1} more stable than those with C^4/C^5-metalated NHC ligands.[289]



Scheme 89. Synthesis of complex **167** with an abnormal NHC ligand.

Subsequent detailed studies by Crabtree et al. demonstrated[290] that N-pyridyl functionalized imidazolium salts can form iridium complexes with C^2- or C^5-metalated NHC ligands depending on the type of N′-substituent, the counterion, and the bite-angle of the bidentate ligand (Scheme 90). When the N′-substituent is methyl and the anion bromide,



Scheme 90. Syntheses of iridium complexes with C^2- and C^5-metalated NHC ligands.

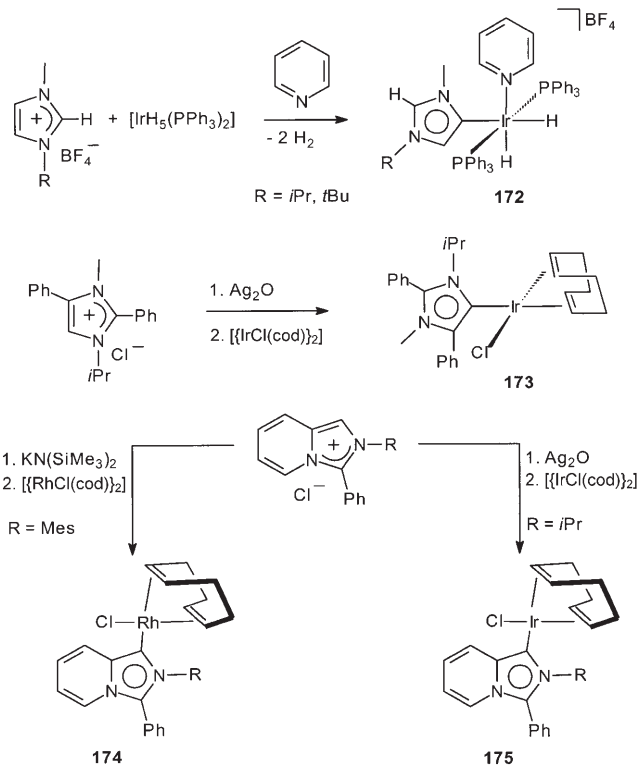
complexes **168** and **169** are obtained in a 91:9 ratio. Change of the counterion to tetrafluoroborate changes this ratio to 45:55 (Scheme 90).[290a] A similar dependence on the counterion was observed for the N′-isopropyl substituent. Decreasing the bite angle leads to the exclusive formation of complex **170** with the C^5-metalated NHC ligand.[290b] Complex **171** containing a C^2-metalated NHC ligand is obtained when the C^4 and C^5 positions of the carbene heterocycle are blocked as in the benzimidazolium salts.[290b]

Complexes with abnormal carbene ligands are formed under kinetic control. The transformation of a C^5-coordinated NHC ligand into the C^2-coordinated ligand was not observed even after exchange of the anion. The abnormal carbene ligands of the iridium complexes **167**, **169**, and **170** exhibit typical signals in the ^{1}H NMR ($\delta(C^2\text{–}H) = 8.7$ ppm, $\delta(C^4\text{–}H) = 5.1$ ppm) and in the ^{13}C NMR spectra ($\delta(C^5) = 140$ ppm, for comparison: $\delta(C^2) = 170$ ppm for the C^2-metalated imidazolin-2-ylidene).[290b] The IR spectra of complexes of type $[IrCl(CO)_2(NHC)]$ indicate that C^5-metalated NHC ligands are significantly stronger electron donors than their C^2-metalated analogues.[290]

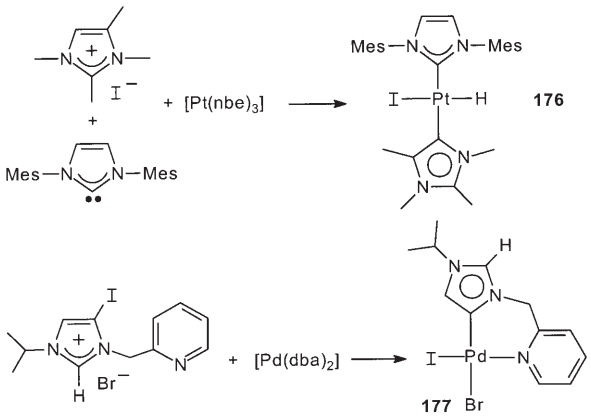
The specific type of donor in the donor-functionalized imodazolium salts appears to be of some importance for the course of the metalation. Peris et al.[259] and Danopoulos et al.[291] prepared iridium NHC complexes using pyridyl-functionalized imidazolium salts. The complexes contain exclusively C^2-metalated NHC ligands. However, the use of a very similar phosphine-functionalized imidazolium salt afforded the iridium complex with the C^5-metalated NHC ligand.[291]

Not only donor-functionalized but also monodentate imidazolium salts have been reported to form complexes with abnormal bound NHC ligands. The Ir^{III} complex **172** is formed in good yield by selective metalation of the sterically least-hindered ring carbon atom, C^5 (Scheme 91).[290d] For the preparation of the Ir^I complex **173** with an abnormal NHC ligand, it proved necessary to block the C^2 and C^4 positions at the carbene heterocycle with phenyl groups (Scheme 91). A similar approach was used in the synthesis of the rhodium(I) and iridium(I) complexes **174** and **175** containing abnormal pyrido[*a*]-annulated NHC ligands (Scheme 91).[103] The preparation of these complexes depends on the substituents at C^2. Crabtree et al. have shown that imidazolium salts with Me, Et, or CH_2Ph groups at C^2 react with Ag_2O through oxidative cleavage of the $C^2\text{–}C_{alkyl}$ bond and give Ag–NHC complexes containing C^2-metalated NHC ligands.[292]

The oxidative addition of a C–X bond is an alternative approach to complexes with abnormal NHC ligands. Cavell et al. reported that the oxidative addition of the C^4–H bond to Pd^0 with formation of complex **176** is possible, if the C^2 position of the imidazolium salt is blocked (Scheme 92).[293] Imidazolium salts with a blocked C^2 position and non-blocked C^4 and C^5 positions can react by metalation of either of the available carbon atoms. Blocking of the C^2 position of the imidazolium salt is not necessary if a more reactive C^5–I bond is offered for the oxidative addition (Scheme 92).[294] This approach was used for the preparation of complex **177**. The presence of an additional N-donor group facilitates the formation of complex **177**.

