Synthesis and properties of heteroaromatic carbenes of the imidazole and triazole series and their fused analogues

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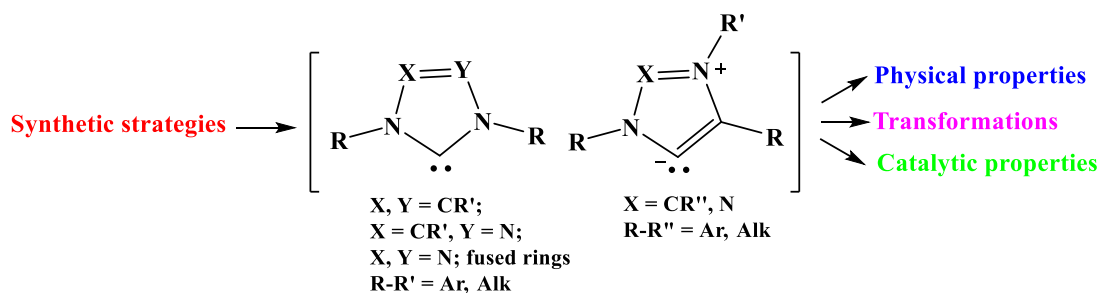*E-mail: nkorotkikh@ua.fm*

Abstract

The present review deals with the syntheses and properties of individual heteroaromatic carbenes of the imidazole, 1,2,4- and 1,2,3-triazole series, their fused analogs and mesoionic carbenes including unprecedented structures such as hyperbasic and hypernucleophilic carbenes. Particular emphasis is placed on their physical properties, novel chemical transformations, and catalytic properties.

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1. Introduction

A quarter of a century has elapsed since Bertrand and Arduengo discovered and then synthesized the first disubstituted derivatives of stable carbenes.[1-5] In turn, this provided a strong impetus for increased research activity in the field. Particular emphasis was placed on the synthesis of carbenes and their derivatives, and studies of their structures, transformations, biological and catalytic properties proliferated. Prior to these results only inorganic and monosubstituted organic analogues of carbenes were known (carbon(II) monoxide CO, carbon(II) thioxide CS and isocyanides, RNC). Although not normally identified as carbenes, these compounds had long been used as ligands and reagents for organic synthesis. The preparation of other types of individual carbenes took longer to materialise.[6,7] However, today a large number of compounds have been isolated; these are predominantly heterocyclic species and include heteroaromatic carbenes, phosphanyl-silylcarbenes, aminoalkyl- and diamino-carbenes of cyclic and acyclic series, borazino- and borazolo-carbenes, etc.[8-20]

One of the major focuses of carbene applications has been the catalysis of organic reactions.[21-30] The connection between individual carbene structure and function has been reported in many publications. However, there remains a considerable problem in that the leading structures in any particular area have not yet been well identified. Overall, heteroaromatic carbenes of the imidazole, triazole (the 1,2,4- and more recently the 1,2,3-type) and benzimidazole series are the best known in this field.

It is worth noting that in the literature the synthesis of carbene derivatives is often described (e.g., the number of metal carbene complexes is growing very rapidly) without the actual isolation of the individual precursor carbenes (their number is much less). The differences in properties between the two can be very significant. Although *in situ* transformations are sometimes able to do surprising things (see, for example, the recently described[31] formation of carbene complexes of copper(I) from azolium salts and metallic copper), individual carbenes not only catalyse organic reactions but also open up new possibilities for organic synthesis.[32,33]

The present article is concerned with the syntheses, structural studies and transformations of individual heterocyclic carbenes of the imidazole and triazole series, as well as their fused analogues. The catalytic activities of these carbenes, and their derivatives, in some typical organic reactions (transesterification and benzoin condensation) will be discussed, as will carbene complexes of transition metals (haloarene hydrodehalogenation and reduction of multiple bonds). These reactions can be used to study the influence of

catalyst structure on catalytic efficiency. During the discussion of such transformations, attention will be concentrated on structural rearrangements, and reactions with carbon and nitrogen electrophiles, particularly those with multiple bonds or nonmetals. The formation of complex compounds with metals and elemento-electrophiles of the main groups of the periodic table constitutes a very broad area, one that has been described in many reviews (see, for example, the most general of them[34-37]). Therefore, except in those cases where elementoderivatives are used for the synthesis of new types of carbenes or reactions of their ring expansions, the results of these studies are not considered in the present work. Attention has been paid to appropriate methods for the synthesis of carbene precursors (precarbenes), the carbenoid structures of which sometimes allow the achievement of *in situ* reactions. The results of such reactions are often comparable to those of free carbenes.[7]
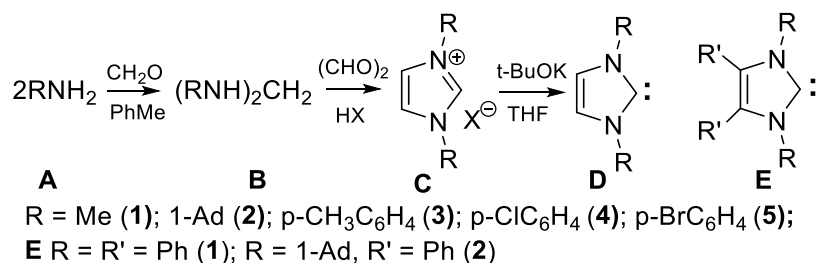
Structures are numbered in this review according to the Scheme in which they first appear, in order to avoid a cumbersome sequence running into the 500s. We hope that this will be found convenient.

2. Synthesis of Carbenes of the Imidazole and Triazole Series and their Fused Analogues

2.1. Imidazol-2-ylidenes

2.1.1. Monoimidazol-2-ylidenes. Current methods for the preparation of imidazol-2-ylidenes involve the deprotonation of *meso*-unsubstituted imidazolium salts under the action of anhydrous and unprotic bases (metal hydrides, alkoxides, hexamethyldisilazanides, diisopropylamides, etc.). Using this approach Wanzlick *et al*.[7] generated carbenes of the heterocyclic series *in situ*. However, Arduengo *et al*. provided the first example of a stable crystalline carbene 1,3-di-(1-adamantyl)imidazol-2-ylidene **1D2** (R = 1-Ad) (Scheme 1).[4] They demonstrated that the method is suitable for the isolation of individual substances and confirmed the lability of carbenes under environmental conditions (to water, oxygen and carbon dioxide). Subsequently, 1,3-disubstituted imidazol-2-ylidenes,[5,38-40] 4,5-dihydroimidazol-2-ylidenes[41] and acyclic diaminocarbenes[42] were prepared and shown to behave in a similar fashion to the first Arduengo compound. In the latter case, there is a significant complexation of alkali metal cations, especially lithium, by the carbene.

The *precursors* of imidazol-2-ylidenes are 1,3-disubstituted imidazolium salts that are obtained by the alkylation of relevant imidazoles. However, this approach is not suitable for the preparation of sterically shielded 1,3-dialkylimidazolium salts such as **1C**. As a consequence, a process that combines amines with formaldehyde (or paraformaldehyde), followed by the reaction of glyoxal with the condensation product **1B** in the presence of acids, was devised (Scheme 1).[43,44] Tetraphenylimidazolium salt **1E1** and 1,3-di(1-adamantyl)-4,5-diphenylimidazolium salt **1E2** were obtained in other pathways: via the oxidation of the corresponding thione with nitric acid[40] and via the quaternization of 4,5-diphenylimidazole with 1-bromoadamantane in the presence of sodium acetate in acetic acid,[45] respectively.

$$2RNH_2 \xrightarrow[\text{PhMe}]{CH_2O} (RNH)_2CH_2 \xrightarrow[\text{HX}]{(CHO)_2} \mathbf{C} \xrightarrow[\text{THF}]{t\text{-BuOK}} \mathbf{D} : \qquad \mathbf{E} :$$

    A   **B**   **C**   **D**   **E**

R = Me (**1**); 1-Ad (**2**); p-CH$_3$C$_6$H$_4$ (**3**); p-ClC$_6$H$_4$ (**4**); p-BrC$_6$H$_4$ (**5**);
E R = R' = Ph (**1**); R = 1-Ad, R' = Ph (**2**)

Scheme 1. Arduengo's method for the preparation of imidazol-2-ylidenes via diaminomethanes.

Subsequently, in some cases this reaction was carried out in a different order. The first step produced the glyoxaldiimines **2B** through the reaction of amines with glyoxal. The resulting diimines were cyclized to the imidazolium salts **2C** by treatment with alkoxymethyl chlorides or paraformaldehyde in the presence of protonating, alkylating or silylating agents (Scheme 2).[44,46] Similarly, the reaction of substituted glyoxals was used to produce alkyl-substituted imidazolium salts.[5]

The cyclization of diimines was effective for the preparation of sterically complicated imidazolium salts such as the mesityl- and Dipp-substituted compounds.[46] The 1,3-diaryl substituted imidazolium salts and their respective carbenes with sterically branched aromatic substituents such as **2E** (2,4-dibenzhydryl-4-methylphenyl- and its analogues) have also been prepared by this method.[47-53]

(i) $(CHO)_2$, i-PrOH; (ii) $ClCH_2OEt$, THF; (ii) NaH or t-BuOK, THF **D** Mes (**1**); Dipp (**2**); Me, 4,5-Me_2 (**3**); CD_3, 4,5-$(CD_3)_2$ (**4**). **E** R = Me, Ar = Ph (**1**), Et, Ph (**2**); MeO, Ph (**3**); Me, 1-$C_{10}H_7$ (**4**).
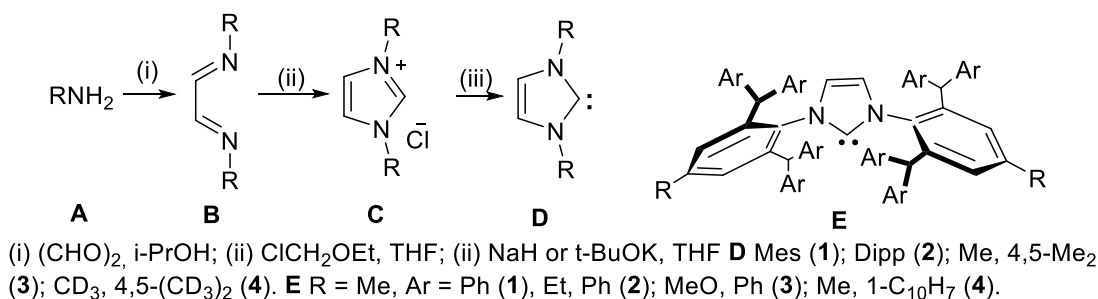
Scheme 2. Arduengo's method for the preparation of imidazol-2-ylidenes via diimines.

For the syntheses of the imidazol-2-ylidenes **3B**, Kuhn and Kratz used the reaction of potassium or a sodium-potassium alloy with the accessible *N*-substituted imidazol-2-thiones by heating them in tetrahydro-furan (Scheme 3).[54] The requisite thiones were prepared via the reaction of hydroxyketones with thioureas or via the reaction of sulfur with imidazolium salts in the presence of bases.

R' = Me; R = Me (**1**), Et (**2**), i-Pr (**3**)
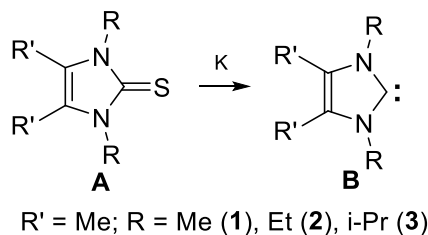
Scheme 3. Synthesis of imidazol-2-ylidenes by reduction of imidazol-2-thiones.

An unusual sterically shielded carbene featuring two imino groups has been synthesized using a sterically hindered acetanilide.[55] Treatment of the latter with PCl_5 readily generated the chloro-imine **4A.** In turn, two equivalents of **4A** reacted with the imidazole, at the NH group and the tertiary nitrogen atom, thereby forming the salt **4C** (Scheme 4). The carbene **4D** was obtained by reaction of **4C** with potassium hexamethyldisilazanide (KHMDS). During crystal growth **4D** was partially converted back into **4B**, followed by further insertion of a second equivalent of **4D** into the C-H bond of the N=C(H)N moiety in the latter.
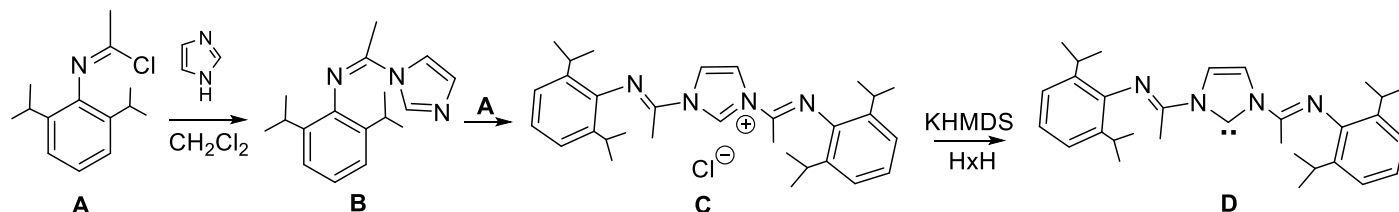
Scheme 4. Synthesis of diiminoimidazol-2-ylidenes.

This new breed of imidazol-2-ylidene carbenes permits significant steric protection of the reaction centers. Moreover, the structures of these compounds are unusual; studies of their catalytic properties could prove to be of significant interest.

Two sterically shielded, bifunctional imidazol-2-ylidenes with 6-trimethylsilylpyridine **5A** and substituted phosphine **5B** fragments have been synthesized using 1-Dipp-substituted imidazolium salts (Scheme 5).[56]
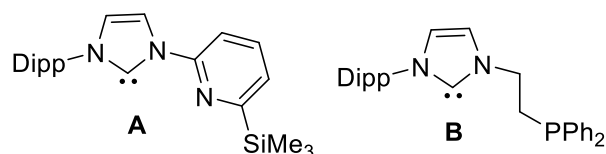
Scheme 5. Stable functionalised imidazol-2-ylidenes.