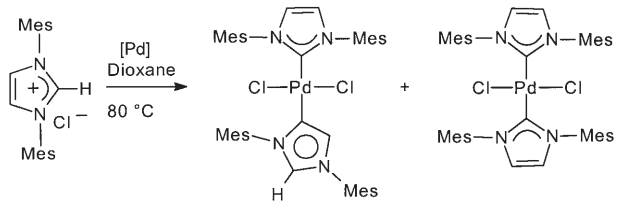


Scheme 91. Syntheses of complexes with monodentate, abnormal NHC ligands.



Scheme 92. Synthesis of complexes with abnormal bound NHC ligands by oxidative addition of C^5–H and C^5–I bonds. nbe = norbornene.

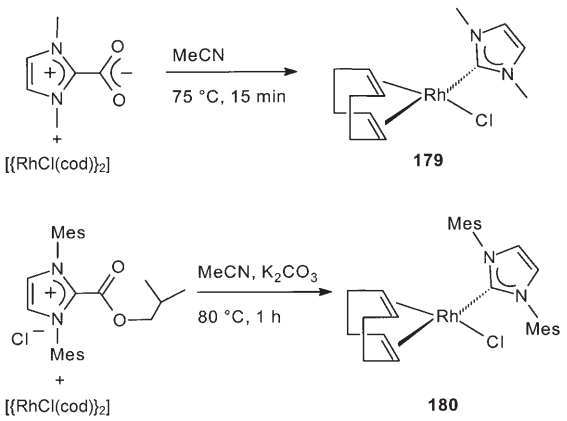
Recent studies by Nolan et al.[295a] and Campeau et al.[295b] emphasize the importance of an unequivocal characterization of carbene complexes generated in situ. The reaction of an imidazolium salt with Pd^{II} afforded, depending on the base used for deprotonation, different complexes with diverging catalytic properties (Scheme 93). The *trans*-dicarbene palladium complex with an abnormal carbene ligand, **178a**, was obtained as the main product from the reaction of *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl) and $Pd(OAc)_2$. Complex **178b** with two classical NHC ligands was formed as the main product when $Pd(OAc)_2$ was treated



Scheme 93. Synthesis of **178a** and **178b** by reaction of $Pd(OAc)_2$ with IMes·HCl in the presence and absence of Cs_2CO_3.

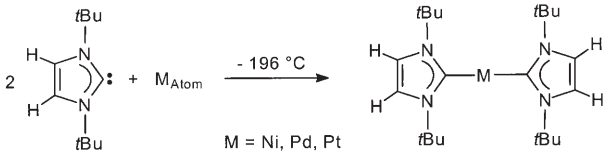
with IMes·HCl in the presence of Cs_2CO_3 (Scheme 93).[295a] The transformation of **178a** into **178b** in the presence of a base was not observed.

Additional complexes with abnormal carbene ligands have been reported.[296] Danopoulos et al. described the synthesis of iron(II) complexes with C-N-C pincer ligands.[296a] Two equivalents of the free dicarbene pincer ligand reacted with $[\{FeCl_2(tmeda)\}_2]$ to afford the octahedral tetracarbene complex where three of the four carbene donors are C^2-metalated while the fourth carbene donor forms a C^5–Fe bond. This C^5-metalation was attributed to the steric demand of the N,N′-aryl substituents of the carbene donors. An analogous, but sterically less-demanding N,N′-substituted pincer ligand does form an octahedral iron tetracarbene complex with four C^2-metalated carbene donors.[297] During the investigation of the coordination chemistry of tripodal tricarbene ligands[169] Meyer et al. isolated a dinuclear copper(I) complex which contains trigonal-planar copper centers each coordinated by two C^2- and one C^5-metalated carbene donors.[166]



Scheme 94. Synthesis of NHC complexes by decarboxylation of C^2.

[Pd(NHC)$_2$] (NHC = *N*,*N*′-di(*tert*-butyl)imidazolin-2-ylidene) (Scheme 95).[299] The method was subsequently further improved.[300] Herrmann et al. described an alternative access to this type of complex, starting from $[Pd(o\text{-tol})_2]$ in hexane solution.[301] Complexes of the type $[M(NHC)_2]$ (M = Pd, Pt) are coordinatively and electronically unsaturated (14-electron complexes). Their properties were studied using DFT calculations.[302] Studies of their reactivity[303] provided important information regarding their catalytic activity.



Scheme 95. Synthesis of M^0 NHC complexes by metal vapor synthesis.

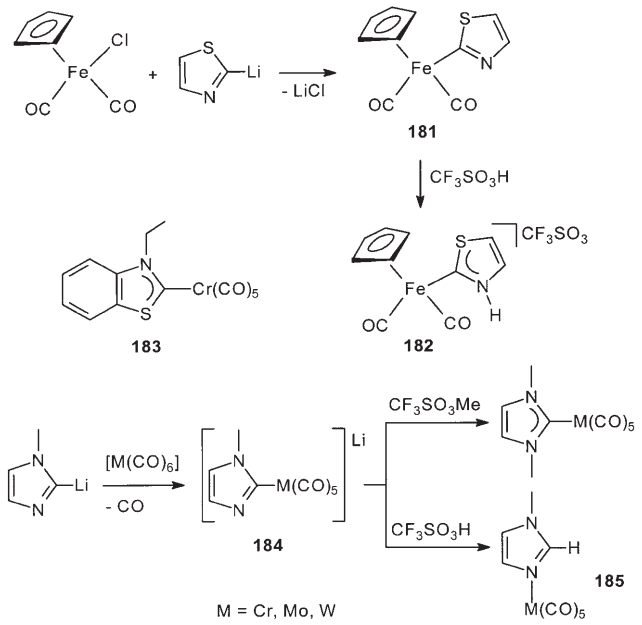
3.5. Additional Methods for the Synthesis of NHC Complexes

Crabtree et al. reported that the air and moisture stable *N*,*N*′-dimethylimidazolium-2-carboxylate[298a,b] can act as a carbene transfer agent for various metals, such as Rh, Ru, Ir, and Pd (Scheme 94).[298c,d] The NHC complexes are formed in very good yield. Exclusion of air and moisture is not necessary, provided the metal precursors used are stable against these reagents. The preparation of **179**, for example, proceeds readily in H_2O/MeCN (90:10, v/v). The preparative access to imidazolium-2-carboxylates is, however, limited. Readily available *N*,*N*′-dimesitylenimidazolium-2-isobutylester was therefore used in an alternative synthesis for the preparation of **180** (Scheme 94).[298c,d] Since the carbene transfer is not hampered by the presence of water, free carbenes are unlikely to be intermediates in this reaction. In general, carbene transfer from NHC-2-carboxylates constitutes an alternative high-yield procedure for the preparation of NHC complexes under mild reaction conditions.