The functionalized 4,5-dichloro-substituted 1,3-dimesitylimidazol-2-ylidene **6G** was obtained via the reaction of CCl_4 with its 4,5-unsubstituted analogue **6A** (Scheme 6).[57] The reaction proceeds by the sequential chlorination of carbene **6A** with CCl_4, deprotonation of the 4 and 5 positions of the intermediate salt **6B** by the $[Cl_3C]^-$ anion (generated during the reaction with CCl_4) followed by chlorination of the anions **6C,E** with CCl_4 in these positions. This transformation provides a useful pathway for the introduction of substituents at the 4- and 5-positions of the imidazol-2-ylidene ring. The sterically complicated 4,5-dibromo-substituted imidazol-2-ylidenes (IPrHBr, IMesHBr) were synthesized in a similar fashion using CBr_4.[58] Along with the dichloro derivatives, these are all relatively stable on air.
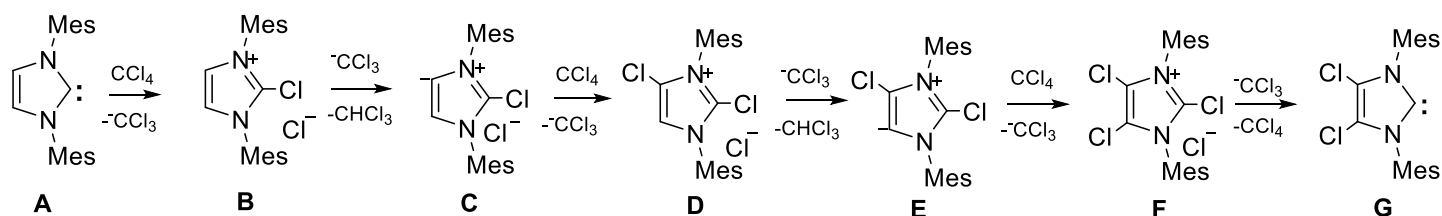
Scheme 6. Synthesis of 4,5-dichloroimidazol-2-ylidenes by chlorination of 4,5-unsubstituted imidazol-2-ylidenes with CCl_4.

Gates *et al.* have developed a method for the phosphaalkylation of the imidazol-2-ylidene **7A** by reacting phosphaalkenes at the 4-position of the ring (Scheme 7).[59] The reaction proceeds via a mesoionic state (carbene **7B**), with addition of the phosphaalkene forming the phosphanylcarbene **7D**.
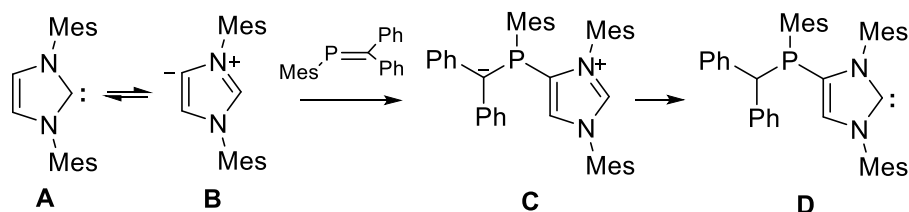
Scheme 7. Phosphanylation of imidazol-2-ylidenes with phosphaalkenes.

In order to obtain similar phosphanyl, as well as 4-aryl-, acyl-, alkylsulfonyl-, silyl-, and halogen-substituted imidazol-2-ylidenes (**8C**, Scheme 8), Bertrand *et al.* used a carbene rearrangement of the deprotonated products of the appropriate 2-substituted imidazolium salts **8B**.[60,61] Silyl derivatives of the imidazol-2-ylidene have also been used for carbene functionalization, without changes at the carbene center, using 1-adamantylamine (structure **8D**).[62]

$E = Ph_2P, Me_3Si, RCO, CF_3SO_2, Cl, Br$
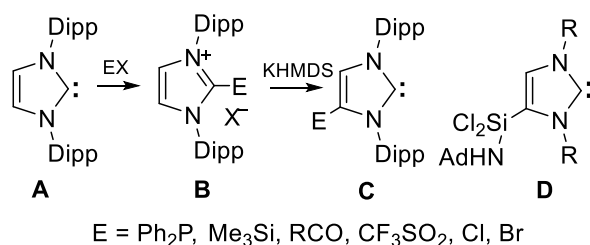
Scheme 8. Synthesis of 4-substituted imidazol-2-ylidenes by rearrangement of carbene adducts with electrophiles.

The difunctionalized derivative, 1,4-dimethyl-4,5-diphosphanylimidazol-2-ylidene **9F**, was synthesized in a similar fashion, namely by deprotonation of the corresponding imidazolium salt with LiHMDS (Scheme 9).[63]

(i) LiHMDS; (ii) Ph₂PCl; (iii) HX
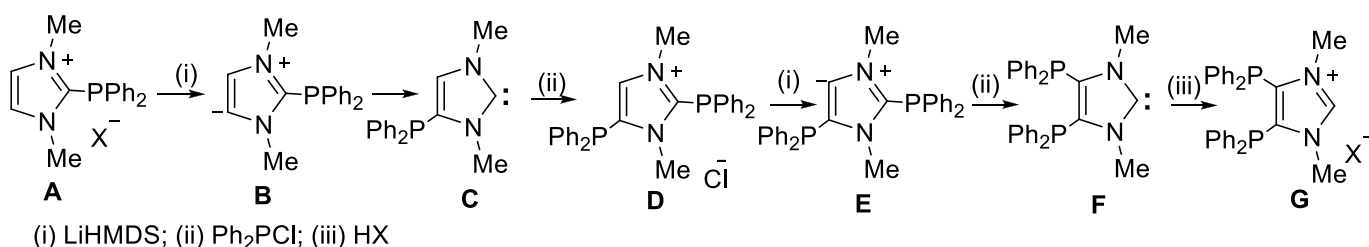
Scheme 9. 4,5-Diphosphanylation of imidazol-2-ylidenes.

A precursor for the synthesis of carbenes was obtained using a method similar to that employed by Arduengo *et al*. This involved sequential phosphanylation of the 1,3-dimethyl-2-phosphanylimidazolium salts **9B,E** with diphenylphosphanyl chloride in the presence of LiHMDS.[63] All attempts to isolate the 4-phosphorylated carbenes of similar type were unsuccessful. However, it was possible to obtain a number of carbene complexes of rhodium and iridium.[64]

The N-phosphorus containing carbenes **10C** were synthesized by the direct phosphanylation of the azole lithium derivatives **10B**, to which a carbene structure was assigned (Scheme 10).[65] The syntheses of phosphanyl substituted carbenes have been described in the review by Gaillard *et al.*[66]

Polymeric derivatives of 4-lithiumimidazol-2-ylidenes of the type **11B** were prepared via the reaction of butyllithum with the imidazol-2-ylidene **11A**. These were used for the synthesis of the chiral silyl substituted mono- (**11E**) and bis-imidazol-2-ylidenes,[67] and also via the reaction with dimesitylborofluoride for the synthesis of the boryl substituted carbene **11C** (Scheme 11).[68] The latter product could also be obtained via the reaction of dimesitylborofluoride with carbene **11A**, followed by the deprotonation of the zwitterion **11D** using potassium hexamethyldisilazanide.
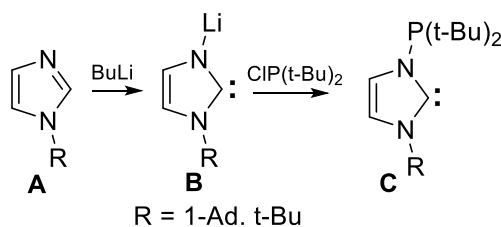
Scheme 10. Synthesis of 3-phosphanylimidazol-2-ylidenes via phosphanylation of Li-azoles.
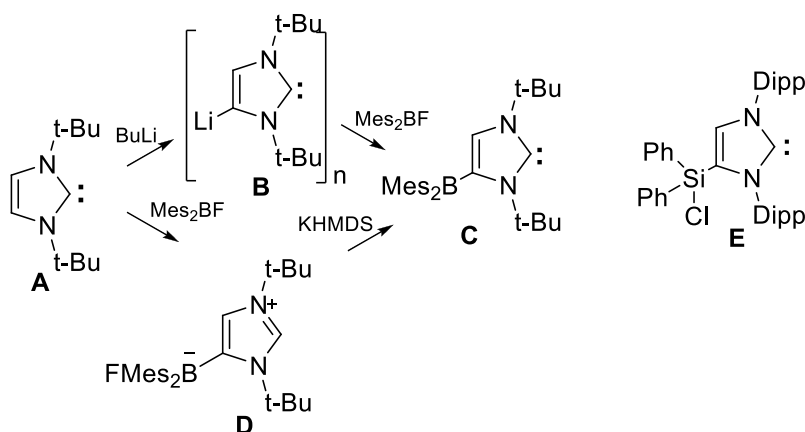
Scheme 11. Borylation and silylation of imidazol-2-ylidenes.

The 4,5-bisdimethylaminoimidazolium and tetrasubstituted bisdimethylaminoimidazolium derivatives **12C** were prepared by the interaction of lithium amidines with the diphosphonium salts **12B** (Scheme 12).[69] The reaction of potassium hydride with the salts **12C** in THF resulted in the formation of the carbenes **12D**. The strongly polarized carbenes **12D** are good representatives for Umpolung reactivity. The corresponding reaction of butyllithium with **12C** resulted in the formation of the lithium salt complexes **12E** that were characterized by chemical transformations.

Ar = Ph, p-MeC$_6$H$_4$, p-Me$_2$NC$_6$H$_4$
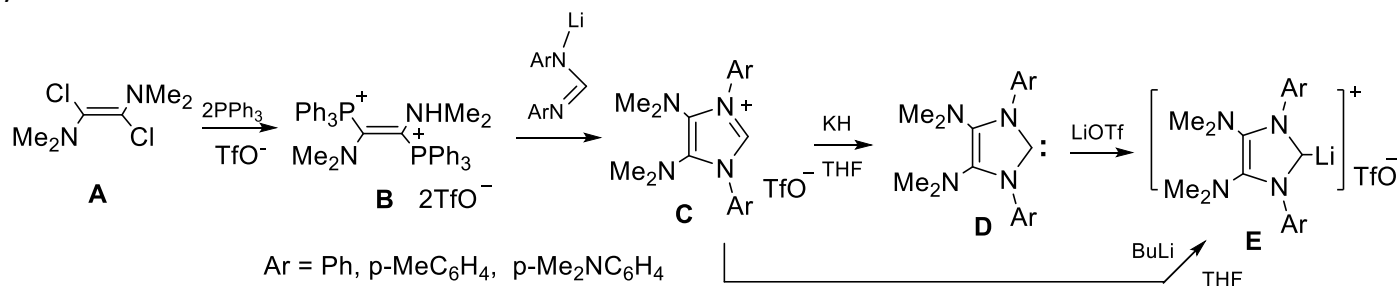
Scheme 12. Synthesis of 4,5-diaminoimidazol-2-ylidenes.

4,5-Dicyano-substituted imidazol-2-ylidenes have been used for the preparation of palladium complexes. However, the free carbenes were not isolated.[70,71]

Cyclosilanyl derivatives of the imidazol-2-ylidenes were obtained from the reaction of carbenes with stable silylenes **13A**.[72] These, in turn, gave rise to the stable carbenes **13C** due to ylide formation at the methyl group (**13B**) (Scheme 13). The resulting compounds were then used for carbene-silylene complexation of transition metals.[73]
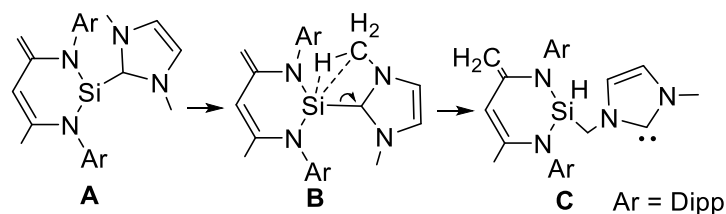
Scheme 13. Synthesis of silanyl derivatives of imidazol-2-ylidenes.

Hydrocarbon derivatives that had been introduced on the nitrogen atoms of imidazolium salts have been converted to the respective carbene complexes by known methods. However, the free carbenes were not isolated.[74] Instead, complexation afforded a series of neutral Rh(I) compounds that showed promising activity for enantioselective ketone hydrosilylation.

Carboranyl substituted compounds have been synthesized using a method similar to that described by Arduengo *et al.*[75] A cesium (anionic) derivative of a carboranylamine was synthesized via the appropriate dicesium-diimine followed by further cyclization of the latter with paraformaldehyde in the presence of hydrogen chloride (Scheme 14). The resulting salt **14A** could be deprotonated under a variety of conditions to give a mixture of products. After optimization of the syntheses it became clear that the normal carbene complex with lithium at the 2 position **14B** is formed by treatment with LiHMDS (2 eq.) at −78°C (C^2 signal in the ^{13}C NMR spectrum, δ 196.9 ppm). The reaction with LDA leads to the product under thermodynamic control, namely the mesoionic complex **14C** (δ C^4 174.7 ppm). In solution compound **14B** was converted (50%) to complex **14C** after 2 weeks, while at 50°C the reaction was complete in 24 hours. The biscarbene complex **14D** was formed (δ C^{2,4} 195.6, 169.5 ppm) by the addition of three equivalents of butyllithium to **14A**.
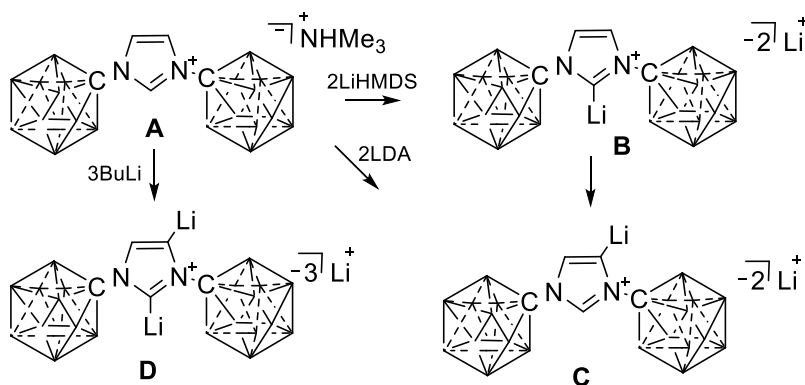
Scheme 14. Synthesis of lithium complexes of carboranylimidazol-2-ylidenes.

Non-aromatic fused derivatives of the imidazol-2-ylidenes **15C,D** were obtained by Glorius *et al*. starting from the appropriate oxazolines and bisoxazolines **15A**[76-78] (Scheme 15). The carbenes were characterized in

solution on the basis of their spectral data. Compounds of type **15D** exhibit high steric shielding of the carbene center. In fact, the steric shielding exceeds those reported for the *tert*-butyl and adamantyl substituted imidazol-2-ylidenes.[79]

(i) AgOTf, ClCH$_2$OCOt-Bu; (ii) KH, t-BuOK, THF
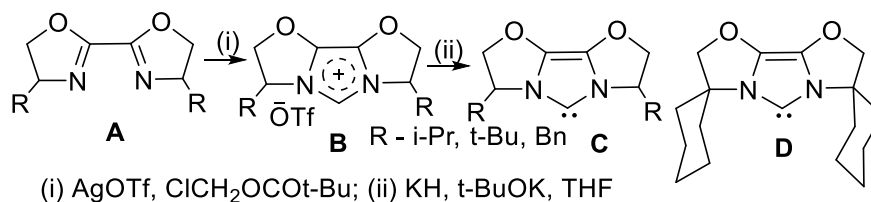
Scheme 15. Synthesis of sterically hindered dioxazolinoimidazol-2-ylidenes.

Bildstein *et al.* proposed the use of ferrocene containing imidazol-2-ylidenes[80] for the synthesis of transition metal complexes, thus taking into account the useful electrochemical properties of metallocene derivatives such as their high chemical stability and reversible redox behaviour. However, only salt precursors were obtained using the classical method of Arduengo for ferroceneimines. The cyclization of diimines was carried out via the reaction of paraformaldehyde with zinc triflate. After treatment with bases, the isolation of stable carbenes was unsuccessful.

The precursors and complexes of chiral ferrocenes containing imidazol-2-ylidenes were also synthesized via the reaction of chiral alcohols with imidazoles in acetic acid.[81] Chiral phosphine and sulfide containing ferroceneimidazol-2-ylidenes were obtained starting from the reaction of the corresponding amines with triethylorthoformate to form formamidines **16A.** This was followed by the alkylation of the latter with bromoacetal and cyclization of the substituted formamidine **16B** with boron trifluoride to form the salts **16C** (Scheme 16).[82-84]

The synthesis of the 1,3-diferrocene containing imidazol-2-ylidene **16D** was reported initially by Broggini and Togni.[85] The carbene was identified as a monomer and the structure was determined by means of X-ray diffraction. Compound **16E** was isolated and analyzed by NMR spectroscopy.[86] 1-Methyl-3-(2-dimethylamino-methylferrocenyl)imidazol-2-ylidene **16F** was synthesized by reaction with the corresponding amino- (via diimino formation) or halogeno-ferrocenes (via alkylation of imidazoles).[87]

(i) BrCH$_2$CH(OEt)$_2$, NaH, DMF
(ii) BF$_3$, NaI, CH$_3$CN
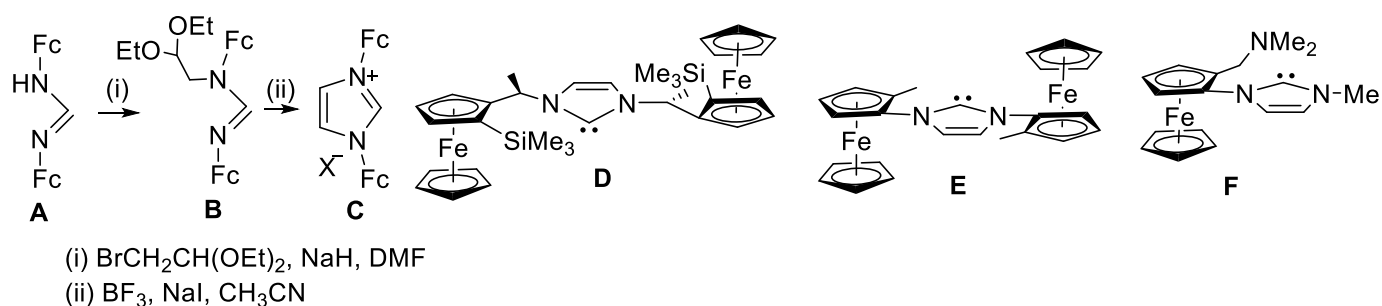
Scheme 16. Synthesis of ferrocenyl substituted imidazol-2-ylidenes.

Carbenes of the imidazol-2-ylidene series have also been obtained from the corresponding azolium salts using electrochemical synthesis.[88] The ability of carbenes to be electrochemically reduced to anion radicals[89] had already been demonstrated on the compound 1,3,4-triphenyl-1,2,4-triazol-5-ylidene.

2.1.2. Bis- and tris-imidazol-2-ylidenes. Herrmann *et al*. first isolated bisimidazol-2-ylidene **17A1** (R = Me, X = (CH₂)₂) by deprotonation of a bisimidazolium salt with sodium hydride in liquid ammonia (Scheme 17).[90] However, the crystal structure has not yet been determined. The most stable carbenes **17A2** (R = Mes, Dipp, X = CH₂) were synthesized much later via the reaction of 3,3'-diarylbisimidazoliummethanes with potassium *tert*-butoxide in THF.[91] The triscarbene **17B** was isolated in a crystalline state by Dias *et al*. as a result of deprotonation of the corresponding trisimidazolium salt with potassium *tert*-butoxide in THF.[92] However, in this case an X-ray diffraction study was not carried out. The first bisimidazol-2-ylidenes **17A3** (X = pyridine-2,6-diyl) with precisely defined structures were synthesized by Danopoulos *et al*.[93] using pyridine-2,6-diimidazolium salts (the condensation products of 2,6-dibromopyridine with the corresponding 1-substituted imidazoles). These biscarbenes are stable at room temperature for several hours and indefinitely stable when cooled (–30 °C). The triscarbene **17C** was synthesized via the reaction of the appropriate trisimidazolium salt with potassium *tert*-butoxide in THF solution.[94]

A R = Me, X = (CH₂)₂ (**1**);
Mes, CH₂ (**2**);
Mes, pyridine-2,6-diyl (**3**)

B-D R = t-Bu
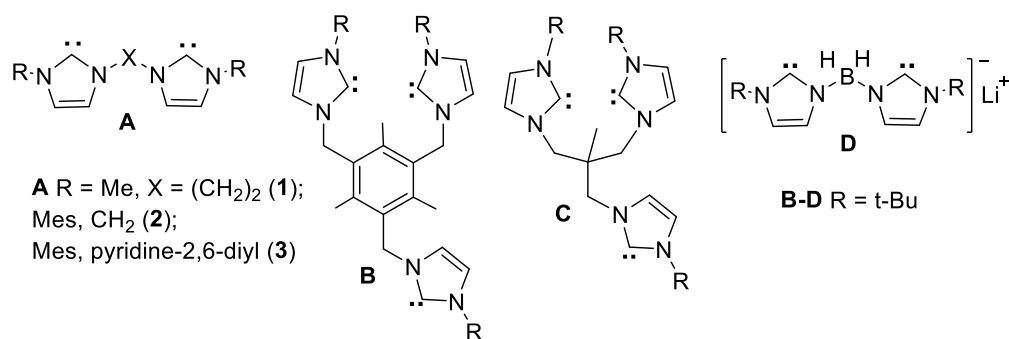
Scheme 17. Stable bis- and trisimidazol-2-ylidenes.

The *precursors* to the bis- and triscarbenes **17A-C** were synthesized by quaternization of the corresponding N-substituted imidazoles with the respective haloalkanes.[90-94]

The borane derivatives of the bisimidazol-2-ylidenes **17D** were generated from the corresponding salts in order to obtain their transition metal complexes.[95-98] Synthesis of the precursors takes place easily via the reaction of haloboranes with N-substituted imidazoles (or alternatively with *tert*-amine complexes of haloboranes) or via the reaction of metal borohydrides with imidazoles followed by subsequent quaternization. Lithium complexes of boranbisimidazol-2-ylidenes have also been prepared.[98] Furthermore, the corresponding potassium complexes can be used for the synthesis of stabilized germylenes.[99,100]

The lithiated carbene **18A** was used for the preparation of the silylene-containing biscarbene **18B** (Scheme 18).[67] An alternative route to similar structures (**19D**) was proposed by Schneider *et al.* (Scheme 19),[101] involving the direct silylation of carbene **19A**. The adduct **19B** is further transformed by heating to form the bridged silylene imidazolium salt **19C** (obtained from Ph₂SiCl₂ with two equivalents of the carbene) followed by deprotonation of **19C** with sodium hydride in the presence of potassium *tert*-butoxide in THF solution.
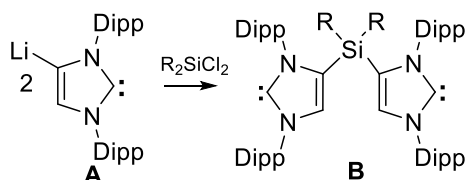
Scheme 18. Synthesis of bis-imidazol-2-ylidenes by silylation of Li-imidazol-2-ylidenes.
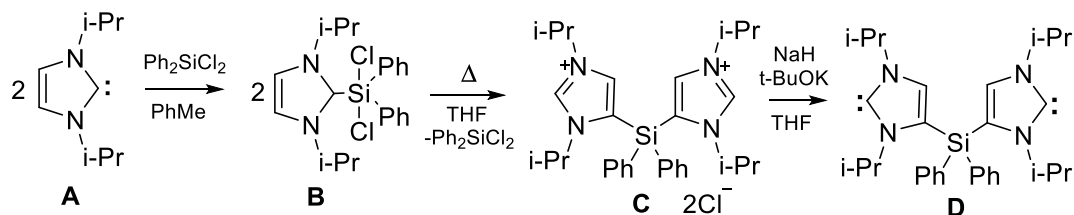
Scheme 19. Synthesis of bis-imidazol-2-ylidenes by silylation of imidazol-2-ylidenes.

2.2. Fused aromatic analogues of imidazol-2-ylidenes

2.2.1. Fused monoimidazol-2-ylidenes. The following alkylation methods were used to obtain precursors for the simplest 1,3-disubstituted, 10-n,π-electron benzimidazol-2-ylidenes. The benzimidazolium salt **20C** was synthesized in high yield by alkylation of 1-(1-adamantyl)benzimidazole **20B** with 1-bromoadamantane.[102] The reaction of sodium hydride with salt **20C** in acetonitrile resulted in formation of the carbenoid 2-cyanomethyl derivative of the corresponding 2*H*-benzimidazoline **20D**, which then decomposes to form the pure 1,3-di-(1-adamantyl)-benzimidazol-2-ylidene **20E** (Scheme 20).[103,104]

Subsequently, adamantyl substituted salts of the type **20C** were obtained starting from 1-adamantylamine and substituted *o*-dibromobenzenes in the presence of sodium *tert*-butoxide, palladium acetate and racemic BINAP followed by cyclization of the resulting diamines with triethylorthoformate in the presence of concentrated hydrochloric acid.[105]

(i) AdBr, K$_2$CO$_3$, o-DCB; (ii) AdBr, o-DCB; (iii) NaH, CH$_3$CN; (iv) 180 °C, -CH$_3$CN
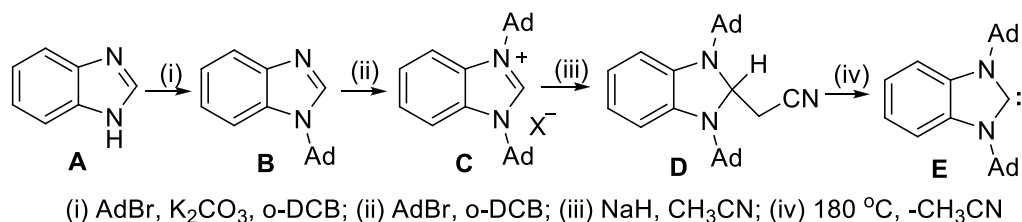
Scheme 20. Synthesis of 1,3-diadamantylbenzimidazol-2-ylidene via decomposition of 2-cyanomethyl-2*H*-benzimidazoline.

A modification of the method of Kuhn and Kratz that uses a potassium-sodium alloy and azolethiones in toluene solution[106] was utilized for the synthesis of 1,3-dineopentylbenzimidazol-2-ylidene **21D** (R = Np, as a mixture of stereoisomers). Its formation takes place at room temperature over a period of 20 days (Scheme 21) in a 60% yield. It is interesting that if the reaction is carried out in THF under the same conditions, the carbene is reduced to the 2*H*-azoline. However, this outcome may have been due to insufficient drying of the solvent.

Np = CH$_2$t-Bu

(i) ClCOt-Bu; (ii) LiAlH$_4$, THF; (iii) CSCl$_2$; (iv) K/Na, PhMe
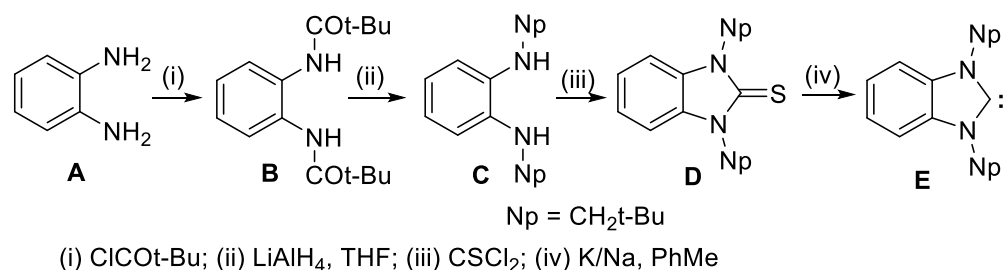
Scheme 21. Hahn's synthesis of 1,3-dineopentylbenzimidazol-2-ylidene.

The *precursor* **21D** was obtained from the diamide **21B**, which was then reduced by lithium aluminium hydride followed by treatment of the resulting diamine **21C** with thiophosgene.