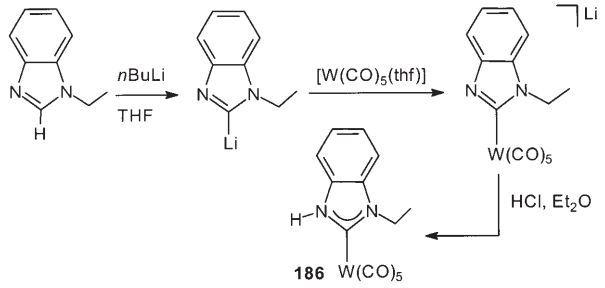
Linear 14-electron dicarbene M^0 complexes (M = Ni, Pt)[263] had been known for some years, when Cloke et al. presented in 1999 the elegant metal-vapor synthesis for the preparation of the hitherto unknown complexes of type

Comprehensive studies by Raubenheimer et al. demonstrated that *N*-alkylimidazoles and thiazoles can be deprotonated at the C^2 carbon atom.[242] Lithiated azoles are readily C^2 metalated by transition metals. Alkylation or protonation of the remaining ring nitrogen atom leads to stable transition-metal NHC complexes. Lithiated thiazole reacts with $[Fe(Cp)Cl(CO)_2]$ to give the neutral complex **181**. This complex can be protonated with CF_3SO_3H to yield the cationic derivative **182** (Scheme 96).[304] Starting from lithiated benzothiazole, complex **183** with the *N*-ethylbenzothiazolin-2-ylidene ligand was obtained after N-alkylation.[305] Lithiated *N*-methylimidazole reacts with Group 6 transition-metal carbonyl compounds to yield anionic complexes of type **184**. N-methylation of **184** yields the known complex with the *N*,*N*′-dimethylimidazolin-2-ylidene ligand, whereas attempts to protonate the ring nitrogen atom in **184** failed resulting in formation of the imino complex **185** (Scheme 96).[306]

Hahn and Waldvogel et al. have found that *N*-ethylbenzimidazole reacts regioselectively after deprotonation of C^2 with $[W(CO)_5(thf)]$ resulting in C^2 metalation. The subsequent reaction with HCl yields complex **186** with an NH,NR-stabilized benzimidazolin-2-ylidene ligand (Scheme 97).[307] Rhodium complexes with similar benzimidazolin-2-ylidene



Scheme 96. Reactions of lithiated azoles with transition-metal complexes.



Scheme 97. Synthesis of **186** with an NH,NR-stabilized NHC ligand.

ligands have been observed by Bergman and Ellman et al. as catalytically active species in the C^2–C coupling reaction of azoles with alkenes or aromatic compounds.[282]

The formation of a hydrogen bond between the NH group of an NH,O-stabilized benzoxazolin-2-ylidene ligand and triphenylphosphine oxide has been described.[308] Little is known about similar hydrogen bonds involving NH,NR-stabilized carbene ligands as found in **186**. The NH group of such an NH,NR-stabilized carbene, which acts as spectator ligand at a metal center, could simultaneously function as a supramolecular recognition unit and thus influence the regisolectivity of a catalytic reaction in solution.

The NMR titration of **186** with 1,3-dimethyl hexahydro-2-pyrimidinone (DMPU) indeed indicates the presence of an N–H···O hydrogen bond in solution. Addition of DMPU to a solution of **186** in dichloromethane leads to a downfield shift of the resonance of the NH proton from $\delta = 9.25$ to 10.45 ppm, while the chemical shifts for all other protons remain essentially unchanged. Addition of more than one equivalent of DMPU causes only a broadening of the NH signal (Figure 6).[307]

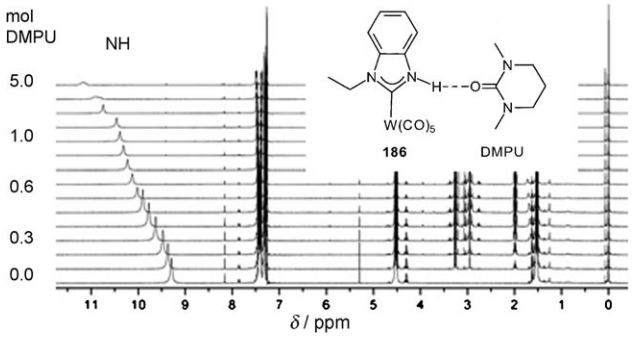
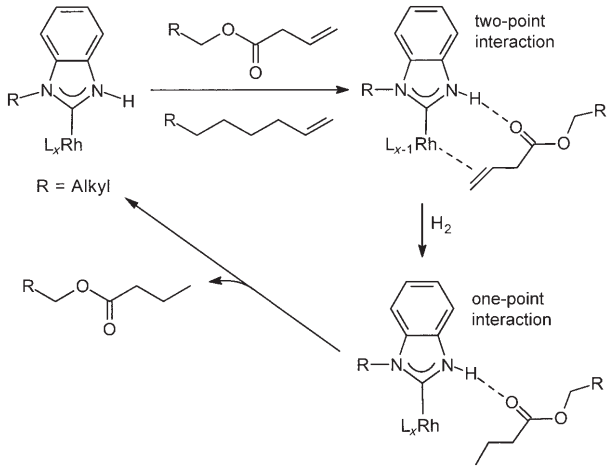


Figure 6. Hydrogen bond between complex **186** and DMPU.