Decreasing the steric hindrances in **21E** results in dimerization of the carbene. A good example of relatively slow dimerization is provided by 1,3-diisobutylbenzimidazol-2-ylidene.[107]

The *o*-phenylenediamine required for the synthesis of 1,3-dimesitylbenzimidazol-2-ylidene was prepared by catalytic routes according to the Buchwald and Hartwig method, namely: (1) the arylation of *o*-phenylene-diamine with mesitylbromide (and related haloarenes) in the presence of Pd_2dba_3, BINAP and sodium *tert*-butoxide;[108] or (2) the amination of *o*-dibromobenzene with mesitylamine in the presence of palladium acetate, BINAP and sodium *tert*-butoxide.[104] The actual syntheses of these carbenes have not yet been described.[109]

The salt precursors for the benzimidazol-2-ylidenes **22A** were synthesized by quaternization of N-methyl-benzimidazole with di-*tert*-butylphosphanyl bromide (Scheme 22). Similar compounds were isolated by direct phosphanylation of lithium benzimidazoles with di-*tert*-butylphosphanyl chloride according to Scheme 10 or by deprotonation of the appropriate N-phosphanylbenzimidazolium salts with NaHMDS, Me_2NLi or MeLi.[65,110]

A R = t-Bu, i-Pr_2N; R' = Me, i-Pr;   (i) CH_2O, H_2O; (ii) Ph_3C BF_4
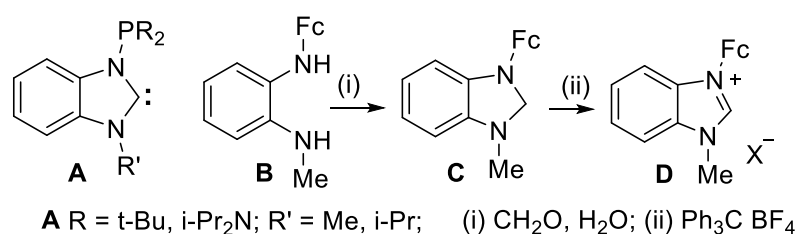
Scheme 22. *N*-phosphanylbenzimidazol-2-ylidenes and synthesis of *N*-ferrocenylbenzimidazolium salts.

The ferrocene-containing benzimidazolium salts **22D** were first synthesized by Bildstein *et al.* and used for the preparation of metal complexes.[111] The key stage of the reaction involves the cyclization of the ferrocenediamines to azolines **22C** and the elimination of a hydride ion from each of them. Isolation of the individual carbenes was impossible in this case due to their tendency to dimerize (note, however, that the coupled product that was formed by deprotonation of the salts **22D** was isolated in high yields).

Bielawski *et al*. added two benzimidazolium fragments to ferrocene according to Scheme 23.[112]

(i) o-O_2NClC$_6$H$_4$, DMSO, NaHCO$_3$; (ii) Pd/C, HCOOH / HCOONa; (iii) Et$_3$O BF$_4$, DCM
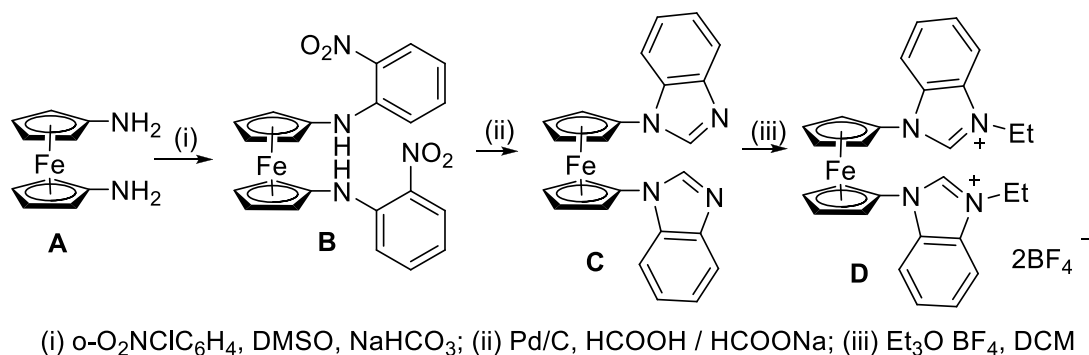
Scheme 23. Synthesis of ferrocene-bridged benzimidazolium precarbenes.

The 2-aza-analogues of the benzimidazol-2-ylidenes **24A1,2**, with sterically shielding neopentyl substituents, were synthesized from the corresponding diamines by cyclization with triethyl orthoformate in

the presence of ammonium salts. This was followed by deprotonation of the quaternary salts with potassium hydride in THF (Scheme 24).[113] The authors evaluated carbenes **24A1,2** and found them to be less stable with respect to their analogs: silylenes, germylenes and stannylenes, the observed order of stability being: Sn > Ge > Si > C.

The fused carbene **24B** (80% purity in an admixture with the corresponding 2*H*-azoline) was obtained by deprotonation of the appropriate naphthoimidazolium salts with potassium-graphite KC_8 in THF.[114] A purer carbene (90% content) was obtained in this work by Kuhn's method using a mixture of the corresponding thione and potassium in THF.

A new carbenoid system based on 2,3-dichloroquinoxaline (precursor to carbene **24C**) was successfully prepared by its reaction with isopropylamine or neopentylamine, followed by further cyclization of the intermediate diamine with triethyl orthoformate. Deprotonation of the intermediate salt with potassium hydride in THF was used *in situ* for the syntheses of the carbene complexes of rhodium and silver.[115] However, the preparation and isolation of free carbenes **24C** has not yet been reported.

A1,2: Y = CH, Z = N (**1**); Y = N, Z = CH (**2**); **B, C** R = i-Pr, Np; **E1,2** R = C*H(Me)(Ph), R' = Bu (**1**); R' = Bn (**2**); R = R' = Bu (**3**); R = R' = o-Tol (**4**).
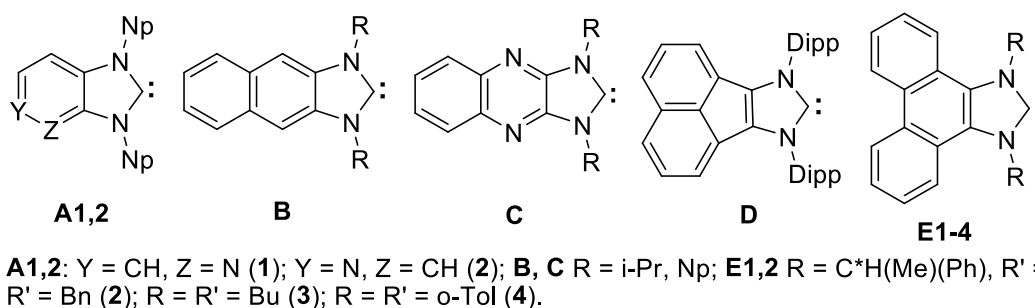
Scheme 24. Fused analogues of imidazol-2-ylidenes.

The Dipp-protected, fused 16-n,π-electron acenaphthyleneimidazol-2-ylidene **24D** was synthesized using acenaphthylenediimine and methoxymethyl chloride[116] according to the classical Arduengo scheme. The carbene that is formed via the reaction of potassium *tert*-butoxide with the fused imidazolium precursor in THF has a very high melting point (approximately 300 °C). It readily forms complexes with transition metal salts,[116-118] including palladium complexes that are efficient as catalysts for the Suzuki-Miyaura reaction.[119]

The phenanthrene-fused, aromatic 18-n,π-electronic imidazol-2-ylidenes **24E1-4** were generated as described in the referenced works.[120-123] However, these compounds were not isolated in a crystalline state. The authors[121] believe that the butyl and benzyl derivatives are stable for some time, and that the latter does not form ylides. The oily di-*o*-tolyl-substituted compound **24E4** is considered to be the most stable of these compounds.[122]

Butyl-substituted pyreneimidazol-2-ylidenes[124,125] and Dipp-substituted pyranocenes[126,127] were generated from the corresponding salts **25A,B** with a view to obtaining carbene complexes (Scheme 25). However, the isolation of these carbenes has not been carried out (the carbenes derived from the **25A** precursors probably exist as dimers). Polymeric complexes of these compounds were studied for their catalytic behavior.[128]
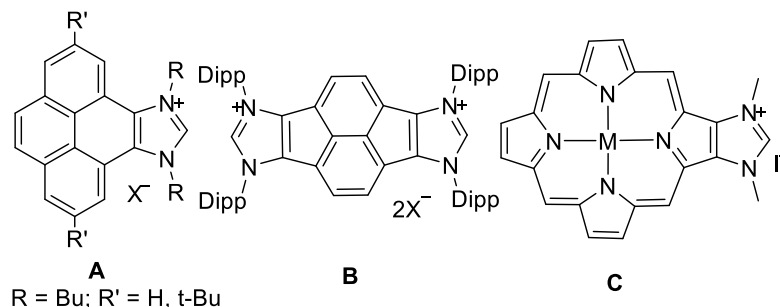
Scheme 25. Pyrene, pyranocene and porphyrine precarbenes.

Complexes of condensed imidazoliumporphyrins **25C** with a variety of metals in the porphyrin ring and rhodium in the carbenoid have been obtained[129]. However, individual carbenes of these types have not yet been isolated. The desired imidazoporphyrins were synthesized by nitration of the related porphyrin complex with LiNO$_3$ in the presence of AcOH and Ac$_2$O. This is followed by amination of the 1-nitroporphyrins with 4-amino-1,2,4-triazole in a basic medium, reduction of the 2-amino-1-nitroporphyrins with sodium borohydride and cyclization of the 1,2-diaminoporphyrins with triethyl orthoformate or by other methods.[130] The *precarbene* quaternary salts are easily prepared by quaternization of imidazoporphyrins with alkylating agents. The carbenoid analogue salts **26C** were synthesized by derivatizing the aldehyde function of azaquinolines (Scheme 26).[131]
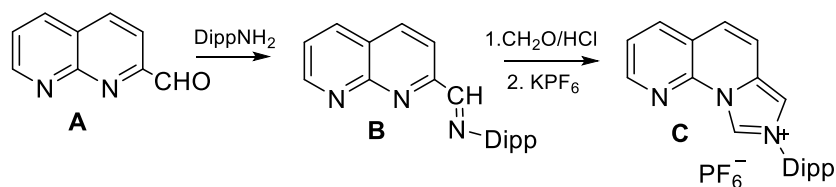
Scheme 26. Synthesis of precarbene phenanthroline analogues.

The analogues of benzimidazol-2-ylidenes are the *N*-annulated carbenes (pyridoimidazol-2-ylidenes) **27C** (Scheme 27). Typically they are synthesized by cyclization of the formylaminomethylpyridines **27A** in POCl$_3$ in the presence of KPF$_6$, followed by deprotonation of the salts **27B** with sodium hydride in the presence of catalytic amounts of potassium *tert*-butoxide.[132] The resulting compounds are either oils or amorphous solids. They have been characterized on the basis of their ^{1}H and ^{13}C NMR spectra and remain stable for long periods of time at room temperature. The structure of the methyl substituted compound (R = Me, R', R'', R''' = H) was established on the basis of a single crystal X-ray diffraction study.[133] Transition metal complexes from the salt precursors **27B** can also be prepared from the corresponding pyridinealdehydes **27D** via the imines **27E** according to a published method.[134]

(i) POCl$_3$, KPF$_6$; (ii) NaH, THF; (iii) MesNH$_2$, PhMe;
(iv) AgOTf, ClCH$_2$OCOt-Bu, DCM
R = Me, Mes; R' = R'' = R''' = H; R', R'' or R'', R''' = (CH)$_4$
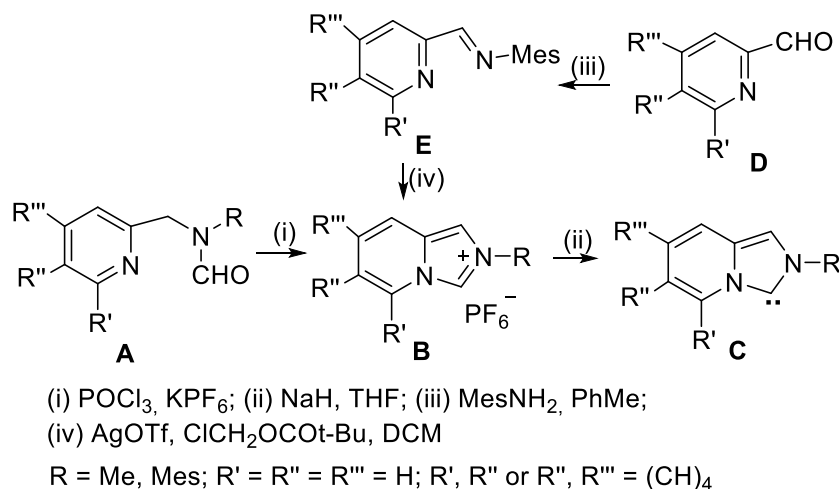
Scheme 27. Synthesis of N-annulated pyridoimidazol-2-ylidenes.

A similar reaction sequence was used to prepare an annulated carbenoid derivative **28C** from quinoline-2-aldehyde (Scheme 28).[135] The sulfur containing analogues of **27B, 28C** and their related complexes are also known.[136]

Cyclophane derivatives of the imidazolium salts **28D**, including those that are chiral, have been described.[137,138] The cyclophane carbene ligands (R = H, OMe) in complexes of the type described therein possess notedly higher donor abilities than their non-cyclophane analogues. But fluoro-containing carbene (R = F) exhibits lower electron donating ability (at the level of non-cyclophanes). Chiral compounds **28E** have been synthesized for asymmetrical catalysis of the Miyaura reaction of arylboronic acids with aromatic aldehydes to form chiral diarylcarbinols. However, individual carbenes of both types (**28D,E**) have not yet been synthesized.

R = H, F, OMe

R = Me, R-CHMePh,
S-CHMePh, Mes;
R' = OMe, Ph$_2$PO
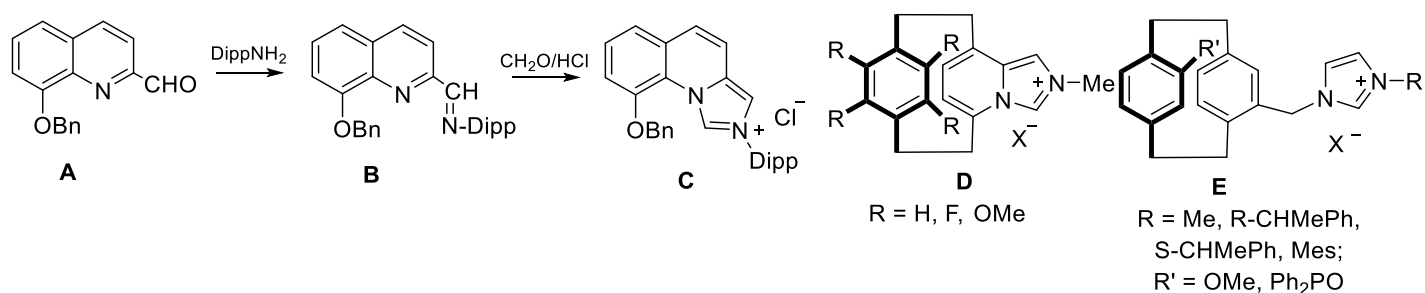
Scheme 28. Synthesis of precarbenes of N-annulated quinolinoimidazol-2-ylidenes.

The development of a method for the preparation of 1,10-diazafluorenylium bistriflate **29C**, via the reaction of trifluoromethanesulfonic acid with a diazoarsonium derivative **29A**, preceded the synthesis of the 14 n,π-electronic 1,10-diazafluoren-11-ylidene **29D** (R = H) (Scheme 29).[139] It can be considered as an aromatic biPy complex of carbon(0). The reaction proceeds via the intermediate arsonium methyltriflate **29B** which effectively generates methylene to connect with 2,2'-bipyridyl and thereby form the bisalt **29C**. The triflate anion was easily exchanged for bromide via reaction with tetrabutylammonium bromide, allowing isolation and characterization of a solid bromide derivative of **29C**. Deprotonation of the former with potassium *tert*-

butoxide in THF solution produced the carbene **29D**, which, however, failed to form in a crystalline state.[139-141] A more stable version of the carbene (di-*tert*-butyl-substituted, R = *t*-Bu) was also prepared.[133]
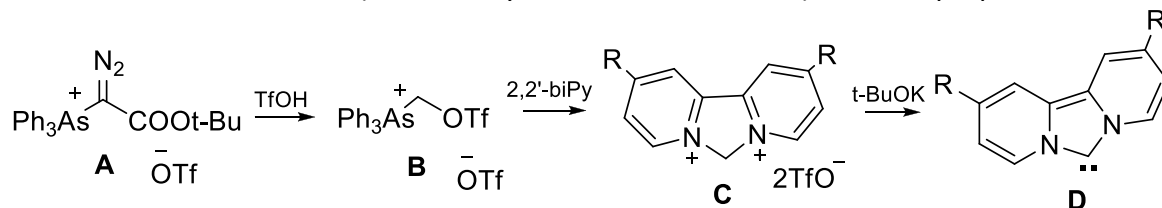
Scheme 29. Synthesis of stable 1,10-diazafluoren-11-ylidenes.

Attempts have been made to prepare related carbene complexes using 2,8-dichloro- and sulfur-containing precursors. However, the isolation of carbenes was unsuccessful[142] due to decomposition of the carbene during deprotonation of the precursor salt.

The syntheses of carbenoid imidazolium salts **30D**, for the preparation of anion-fused imidazol-2-ylidenes of the Arduengo type (pentalene analogues), were implemented using a substitution reaction on imidazole rings (Scheme 30). However, after the addition of potassium *tert*-butoxide to the salt in THF solution only the pentalene **30E** was formed, and further attempts at deprotonation were unsuccessful.[143] Nevertheless, desired compounds of ferrocene containing the imidazol-2-thione **30F**[144] and related transition metal complexes[145] have been obtained. Using the chloro-substituted derivative **30C** and an appropriate salt the ruthenium complex **30G** was synthesized, it being nearest to the target pentalene-carbene in terms of its structure.[146]

The syntheses of salts and complexes of the fused derivatives of imidazol-2-ylidene and analogues of the type **31A,B** have been carried out in studies by Metallinos,[147-149] and Grubbs *et al.*[150] (Scheme 31).

Following the publication of a paper[151] in which 5-substituted palladium complexes of benzimidazolium-5-ide have been described, the syntheses of mesoionic carbenes of the annulated type **31C** can be anticipated.

(i) BuLi, 3-Me-3-penten-2-one;
(ii) TsOH, DCM; (iii) LiAlH$_4$, THF;
(iv) Me$_3$O BF$_4$, DCM; (v) t-BuOK, THF
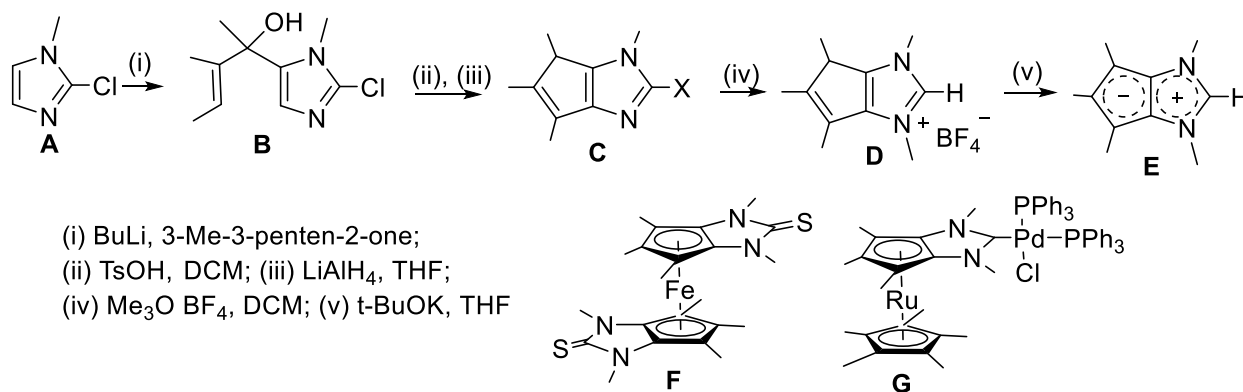
Scheme 30. Synthesis of a precarbene imidazolium annulene.
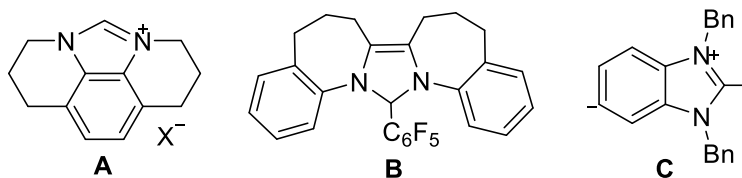
Scheme 31. Aliphatic and aromatic fused carbenoids of the imidazole series.

2.2.2. Bis- tris- and polybenzimidazol-2-ylidenes. The syntheses of aromatic derivatives of the sterically shielded benzimidazol-2-ylidenes were carried out on selected annulated bisimidazol-2-ylidenebenzenes. Initially, the tetramines **32B** were obtained by means of treatment of tetrabromobenzene **32A** or its chloro-analogue with the respective amines, in the presence of an alkoxide and a catalytic complex of the carbene IPr with palladium acetate (Scheme 32).[152] The desired bisimidazolium salts **32C** were then synthesized by treatment of **32B** with triethyl orthoformate in the presence of an acid capable of undergoing deprotonation by strong bases (potassium *tert*-butoxide, sodium hydride or KHMDS),[153,154] thereby forming the stable carbenes **32D**. Deprotonation of the asymmetric derivative **32D4** resulted in the formation of a dimer in which there are two sterically shielded carbene centers **32E**.

B-D R = R' = 1-Ad (**1**),
t-Bu (**2**), t-Am (**3**); **B-D** (**4**),
E R = t-Bu, R' = Me

(i) RNH$_2$ or R'NH$_2$, t-BuONa, Pd(OAc)$_2$, IPr·HCl; (ii) CH(OEt)$_3$, HX; (iii) LDA, PhMe;
(iv) NaH, t-BuOK, PhMe
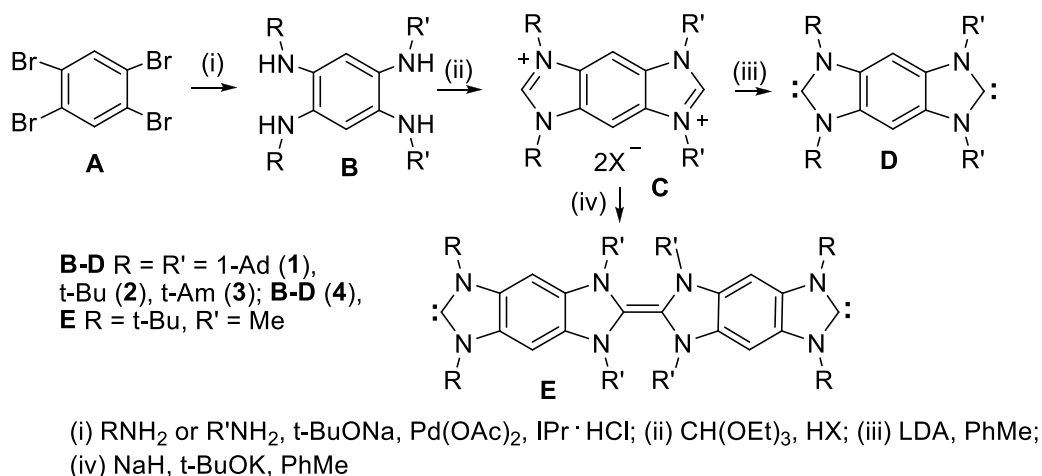
Scheme 32. Synthesis of bisbenzimidazol-2-ylidenes.

The building blocks of bisbenzimidazolylidene borate and bisbenzimidazol-2-ylidene phthalimide were created by reaction of the 5,6-dihydroxybenzimidazolium salt with benzene diboronic acid or from imidazo[5,6-d]phthalic anhydride with aromatic polyamines (e.g., tris-(4-aminophenyl)methane or its tetrakis-analogue).[155,156] Only one individual carbene was isolated (compound **33E**, Scheme 33). Unfortunately, it was not possible to characterize this compound by means of X-ray diffraction.

Trisbenzimidazol-2-ylidenes of the triptycene series **34D** were obtained from the 9,10-dibutylhexabromo-tripticenes **34A** by heating with *tert*-BuNH$_2$ in toluene solution in the presence of carbene complex Pd(OAc)$_2$. This was followed by cyclization of the resulting diamines **34B** with triethyl orthoformate in the presence of HBF$_4$·OEt$_2$ and subsequent deprotonation of the salts **34C** with sodium hydride in the presence of potassium *tert*-butoxide (Scheme 34).[157]

a. Pd(OAc)$_2$, IPr.HCl, t-BuOK, MesNH$_2$ / PhMe;
b. CH(OEt)$_3$, HBF$_4$; c. (i) BBr$_3$, DCM; (ii) MeOH
BI = 1,3-Mes$_2$-benzimidazol-2-ylidene 5,6-disubstituted
d. BDBA - 1,4-(HO)$_2$BC$_6$H$_4$B(OH)$_2$, EtOH
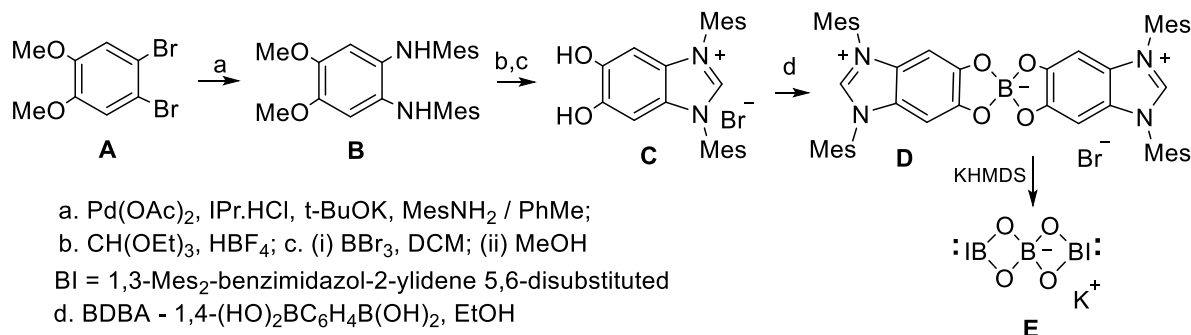
Scheme 33. Synthesis of boron containing bisbenzimidazol-2-ylidene and its precarbene.

Complexes of the conjugated 30-n,π-electron trisbenzimidazol-2-ylidenes **34E** were obtained in a similar fashion starting from hexabromotriphenylene.[158,159] The isolation of the triscarbenes **34E** was effected by treatment of the appropriate tetrafluoroborate salts with potassium hydride in tetrahydrofuran.[160]

R = Bu (**1**), Hx (**2**)
(i) t-BuNH$_2$ / Pd(OAc)$_2$-IPr·HCl-
t-BuONa / PhMe; (ii) CH(OEt)$_3$ /
HBF$_4$.OEt$_2$; iii NaH, t-BuOK / THF

E   R = t-Bu, Mes
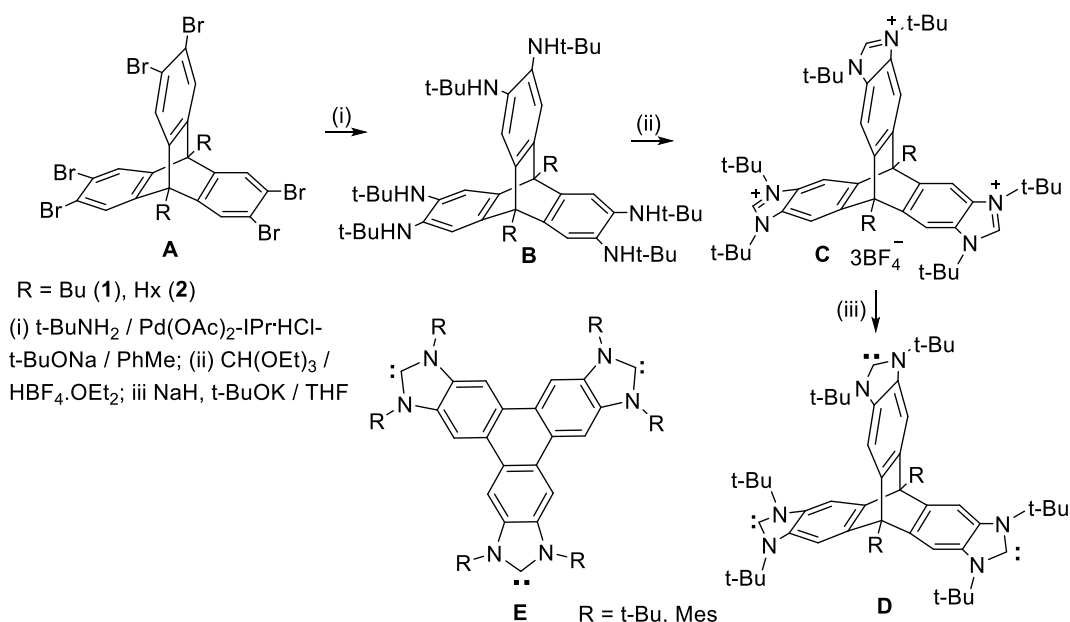
Scheme 34. Synthesis of fused trisbenzimidazol-2-ylidenes.