The association constant $\Delta G_{ass} = 2.2\ kcal\,mol^{-1}$ for the process is of a magnitude that suggests the formation of this type of hydrogen bond could be a means of controlling the selectivity of a chemical reaction. The rhodium complex bearing an NH,NR-stabilized benzimidazolin-2-ylidene ligand, for example, can coordinate carbonyl-functionalized olefins selectively through formation of a two-point interaction, while unfunctionalized olefins can only coordinate through the C=C double bond. The catalytic hydrogenation of the C=C double bond results in a one-point interaction which allows a fast exchange of the substrate (Scheme 98). First catalytic tests confirm that rhodium complexes with NH,NR-functionalized benzimidazolin-2-ylidene ligands can be used as catalysts for selective hydrogenation reactions.[307]

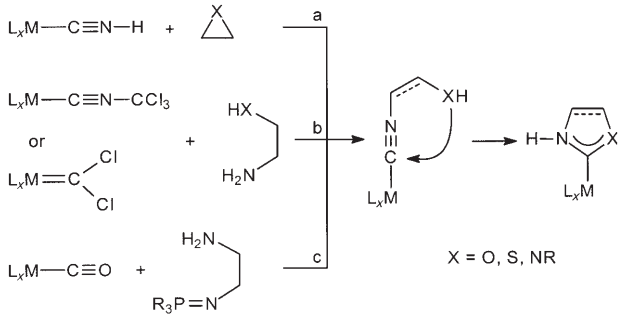


Scheme 98. Selective hydrogenation using rhodium complexes with NH,NR-stabilized benzimidazolin-2-ylidene ligands.

3.6. Template Syntheses of NHC-Complexes

The majority of N-heterocyclic carbenes and their metal complexes are obtained from cyclic azolium derivatives (Scheme 66). However, it is also known that coordinated isocyanides are attacked by proton bases HX (X = OR, RNH) in a nucleophilic reaction which leads to heterocarbene complexes (Scheme 3).[17,18] Whereas the attack of a nucleophile HX at a coordinated isocyanide leads to an acyclic heterocarbene complex, the use of functionalized isocyanides

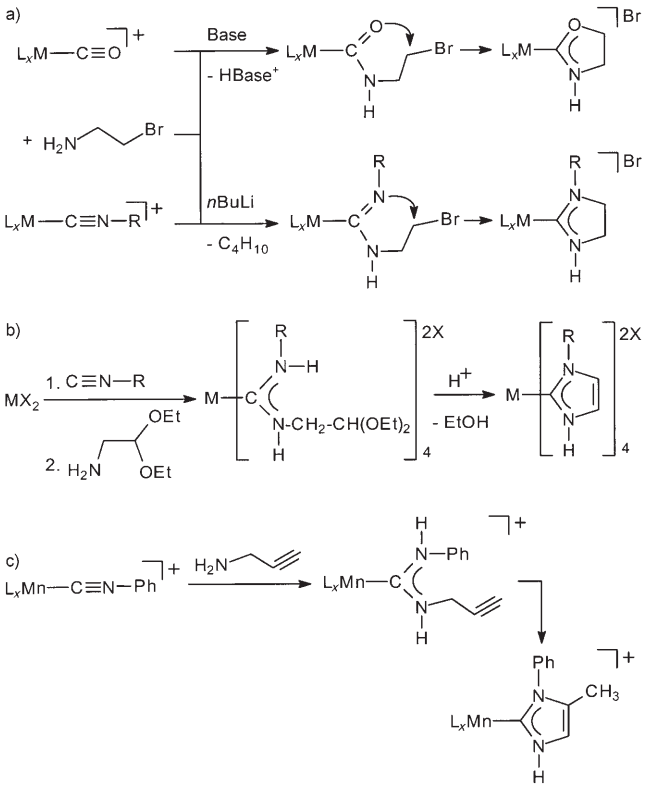
containing both the isocyanide function and the nucleophile gives complexes with heterocyclic carbene ligands through a 1,2-addition across the C≡N triple bond. Various research groups have been active in the development of nucleophile functionalized isocyanides in metal-template-controlled reactions. Beck et al.,[309] Fehlhammer et al.,[310] and Michelin et al.[311] described the reactions of complexes bearing isocyanic acid or isocyanide ligands with epoxides or aziridine (Scheme 99a). Complexes with nucleophile-substituted isocyanide ligands can also be obtained by the reaction of ethylendiamine or ethanolamine with trichloromethyl isocyanide[312] or dichlorocarbene complexes[313] (Scheme 99b). A particularly interesting reaction with a broad scope of applications has been developed by Liu et al. It involves the initial reaction of an amine phosphinimine with a metal carbonyl complex. The phosphinimine reacts with a carbonyl group to give an isocyanide and $R_3P{=}O$. The amine-functionalized isocyanide can then be cyclized to yield a heterocarbene ligand (Scheme 99c).[314]



Scheme 99. Synthesis of heterocarbene complexes by template-controlled cyclization of β-functionalized isocyanides.

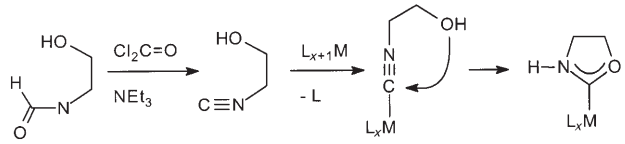
Additional template syntheses of complexes with cyclic heterocarbene ligands using isocyanide or carbonyl complexes as starting material have been described. Special attention deserve the reactions of carbonyl[315] or isocyanide complexes[316] with 2-bromoethyl amine which lead to complexes with oxazolidin-2-ylidene or imidazolidin-2-ylidene ligands, respectively (Scheme 100a). The nucleophilic attack of the diacetal-protected amino acetaldehyde at a tetraisocyanide palladium complex followed by an acid-catalyzed cyclization reaction resulted in the formation of the complex bearing four imidazolin-2-ylidene ligands. (Scheme 100b).[317] A recent report describes the metal-template-controlled coupling of propargyl amine with phenyl isocyanide to yield an NHC ligand (Scheme 100c).[318] In addition, Fehlhammer et al. prepared coordinated NHC ligands by α-metalation of coordinated isocyanides followed by the reaction with 1,2-dipolar substrates under cyclization.[319] This method resembles the organic heterocycle synthesis of Schöllkopf and Hoppe.[320]

Much simpler than the template-controlled generation of β-functionalized isocyanides is their direct use. Fehlhammer et al. used 2-hydroxyalkyl isocyanides in which the nucleophilic group and the isocyanide are linked together before the coordination of the isocyanide to a metal center. Upon