The polymeric carbenes **35A** can be synthesized from Bielawski biscarbenes using B$_2$Br$_4$ followed by reaction of the carbene adducts with sodium naphthalenide (Scheme 35).[161] Other polymeric structures have also been prepared.[162] However, their structures are different due to the absence of terminal carbene fragments.

Promising precursors for benzimidazol-2-ylidene derivatives can be prepared from ionic benzimidazolium and imidazolium crown derivatives. These can be synthesized using benzimidazole and 1,5-dichloro-3-oxapentane or 1,8-dichloro-3,6-dioxaoctane in an alkaline medium under the conditions required for phase transfer catalysis by quaternary ammonium salts, followed by quaternization of the intermediate alkylene-bisbenzimidazoles with same reagents in *o*-dichlorobenzene.[163,164] However, it was found that the deprotonation of the benzimidazolium compounds **35B** resulted in the formation of carbene polymers **35C**.[165]

Recent reviews of the syntheses and properties of annulated imidazolylidenes are available in the cited papers.[166,167]

R = 1-Ad, t-Bu, t-Am   **A**

B: R,R = $(CH)_4$, n = 1 (**1**); R,R = $(CH)_4$, n = 2 (**2**); R = H, n = 1 (**3**); R = H, n = 2 (**4**); X = Cl, ClO_4;
C: R, R = $(CH)_4$, n = 1
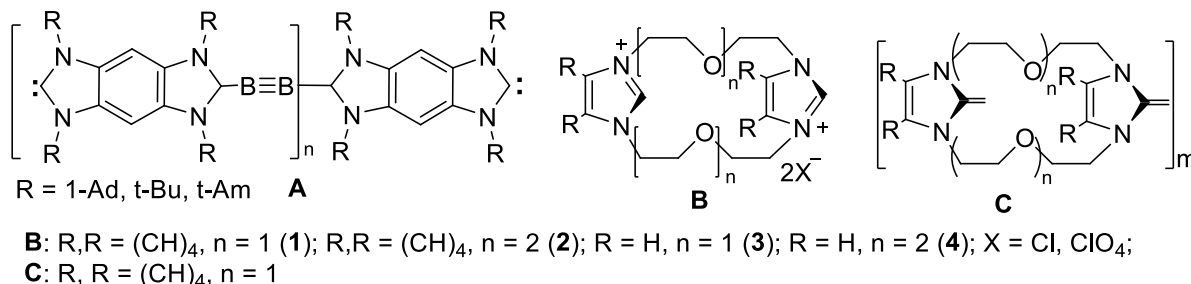
Scheme 35. Boron containing carbene polymers and new carbenoids of crown type.

2.3. 1,2,4-Triazol-5-ylidenes

The first 1,2,4-triazol-5-ylidene **36C** was synthesized by Enders *et al*. via deprotonation of the 1,3,4-triphenyl-1,2,4-triazolium salt **36A** with sodium methoxide. Further decomposition of 5-methoxytriazoline **36B** occurred upon heating under vacuum at 80 °C for 24 h (Scheme 36).[168]
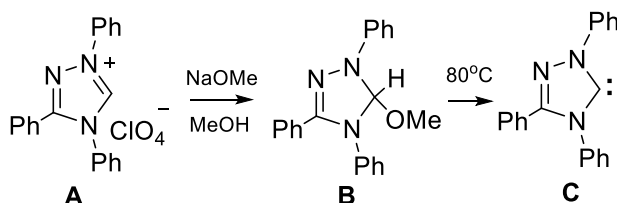
Scheme 36. Enders' synthesis of 1,3,4-triphenyl-1,2,4-triazol-5-ylidene.

For the synthesis of the *precarbene* 1,3,4-triphenyl-1,2,4-triazolium salt **37D**, a route was developed starting from aniline and benzoyl chloride (Scheme 37).[169] The overall yield of salt from aniline is 45%. However, the carbenes of other derivatives of *meso*-unsubstituted triaryltriazolium salts have not yet been prepared and if used are generated *in situ*.

Recently the authors of this review have developed an alternative method for preparing the 1,3,4-triaryl-1,2,4-triazolium salts **38C**, which is based on the reaction of phenylhydrazine with benzoyl chloride and the subsequent acylation of the product with formic acid. Vilsmeier reaction of the intermediate **38B** sequentially with $POCl_3$ and aniline (Bredereck amino-version) generates **38C** (Scheme 38).[170] This method permits the introduction of sterically shielding aryl groups (Mes, Dipp) to the four position of the cycle and results in a yield of salts from phenylhydrazine of 62–70%. Deprotonation of these salts results in the formation of the carbenes **38D**.
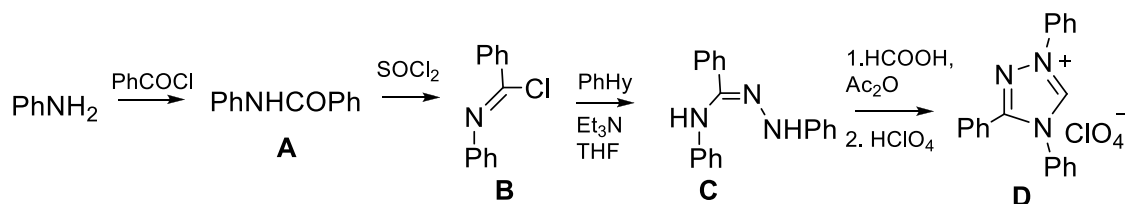
Scheme 37. Enders' synthesis of the 1,3,4-triphenyl-1,2,4-triazolium precarbene.
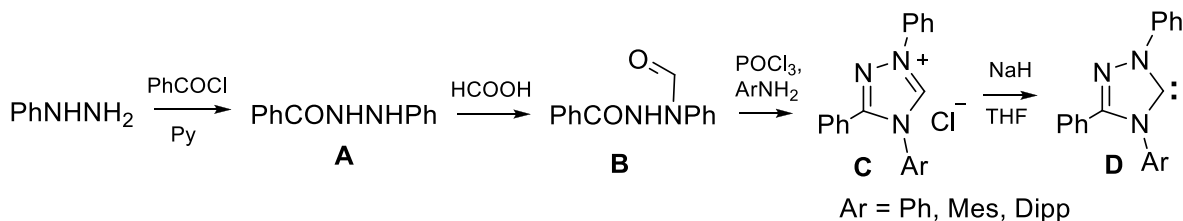
Scheme 38. Synthesis of 1,2,4-triazol-5-ylidenes from phenylhydrazine.

A related approach (to pathway 37) had been used previously for the synthesis of 1-alkyl-3,4-diaryl-, 1,4-dialkyl-3-aryl- and 1,3,4-trialkyl substituted 1,2,4-triazolium salts **39D**, which were obtained in 41-84 % yields. The 1-methyl-3-phenyl-4-(1,6-hexylene) substituted bis-salt was also isolated in 11% yield. In this case the reaction of chloroimidoyl chloride **39B** was carried out with 1-formyl-1-alkylhydrazines **39C** (Scheme 39).[171]

R = Me; R' = Me, Ph; R'' = Me, chiral Alk
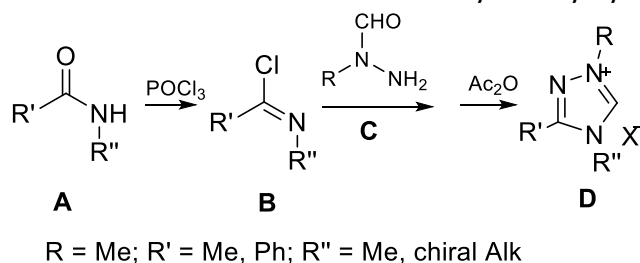
Scheme 39. Synthesis of 1,2,4-triazolium precarbenes from amides.

Similar transformations (to pathways 37 and 39) were carried out to obtain fused analogues of triazolium salts of the type **40A-E** (Scheme 40).[172-181] For example, salt **40D** was prepared by the methylation of amides with trimethyloxonium tetrafluoroborate. This was followed by further hydrazination of the resulting methoxyazine **41B** and finally cyclization of the hydrazino derivative **41C** with triethyl orthoformate (Scheme 41).[172] Similarly, compound **40A** was prepared from the corresponding azolidone.[172] Carbenes from compounds **40A-D** and their analogues have not yet been isolated.

C R = Ph, Me; R' = TMS, TBS
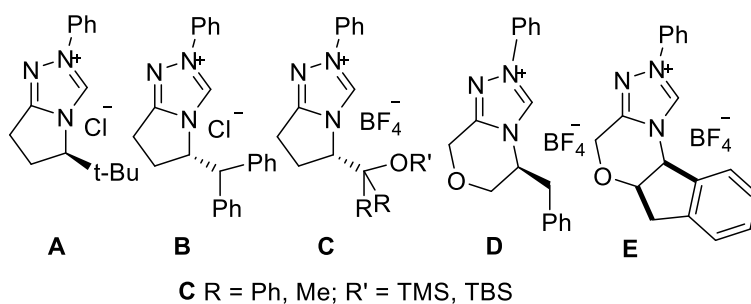
Scheme 40. Fused 1,2,4-triazolium precarbenes.
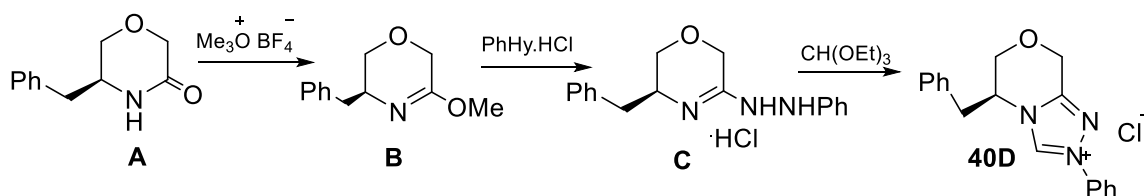
Scheme 41. Synthesis of one of the fused 1,2,4-triazolium precarbenes.

The fused systems just described have been used for carbene catalysis of organic reactions. Stable carbenes were generated in the reaction mixture in the presence of bases (alkoxides, hexamethyldisilazanides of metals, etc.)[24,177,82-194]

Syntheses of the 1-alkyl-3,4-diaryl-1,2,4-triazol-5-ylidenes **42D** have now been developed in more detail. Substituents in the 1-, 3- and 4-positions have all been varied, including the formation of fluoroaryl substituted compounds (Scheme 42).[32,51,85,104,195-198]
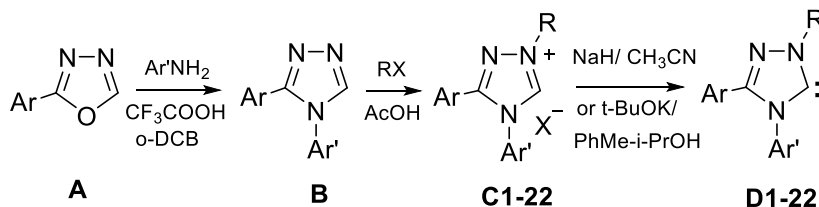
C,D: R = 1-Ad, Ar = Ar' = Ph (**1**); R = 1-Ad, Ar = Ph, Ar' = p-Br-C$_6$H$_4$ (**2**); R = 1-Ad, Ar = Ar' = p-Br-C$_6$H$_4$ (**3**);
R = 1-Ad, Ar = Ph, Ar' = C$_{10}$H$_7$ (**4**); R = t-Bu, Ar = Ar' = Ph (**5**); R = t-Bu, Ar = Ph, Ar' = p-Br-C$_6$H$_4$ (**6**); R = t-Bu,
Ar = Ar' = p-Br-C$_6$H$_4$ (**7**); R = t-Bu, Ar = o-Cl-C$_6$H$_4$, Ar' = Ph (**8**); R = t-Bu, Ar = Ph, Ar' = p-F-C$_6$H$_4$ (**9**); R = t-Bu,
Ar = o-Cl-C$_6$H$_4$, Ar' = p-F-C$_6$H$_4$ (**10**); R = t-Bu, Ar = Ph, Ar' = m-F-C$_6$H$_4$ (**11**); R = t-Bu, Ar = o-Cl-C$_6$H$_4$, Ar' = m-F-C$_6$H$_4$
(**12**); R = t-Bu, Ar = Ph, Ar' = 2,4-F$_2$-C$_6$H$_3$ (**13**); R = t-Bu, Ar = Ph, Ar' = 2,3,4-F$_3$-C$_6$H$_2$ (**14**); R = 1-Ad, Ar = Ph, Ar' =
Mes (**15**); R = t-Bu, Ar = Ph, Ar' = Mes (**16**); R = t-Bu, Ar = Ph, Ar' = Dipp (**17**); R = 1-Ad, Ar = Ph, Ar' = Dipp (**18**); R
= 1-Ad, Ar = Ph, Ar' = Dbmp (**19**); R = Ar = Ar' = Ph (**20**); R = Ar = Ph, Ar' = Mes (**21**); R = Ar = Ph, Ar' = Dipp (**22**).

Scheme 42. Synthesis of 1-alkyl-3,4-diaryl-1,2,4-triazol-5-ylidenes from 1,3,4-oxadiazoles.

These syntheses require the deprotonation of the salts **42C,** using either sodium hydride in acetonitrile (the acetonitrile method) or metal alkoxides in a mixture of alcohol and an aromatic solvent (the toluene-alcohol method). The first method results in the formation of the pure carbenes **42D**, which precipitate from the acetonitrile solutions in the form of weak solvates. However, when sufficiently soluble, the triazolylidenes react relatively rapidly to form new products after insertion into the C-H bond of the acetonitrile.[104]

The second (toluene-alcohol) method is universal and proceeds well in pure aromatic solvents. The carbene center is protected in the presence of alcohol due to the formation of 5-alkoxyazolines. As a consequence, it becomes less sensitive to environmental factors (traces of moisture, oxygen, etc.) thus permitting the isolation of pure samples of the carbenes.

The *precarbenes* **42C** were obtained after ring transformations of the 2-aryl-1,3,4-oxadiazoles **42A** with anilines,[199] followed by quaternization of the intermediate triazoles with 1-adamantyl bromide **42B** or *tert*-butyl iodide in acetic acid. The quaternization reaction under these conditions is directed solely at position 1, whereas methylation results in a 25% yield of the 2-substituted isomer. Several carbenes, sterically shielded at positions 1 (*tert*-butyl, 1-adamantyl) and 4 (Mes, Dipp and lately Dbmp) **42D9-13**, have been produced using this method, which confirms a wide range of possible uses for this synthetic scheme.[51,169]

New phosphanylated 1,2,4-triazol-5-ylidenes **43A** were synthesized by deprotonation of the respective triazolium sats, which, in turn, were obtained by quaternization of the corresponding triazoles with phosphanyl bromides or phosphanyltriazoles with alkyltriflates [200,201].

The above methods can be used to prepare a number of individual conjugated biscarbenes of the 1,2,4-triazole type (X = *p*-C$_6$H$_4$, *m*-C$_6$H$_4$), as well as for the aliphatic bridged structures (compounds **43B**, **43C**) (Scheme 43).[202-204] The acetonitrile method is best for the synthesis of compounds **43B**. On the other hand, a

mixture of alcohol and toluene is preferred for the synthesis of **43C**. The predominant isomers of the biscarbenes adopt *trans*-configurations. Similar to Arduengo's 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene,[57] these compounds are among the most stable carbenes known, both thermally and chemically (they can be saved, without significant changes, open to the air for several days). Recently, this method has also been used for the generation of carbenes with 4-[2-(dimethylaminomethyl)phenyl] substituted 1,2,4-triazolylidenes. These were then utilized for the preparation of palladium complexes.[205,206]

A: R = t-Bu, R' = Me (**1**), Et (**2**), i-Pr (**3**); **B:** R = 1-Ad, Ar = Ph, X = *p*-C$_6$H$_4$ (**1**); R = 1-Ad, Ar = Ph, X = *m*-C$_6$H$_4$ (**2**); R = 1-Ad, Ar = Ph, X = (CH$_2$)$_4$ (**3**); R = t-Bu, Ar = Ph, X = *p*-C$_6$H$_4$ (**4**); **C:** R = 1-Ad, X = *p*-C$_6$H$_4$ (**1**); R = 1-Ad, X = *m*-C$_6$H$_4$ (**2**);
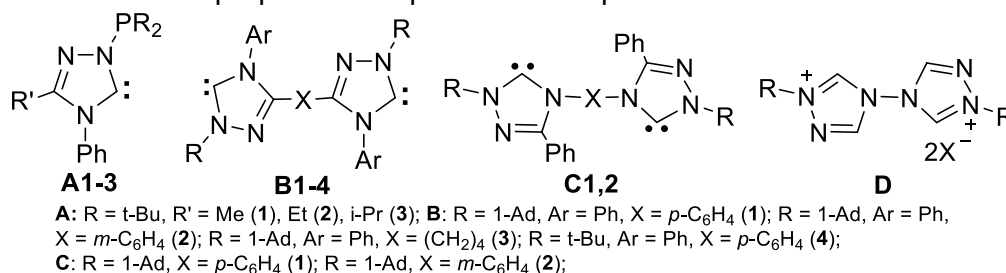
Scheme 43. Stable phosphanyl substituted 1,2,4-triazol-5-ylidenes **A**, conjugated bis-1,2,4-triazol-5-ylidenes **B,C** and precarbene **D**.

Peris *et al.*[207,208] proposed using bistriazolylidene ligands for the synthesis of precursors to **43C,** prior to the generation of metal complexes. However, carbenes of this type have not yet been prepared. Furthermore, the compounds **43C** are the bis-heterocyclic analogues of 3,5-unsubstituted mono-1,2,4-triazolium salts. These undergo deprotonation with strong bases even in aprotic media, thereby resulting in ring closure to 1-cyano-amidines.[209]

1,2,4-Triazolium salts with electron withdrawing groups (3-nitro and 4-(2,4-dinitrophenyl)) have been used for the preparation of rhodium complexes (structures **42C**).[210] Compounds of this type could be some of the least electron donating carbenes known. However, none have yet been isolated.

The only condensed derivatives of 1,2,4-triazol-5-ylidenes were synthesized in the work described in Scheme 44.[211] Synthesis of the salt **44C** was carried out starting from 2-pyridylhydrazine **44A** and trialkyloxonium tetrafluoroborate and triethylorthoformate, enabled the formation of **44B**. Subsequent deprotonation with sodium hydride in THF produced the pure carbenes **44C** that can be stored indefinitely in the solid state. However, if the deprotonation in THF is carried out in the presence of potassium carbonate, irreversible formation of the carbene dimers, as mixtures of the *cis*- and *trans*- isomers, occurs. This data supports the hypothesis concerning the catalytic character of carbene dimerization in a heterocyclic series; protic compounds (water, alcohols, acids, *meso*-unsubstituted azolium salts, etc.) accelerate the process. The cyclization of the related arylsubstituted hydrazines proceeds similarly (in the presence of NH$_4$PF$_6$) to the salts **44B** (R' = Ar).[211]

R = H, Me   (i) R'$_3$OBF$_4$; (ii) CH(OEt)$_3$; (iii) NaH, THF
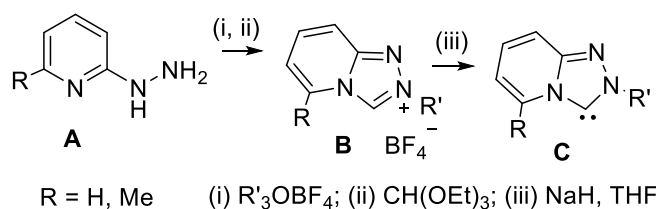
Scheme 44. Synthesis of N-annulated 1,2,4-triazol-5-ylidenes.

2.4. Hyperbasic and hypernucleophilic anionic carbenes

The terms "hyperbasic and hypernucleophilic (HBN) carbenes" were proposed to designate structures in which the introduction of anionic centers to the carbene molecule leads to fundamental changes in the carbene's properties. Included are significant increases of their basicities and nucleophilicities by charge transfer to the carbene center via the conjugation chain.[21,212] This outcome is particularly clear in the cases of oxido-, sulfido-, imido-, phosphido- and other related structures of the type **45A**, all of which exert their influence via an aromatic ring (Scheme 45). The phenoxides and phenothioxides themselves do not possess high basicities and proton affinities (PAs). However, the PA of the carbene center under their influence increases very significantly (PA from 230-285 for neutral carbenes to 330-460 Kcal/mol for hyperbasic systems). In structures with basic nitrogen or carbon-containing anionic centers these centers can be competitive with the carbenic carbon. However, the significant impact of the anionic center on the basicity and nucleophilicity of the carbene is also preserved in these cases.
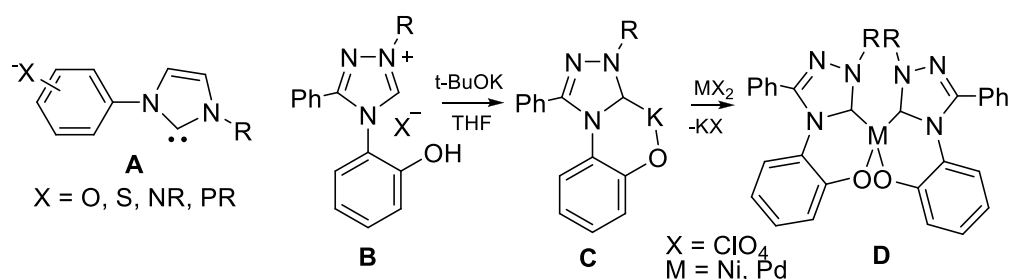
Scheme 45. Synthesis of HBN 1,2,4-triazol-5-ylidene complexes.

Transition metal complexes of such HBN-carbenes on the non-aromatic objects, e.g. 4,5-dihydroimidazol-2-ylidenes were synthesized by Grubbs and Hoveyda,[213,214] and heteroaromatic complexes of HBN-carbenes with alkali metals such as **45C** have been described in the following papers (Scheme 45).[198,215,216] These compounds can be considered to be chelated complexes of anionic carbenes. The heteroaromatic complexes **45D** were obtained by replacing the potassium in the precursor with nickel or palladium.

Bielawski *et al*. developed a synthesis for similar chelated palladium complexes of the benzimidazole series using the reaction of *N*-(hydroxyphenyl)benzimidazolium salts with palladium acetate in THF. This was followed by the addition of sodium carbonate to the intermediate carbene complexes, and finally by their cyclization in a mixture of THF and methanol.[217] Alternatively, bisbenzimidazolium salts in DMSO could be used to form chelated organometallic polymers. Alkali metal complexes of this type have not yet been synthesized.

Attempts to synthesize the HBN-carbene **46B** were made later,[21,218,219] by deprotonation of 1,4-diphenyl-1,2,4-triazolium-3-phenylimide **46A** ("nitron") with potassium *tert*-butoxide in THF (Scheme 46). However, in the presence of small amounts of oxygen the oxidation of carbene **46B** resulted in the formation of the azoamidine **46C**.

It was found that the mesoion **46A** is a generator of the carbene **46D.** The difference in their energies was found to be only 6.2 Kcal/mol. However, this also allowed the generation of carbene complexes of copper(I) **47C,D** upon boiling of **47A** and copper(I) salts in acetonitrile solutions (Scheme 47).

Later, Siemeling *et al*. produced similar rhodium carbene complexes, LRh(CO)$_2$Cl,[220] and phosphinocarbene ruthenium complexes, in which there is bonding participation at the *ortho*-position of the aromatic carbene ring.[221]

Interestingly, intra- and intermolecular anionic carbene generated systems (carbenoids) have been described recently for the imidazolium *N*-uracylides[222] and for the zwitterionic azolium indolides[223,224] (anionic center at the nitrogen atom), the imidazolium-*N*-fluorenides[225] (anionic center at the carbon atom), and the imidazolium carboxylates[224] (and references therein). However, these systems are not related to the HBN anionic carbenes.
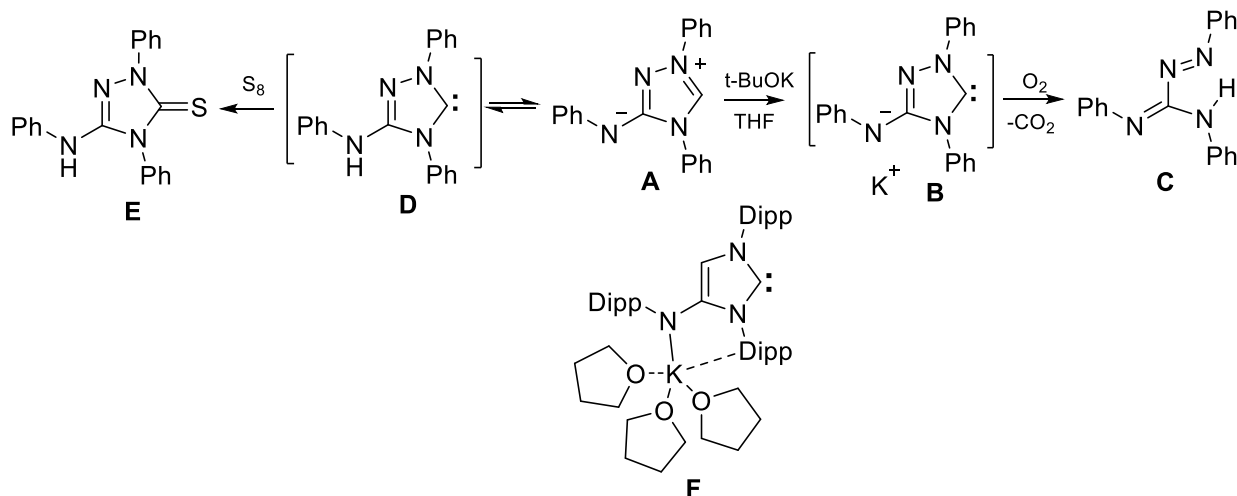
Scheme 46. Reactions of an HBN-carbene with oxygen and its precarbene with sulfur.
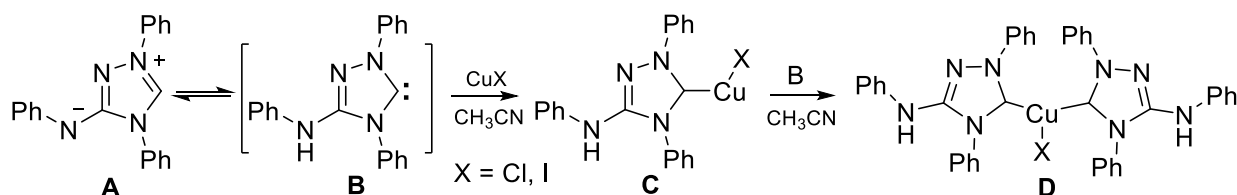
Scheme 47. Carbenoid reactions of 1,4-diphenyl-1,2,4-triazolium-3-phenylimide with copper(I) salts.

An important development in the chemistry of HBN carbenes of the type **46B** was made by Danopoulos *et al.*,[226] who succeeded in synthesizing a similar, but more sterically shielded, structure of the imidazol-2-ylidene series, namely the THF complex **46F**. In this case the precursor zwitterion was treated with benzylpotassium (KBn) in THF solution. If the ratio of the mesoion to KBn was changed, polymer associated structures were formed. The interaction of the potassium cation with the nitrogen atom, rather than the carbene center, is probably due to the hardness of the potassium atom relative to transition metals such as copper, rhodium, etc. Nickel ions (in NiCl$_2$) are also harder and react with the nitrogen atoms of the mesoion.[218] Thus, in the presence of anionic centers on the nitrogen atoms of a hyperbasic carbene, there is a competition between the carbene and the anionic center, the outcome of which depends on the basicity and hardness of the anionic center.