Scheme 100. Template syntheses of heterocarbene complexes.

activation of the isocyanide at an electron-poor metal center the spontaneous cyclization to an oxazolidin-2-ylidene ligand was observed (Scheme 101).[321] Homoleptic tetra-[21a] and hexa-NHC complexes[21b] were obtained by this route. The cyclization of the 2-hydroxyethyl isocyanide ligand is prevented when the ligand coordinates to an electron-rich metal center since enhanced M→CNR π-backbonding deactivates the isocyanide for the intramolecular nucleophilic attack.[321c]

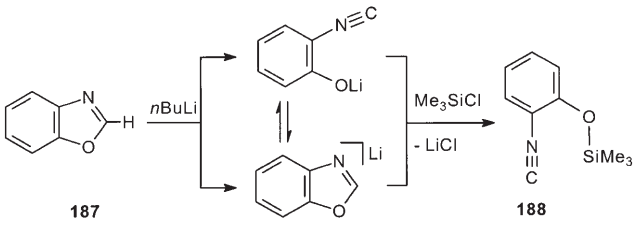


Scheme 101. Cyclization of 2-hydroxyethyl isocyanide at transition-metal complexes.

2-Hydroxyphenyl isocyanides[322] not only contain the isocyanide and the nucleophile within the same molecule, but both groups are already arranged in one plane. This arrangement, in addition to the aromaticity of the five-membered ring obtained after cyclization to the benzoxazolin-2-ylidene ligand, particularly favors the intramolecular nucleophilic attack. Free 2-hydroxyphenyl isocyanide is unstable and cyclizes spontaneously to benzoxazole **187**,[323] in contrast to the stable 2-hydroxyethyl isocyanide. The heterocycle in benzoxazole opens upon treatment with *n*BuLi and the isocyanide obtained this way can be stabilized as 2-trimethyl-

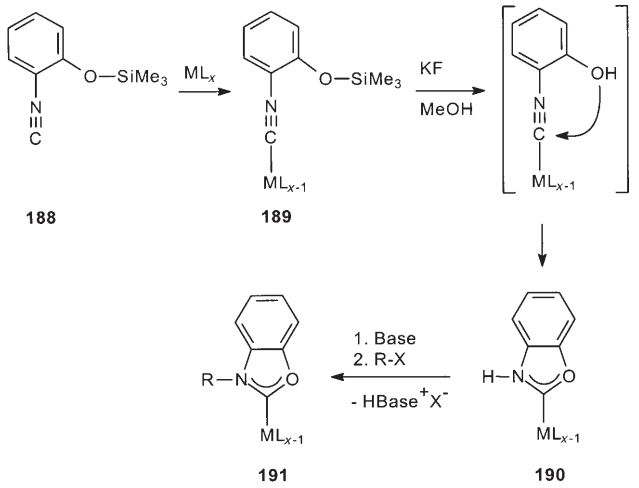
siloxyphenyl isocyanide **188** by reaction with trimethylsilyl chloride (Scheme 102).[324]

Phenyl isocyanide **188** coordinates to electrophilic metal centers to give the isocyanide complex **189**. Cleavage of the



Scheme 102. Synthesis of 2-trimethylsiloxyphenyl isocyanide **188**.

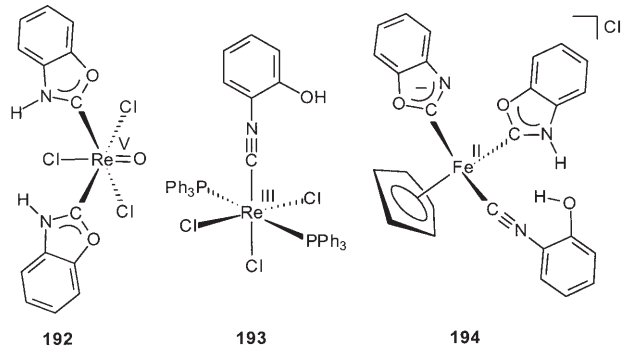
$O-SiMe_3$ bond leads to spontaneous cyclization and formation of complex **190** with the benzoxazolin-2-ylidene ligand. The N-alkylation of the heterocycle to give **191** proceeds readily (Scheme 103). A large number of complexes with



Scheme 103. Cyclization of 2-hydroxyphenyl isocyanide at a metal template.

NH,O- and NR,O-stabilized benzoxazolin-2-ylidene ligands containing W,[325,326] Cr,[326] Pt, Pd,[327] B,[328] Fe,[329] and Re[308] have been prepared. Michelin et al. describe related palladium and platinum complexes with the six-membered benzo-[1,3]oxazin-2-ylidene heterocycle which was also obtained by the cyclization of a β-functionalized phenyl isocyanide.[21d]

The intramolecular nucleophilic attack of the hydroxy group at the isocyanide carbon atom is influenced by $d\rightarrow\pi^*$ backbonding from the metal center to the isocyanide. No cyclization is observed in the case of a strong backbonding and the complexes with the unstable 2-hydroxyphenyl isocyanide ligand, which is now stabilized by coordination to the metal center, can be isolated. Force constants for the $C\equiv NR$ bonds in various complexes calculated from IR data allow a prediction of the behavior of the coordinated ligand **188** after cleavage of the $O-SiMe_3$ bond.[330] 2-Hydroxyphenyl isocyanide coordinated to Re^V cyclizes immediately forming complex **192**, while the same ligand is stable against cyclization when coordinated to the more electron-rich Re^{III} center in **193** (Scheme 104).[308] Cleavage of the $O-SiMe_3$ bonds in



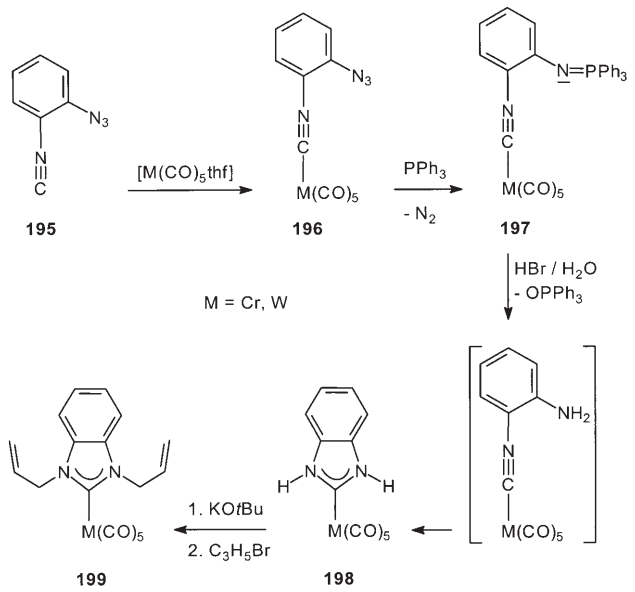
Scheme 104. Reactivity of coordinated 2-hydroxyphenyl isocyanide.

the iron(II) complex with three ligands **188** yields complex **194** with only two benzoxazolin-2-ylidene ligands. These are stronger σ-donors and weaker π-acceptors than the phenyl isocyanide ligands from which they were formed. The electron density at the iron(II) atom is thereby increased and so is the backbonding to the remaining 2-hydroxyphenyl isocyanide ligand, which prevents its cyclization to the benzoxazolin-2-ylidene. Complex **194** contains the ligand isomers 2-hydroxyphenyl isocyanide and benzoxazolin-2-ylidene, which are interconvertable (Scheme 104).[331] The position of the equilibrium between complexes with the 2-hydroxyphenyl isocyanide and the benzoxazolin-2-ylidene ligands can also be shifted by addition of selected bases.[332]

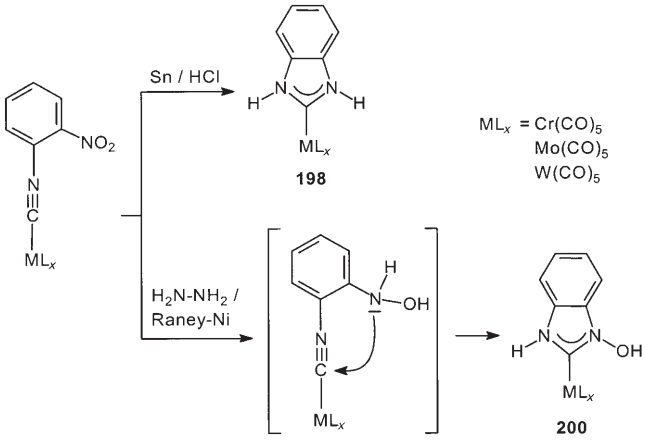
Very strong $M\rightarrow C\equiv N$ backbonding leads to an umpolung of the reactivity of the coordinated isocyanide ligand, which is then attacked by electrophiles at the isocyanide nitrogen atom.[333] The reactivity of β-functionalized isocyanides has been reviewed.[21c,334]

The cyclization of β-functionalized isocyanides can be applied in a template synthesis of cyclic diaminocarbenes. Since free 2-aminophenyl isocyanide spontaneously cyclizes to benzimidazole, a synthon for this unstable NHC precursor is needed. 2-Azidophenyl isocyanide **195** has been shown to be a suitable synthon (Scheme 105).[335] 2-Azidophenyl isocyanide coordinates readily to transition metals giving complexes such as **196**. The required amino function for the intramolecular nucleophilic attack is then liberated by a Staudinger reaction.[336] Complex **196** reacts with a tertiary phosphine to yield the iminophosphine complex **197**. The iminophosphine function in **197** is readily hydrolyzed forming triphenylphosphine oxide and the unstable complex with the 2-aminophenyl isocyanide ligand. As expected, this β-functionalized isocyanide ligand cyclizes spontaneously to give complex **198** with an NH,NH-stabilized NHC ligand. The alkylation of both NH functions to yield complex **199** proceeds readily.[335]

The generation of the NH,NH-stabilized benzimidazolin-2-ylidene ligand is also possible by reduction of the nitro group of coordinated 2-nitrophenyl isocyanide with Sn/HCl (Scheme 106).[337] Under these drastic reaction conditions it is



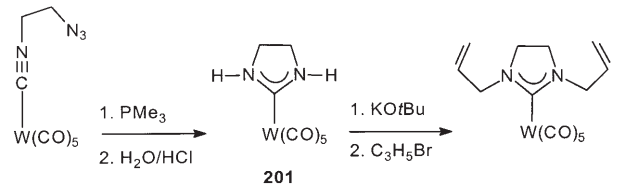
Scheme 105. Template-controlled cyclization of 2-azidophenyl isocyanide.



Scheme 106. Reduction and cyclization of 2-nitrophenyl isocyanide.

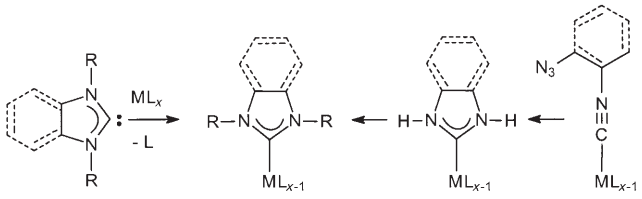
essential that the 2-nitrophenyl isocyanide is coordinated to a redox-inert metal center like the one found in metal pentacarbonyl complexes. The use of raney-nickel and hydrazine in the reduction of the nitro group of 2-nitrophenyl isocyanide did not yield the 2-aminophenyl isocyanide but instead the complex with a 2-hydroxylamine-functionalized isocyanide ligand (Scheme 106). This isocyanide ligand cyclizes producing the complex with an NH,NOH-stabilized NHC ligand **200**. The alkylation of the NH and OH functions in complex **200** proceeds stepwise with the first alkylation occurring at the OH group.[337] A related reaction sequence starting from 2-(azidomethyl)phenyl isocyanide has been reported by Michelin et al.[338]

2-Azidoethyl isocyanide is also readily available. This ligand also cyclizes at a suitable metal center in analogy to 2-azidophenyl isocyanide to give for example complex **201** with an NH,NH-stabilized imidazolidin-2-ylidene ligand (Scheme 107).[339] The *N*,*N*′-alkylation proceeds readily. Complex **201** has been obtained previously by Liu et al. by the reaction of an amine phosphinimine with $[W(CO)_6]$ (Scheme 99c).[314]



Scheme 107. Cyclization of 2-azidoethyl isocyanide at a metal template.

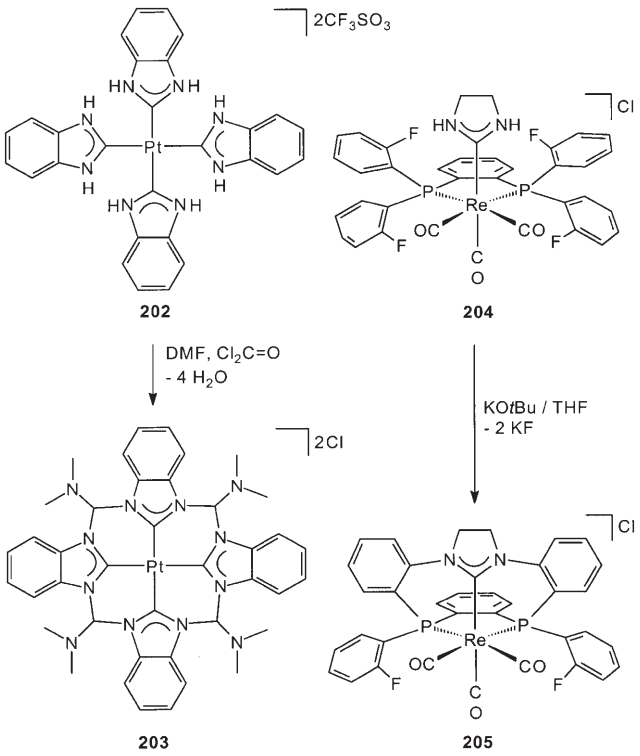
The cyclization reactions of 2-azidophenyl and 2-azidoethyl isocyanides constitute an alternative and complementary method for the preparation of complexes bearing cyclic diaminocarbenes compared to the classic method starting from cyclic azolium salts (Scheme 108). This method is of advantage when the azolium precursor is not readily available or is difficult to deprotonate. In addition, the method allows for the stepwise alkylation of the nitrogen atoms of the carbene heterocycle which gives access to complexes with unsymmetrically N,N′-substituted NHC ligands.



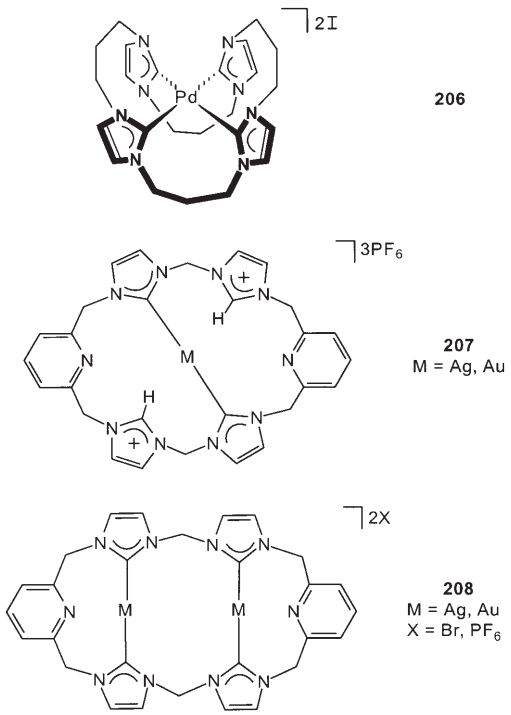
Scheme 108. Alternative methods for the preparation of NHC complexes.

Coordinated NH,NH-stabilized NHC ligands have been shown to be useful building blocks in the synthesis of complexes with cyclic polycarbene ligands. Complex **202**, for example, was obtained in a multistep domino reaction starting from $[Pt(PMe_3)_4](CF_3SO_3)_2$ and 2-azidophenyl isocyanide. The four NH,NH-stabilized benzimidazolin-2-ylidene ligands in **202** can be linked with DMF in the presence of phosgene to yield complex **203** bearing a cyclic tetracarbene ligand with crown-ether topology (Scheme 109).[340] The NH,NH-stabilized imidazolidin-2-ylidene ligand in **204** can be connected to the coordinated diphosphine ligand in a template-controlled reaction[341] giving the complex **205** with the facial-coordinating cyclic P-C^{NHC}-P ligand (Scheme 109).[342]

In this context it is interesting to review recent attempts to generate complexes with cyclic polycarbene ligands from polyazolium precursors. The tetraimidazolium salt **104** (Scheme 60) reacts with PdI_2 and NaOAc as a base giving the palladium tetracarbene complex **206** (Scheme 110). The dinuclear silver and copper complexes with the tetracarbene ligand derived from **104** have also been described.[343] The lutidine-bridged tetraimidazolium salt **106** (Scheme 61) forms mono (**207**) and dinuclear (**208**) complexes with silver(I) depending on the amount of silver salt used in the synthesis. As expected, these silver complexes are excellent carbene-transfer agents and thus have been used for the preparation of



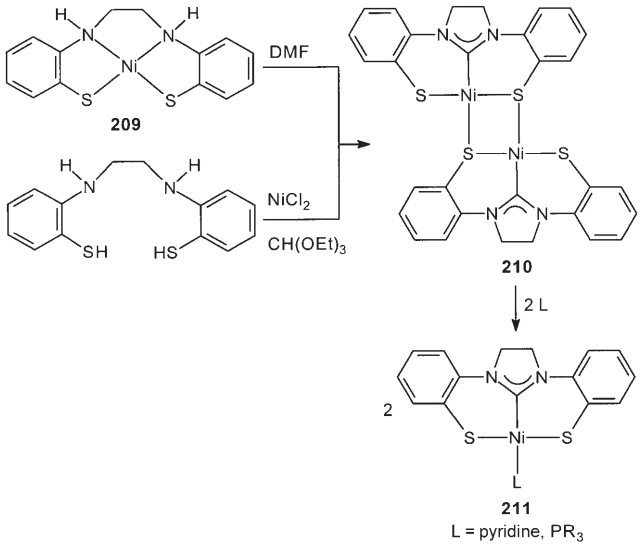
Scheme 109. Template synthesis of complexes with cyclic polycarbene ligands.



Scheme 110. Complexes of cyclic polycarbene ligands.

the mono and dinuclear gold(I) complexes.[194a] The tetraimidazolium salt **106** contains, in contrast to **104**, two additional pyridine donor functions which in principle allow the preparation of endocyclic dinuclear double-pincer complexes (Scheme 57).

The surprising addition of a carbon atom to the ethylene diamine moiety in complex **209**, to give complex **210** has been described by Sellmann et al. The dinuclear nickel NHC complex **210** can be obtained in a rationally devised synthesis from $NiCl_2$, 1,2-ethandiamine-*N*,*N*′-bis(2-benzenethiol), and $CH(OEt)_3$.[344] Nucleophiles cleave complex **210** into two mononuclear, square-planar complexes of type **211** (Scheme 111).



Scheme 111. Synthesis of carbene complexes **210** and **211**.

4. Summary and Outlook

Heterocyclic carbenes have been employed successfully as spectator ligands in organometallic chemistry. The electronic and spectroscopic properties of such ligands can be varied over a wide range by modification of the heteroatoms and the substituents at the heteroatoms. The option of fine tuning the electronic properties makes heterocyclic carbenes interesting ligands for the development of novel and efficient catalytically active complexes.

In spite of the vast amount of data currently available, new methods for the synthesis of heterocyclic carbenes and their metal complexes are regularly reported. New and interesting developments can be expected in the future, particularly regarding the generation of suitable heterocycles for carbene synthesis. Yamamoto et al., for example, recently reported the synthesis of imidazoles by the copper-catalyzed cycloaddition of two different isocyanides.[345] Carbene complexes with isoquinolin-2-ylidene ligands have recently been described[346] and even the "Click" reaction has been used for the preparation of carbene complexes with triazolide ligands.[347]

Tamm et al. described the first chiral diaminocyclopropylidene.[348a] Some years after the discovery of the first carbene with "autoumpolung character" (**28 d**, Scheme 37), the report on the dinitroxide carbene adds a second member to this family of unusual N-heterocyclic carbenes.[348b] A first report on stable N-heterocyclic carbenes derived from a seven-

membered ring (diazepanylidenes) appeared recently.[349a] Fürstner et al. described a planar-chiral N-heterocyclic carbenes with a five-membered heterocycle and a remarkable σ-donor capability.[349b] New C-N-C pincer ligands have been reported[350] and even phosphonium ylide substituted NHCs, which can function as C–C chelate ligands are known.[351] Not surprisingly, the rapid development of the field is occasionally accompanied by irreproducible reports such as the one on the isothiazole carbene.[352]

N-heterocyclic carbenes are not only stable spectator ligands. Activation of the N,N′-substituents or reactions with the solvent have been observed under special conditions.[353] Even more diverse is the reactivity of metal-coordinated NHC ligands. There are a number of reports on the C–H activation of N-aryl or N-alkyl substituents of NHC ligands.[354a–f] The insertion of an NHC ligand into the platinum–olefin bond[354g] and the attack of the C^2 atom of an NHC on the alkylidene of a ruthenium olefin-metathesis catalyst have also been reported.[354h]

A complex with a cage-like tris(imidazolin)2-ylidene[355] is known along with complexes with bidentate bis(imidazolin-2-ylidene) ligands. A recent report describes the preparation and properties of a palladium complex bearing a dicarbene ligand with two abnormally coordinated NHC donor functions.[356] Both the C^4 and C^5 positions are deprotonated and the abnormally bound NHC ligand bridges two metal centers in a trinuclear ruthenium complex.[357] *N*-phenylimidazole has been shown to coordinate with the unsubstituted nitrogen atom to a Mn^I center. Subsequent attempts to deprotonate the C^2 carbon atom led to an intermediate which upon protonation with NH_4PF_6 reacted to give the complex with a C^2 metalated NH,NPh-stabilized carbene ligand.[358] This base-catalyzed tautomerization[359] of an imidazole complex into an NHC complex could be of general applicability for the preparation of NHC complexes. Similar complexes with NH,NR-stabilized benzimidazolin-2-ylidene ligands have been obtained from *N*-alkylbenzimidazole (Scheme 97).[307] Heterocyclic CAAC ligands have been used for the preparation of ruthenium complexes for olefin metathesis[360] and the rhodium chelate complex with a rigid bis(triazolin-5-ylidene) ligand has also recently been described.[361]

The equilibrium between an N-heterocyclic carbene and its entetraamine dimer is still of interest. Denk et al. presented a new study on this equilibrium using a series of symmetrically and unsymmetrically N,N′-substituted imidazolidin-2-ylidenes.[362]

A large number of recent studies deal with the use of N-heterocyclic carbenes as organocatalysts.[363] Such metal-free catalytic procedures constitute an interesting, often atom-economical alternative to classical organic transformations. Initially, C–C coupling reactions, such as the benzoin condensation and the Stetter reaction, got most attention. More recently new applications for NHC organocatalyst, such as the synthesis of homoenolates from α,β-unsaturated aldehydes, transesterification reactions, and 1,2-addition reactions, have been studied. The generation of reactive aryl anions by electron transfer from dibenzotetraazafulvalenes to aryl iodides constitutes the most recent application for NHC organocatalysts.[364]

Bertrand and co-workers demonstrated that CAACs can add CO.[365] Baker et al., searching for compounds for chemical hydrogen storage, discovered that nickel NHC complexes can dehydrogenate an ammonia-borane adduct.[366] Even the dihydrogen molecule itself can be activated by CAACs.[367] In this process, the carbene carbon atom with its filled sp^2_σ and its empty p_π orbitals assumes the function of the metal atom in the long known electrophilic activation of dihydrogen by transition metals. Compared to the electrophilic transition-metal activation, a different mode of dihydrogen activation has been proposed for nucleophilic carbenes. The reaction of a nucleophilic CAAC with H_2 is believed to lead initially to a hydride-like hydrogen which then adds to the positively polarized carbene carbon atom. The same mechanism has been proposed for the nucleophilic activation of ammonia by NHCs, which is a difficult task for transition metals because of the formation of Lewis acid/Lewis base adducts.

Very recently, first reports on carbodicarbenes appeared.[368] Such ligands contain, in analogy to the carbodiphosporanes, a divalent carbon(0) atom which is, at least formally, stabilized by two carbene donors. Compounds of this type can, in principle, be metalated twice at the carbon(0) atom.[369]

The majority of the results summarized in Section 4 has appeared in 2007, indicating the tremendous activity in this research area worldwide. An end to this development is not foreseeable. Surely, the future will bring new and spectacular results regarding heterocyclic carbenes and their metal complexes.

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