The *C*-anionic carbenes are also related to HBNs in that they are formed by the additional deprotonation of heterocyclic azolylidene nuclei. Such carbenes have been used by Liddle and Arnold for *in situ* experiments involving the synthesis of transition metal carbene complexes.[227] Subsequently, Robinson *et al.* succeeded in preparing stable complexes of both anionic carbenes and alkali metals.[228] Initially, the reaction of butyllithium

with the imidazol-2-ylidenes **48A** in THF solution, and in the presence of TMEDA or lithium in the same solvent, produced the oligomeric lithium complexes **48B,C** (Scheme 48).
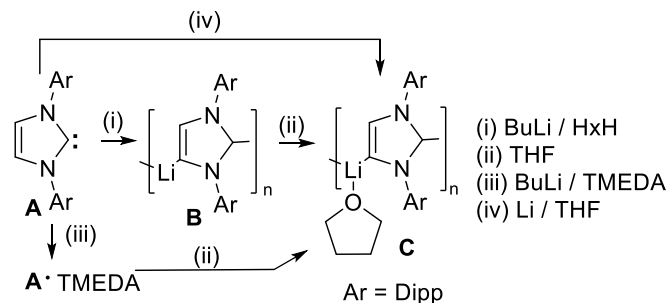
Scheme 48. Synthesis of HBN-carbenes from imidazol-2-ylidenes.

The reaction of the latter with Lewis acids resulted in boron, silicon and aluminum derivatives, etc. Treatment with potassium *tert*-butoxide produced the complexes **48B,C.** The potassium analogues were also synthesized,[229] and it was discovered that potassium can be exchanged for other metals (for example, with their hexamethyldisilazanides).

A new phosphanide containing an HBNC of the imidazol-2-ylidene series was synthesized as a complex with alkali metal cations and 12-crown-4 (Scheme 49).[230] For this purpose the reactions of the phosphanylimidazole-2-thione **49A** or its bis-analogue **49C** with potassium were carried out in THF solution thereby producing the mesoion **49B**. Treatment of the latter with butyllithium or KHMDS resulted in the formation of the HBN-carbene complex **49D**.
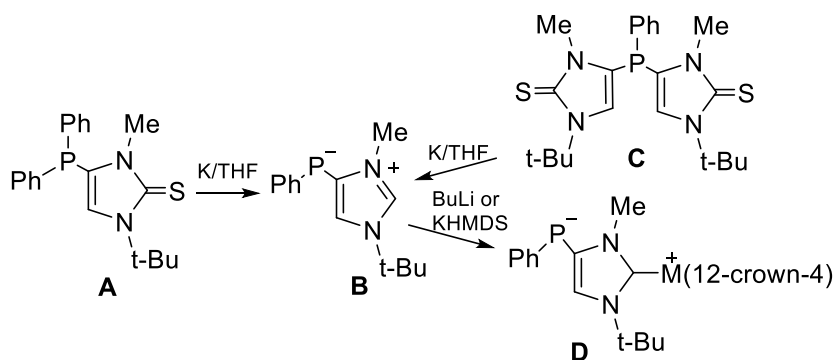
Scheme 49. Synthesis of phosphanide substituted HBN imidazol-2-ylidenes.

Anionic carbenes which have no conjugation between the heterocyclic nucleus and the anionic center are not of the HBN-type. However, a stable structure **50D** that features two potassium cations has been synthesized recently by Arduengo *et al.* (Scheme 50).[231] The basicities of the anions are significantly reduced due to the influence of the trifluoromethyl groups. The aim of the study was to create tridentate carbene ligands. The replacement of the potassium atoms by a nickel cation resulted in the formation of a chelated carbene-alkoxide complex of nickel(II). However, the paper does not include any data regarding the interaction between the potassium atoms and the carbene center in compound **50D**. The syntheses of the precursors for these carbenes were carried out using 1,1-bis(trifluoromethyl)oxirane and imidazole according to Scheme 50.
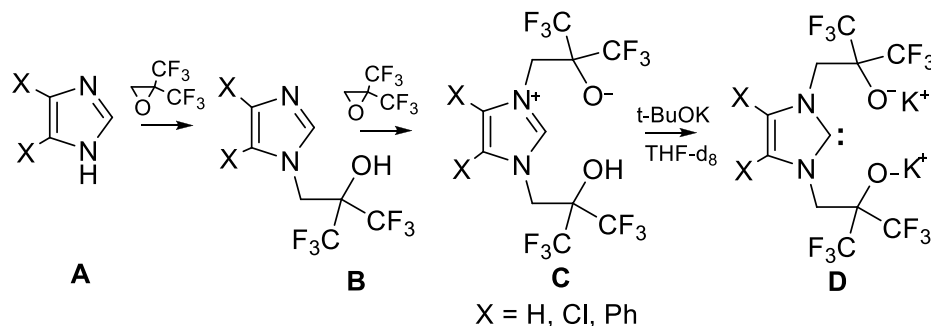
Scheme 50. Synthesis of imidazol-2-ylidene alkoxides.

2.5. Mesoionic carbenes

2.5.1. Imidazolium-4-ides. The so-called mesoionic (abnormal) carbenes (or more precisely intracyclic mesoions) in which the negative charge is localized on a ring carbon atom, were synthesized for the first time by Bertrand[232-235] (for their carbene complexes see refs 236, 237 and reviews[238-242]). Strong bases, such as potassium hexamethyldisilazanide, were used to obtain the imidazolium-4-ides. Weaker bases, such as potassium *tert*-butoxide, were employed to obtain the 1,2,3-triazolium-5-ides. As an example, Scheme 51 illustrates the preparation of the Dipp-substituted imidazolium-4-ides **51D**.[233] Precursors for the imidazolium-4-ides of the type **51D** were synthesized from the corresponding sterically shielded benzamidines **51A** and haloketones, followed by cyclization of the intermediates **51B** under acidic dehydration conditions.[232,233]

R = Dipp; Ar = Ph, 3,5-$(CF_3)_2C_6H_3$; Ar' = Ph, p-FC_6H_4, p-ClC_6H_4, p-BrC_6H_4, p-$CF_3C_6H_4$, Tol, p-$MeOC_6H_4$, 3,5-$(CF_3)_2C_6H_3$;
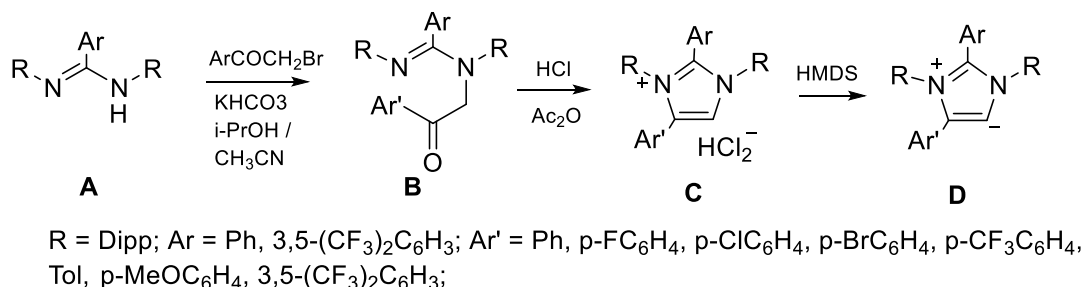
Scheme 51. Synthesis of stable mesoionic carbenes imidazolium-4-ides.

2.5.2. 1,2,3-Triazolium-5-ides. The starting 1,2,3-triazolium salts were obtained by cycloaddition of 1,3-diaryltriazenium salts to acetylenes[235] or by quaternization of the corresponding 1,2,3-triazoles, which in turn were synthesized by click-cycloaddition of azides to acetylenes in the presence of copper(II) compounds.[243] The individual 1,2,3-triazolium-5-ides **52C** were synthesized by deprotonation of the appropriate 1,2,3-triazolium salts **52B** with potassium *tert*-butoxide or KHMDS in THF or ether solutions (Scheme 52).[234] Similarly, the pyrazolium-4-ide **52D** was synthesized from a 3,5-diphenoxypyrazolium salt in which the distribution of electron density is more like that of a conjugated cyclic allene.[232]

Stable potassium carbazolide complexes of 1,2,3-triazolium-5-ides **53C** have been synthesized in a similar fashion (Scheme 53).[244] The replacement of potassium by copper or nickel results in the respective transition metal complexes.

(i) 1. t-BuONO, Me₃SiN₃ / CH₃CN; 2. PhCCH/ CuSO₄, Na ascorbate; (ii) ROTf / DCM;
(iii) KHMDS / Et₂O.   R = Me, i-Pr.
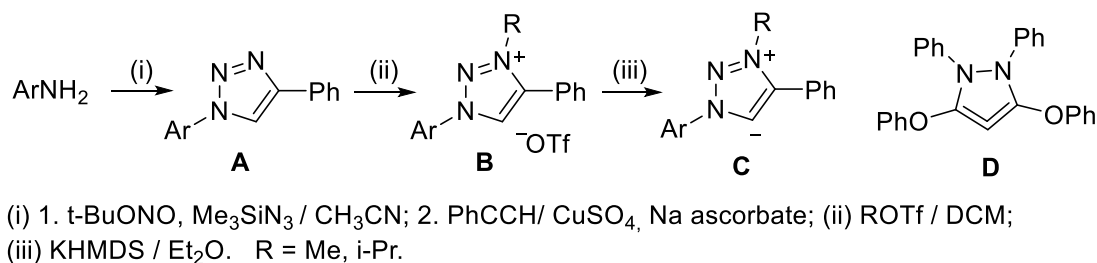
Scheme 52. Synthesis of stable 1,2,3-triazolium-5-ides **C** and structure of a cyclic allene **D**.
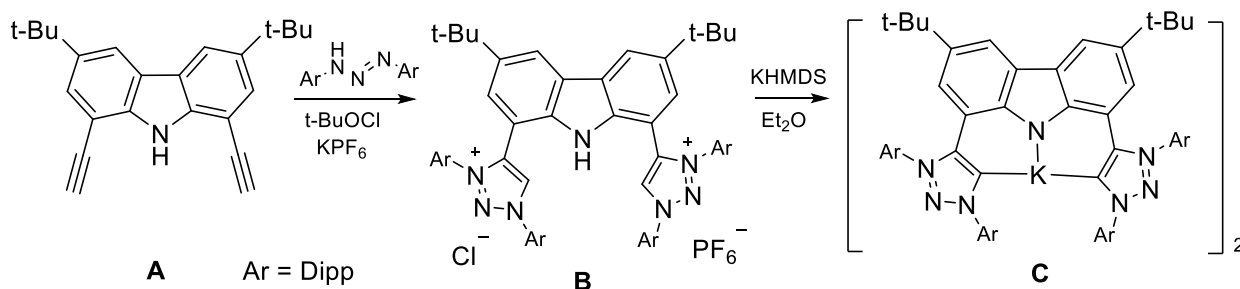
Scheme 53. Synthesis of potassium bis-1,2,3-triazolium-5-ide carbazolide complexes.

3. Physical Properties of Stable Carbenes

3.1. ^{1}H and ^{13}C NMR spectra

In the ^{1}H NMR spectra, the proton signals of virtually all the ring carbene atoms are shifted upfield with respect to those in the spectra of their corresponding salts. Also noteworthy is the unusual deshielding of the nitrogen connected to adamantyl CH₂ protons in the spectra of carbenes **20E** and **42D1-4**, which causes a downfield shift, by 0.2–0.3 ppm, with respect to the signals for their salt analogues.[104]

In the ^{13}C NMR spectra (Table 1) the most important signals are those for the carbenic carbon atoms. In carbenes these are known to cover a wide range, δ 184–381 ppm[245] (for the respective precarbenes 114-193 ppm). However, for the specific group of compounds of the azole series, this range is narrowed significantly, δ 190–235 ppm (for their precarbenes 114-150 ppm).

The *N*-aryl derivatives of the imidazol-2-ylidenes (e.g., **1D4,2D1,2, 2E2**) are typically deshielded by a larger amount than are their aliphatic analogues (**1D2,3,2D4**). The effect of the *N*-substituents on the chemical shift is larger than that for *C*-substituents (*cf*. **1D2, 1E2; 2D1, 6G**). In the NMR spectrum of the imidazol-2-ylidene **2E2** steric shielding should result from the branched aromatic substituents (2,6-dibenzhydryl-4-ethylphenyl, dbep). However, the δ value for C2 is almost the same (218.5 ppm) as that observed for 1,3-dimesitylimidazol-2-ylidene **2D1** (219.7 ppm), implying that there is no significant anisotropic effect of the aromatic nuclei at the carbenic center. The chemical shift of the carbenic carbon atom in the compound **4D** (222.9 ppm) is reminiscent of that for compound **2E2**. The introduction of electron withdrawing groups into a structure (benzoyl, trifluoromethylsulfonyl, diphenylchlorosilyl, dimesitylboryl) causes downfield shifts (**8C1,6,** and **11C,E**). However, the simultaneous presence of electron donors reduces the change in δ (**8C2**). The electron donating influence naturally causes an upfield chemical shift of the C2 signal (δ 190 ppm for **12D**, 195.8 ppm

for   **15C**,   at

Table 1. Typical ^{13}C NMR chemical shifts of the carbenic carbon atoms, bond lengths and angles at the carbenic carbon atoms for individual compounds of the imidazole, 1,2,4- and 1,2,3-triazole, and fused series (carbene numbering and references are as indicated in the text). For notes see end of table

Carbene	R	R', R''or X	δ C$_{carbene}$	N-C or C-C	Bond order*	Ref.
1D2	Ad	H	211.4	1.367	1.615	4
				1.373	1.580	
1D3	t-Bu	H	213.2	1.362	1.644	38
1D4	p-MeC$_6$H$_4$	H	215.8	1.371	1.592	5
				1.375	1.569	
2D1	Mes	H	219.7	1.365	1.626	5
				1.371	1.592	
2D2	Dipp	H	220.6	1.367	1.615	46
2D4	CD$_3$	CD$_3$	212.5	1.364	1.632	39
2E2	Dbep	H	218.5	1.364	1.632	52
				1.368	1.639	
1E1	Ph	Ph	219.6	1.369	1.603	40
1E2	Ad	Ph	211.4	-	-	45
6G	Mes	Cl	219.9	1.364	1.632	57
4D	*1	H	222.9	-	-	55
5A	Dipp. 6-Me$_3$SiPy	H	-	1.366	1.621	56
				1.360	1.655	
5B	Dipp. Ph$_2$P-ethyl	H	-	1.367	1.615	56
				1.378	1.552	
7D	Mes	*2. H	220.3	1.363	1.638	57
				1.366	1.621	
8C1	Dipp	PhCO,H	227.2	1.372	1.586	60
				1.351	1.707	
8C2	Dipp	Ph$_2$P, PhCO	217.7	-	-	60
8C3	Dipp	Cl, H	222.5	-	-	60
8C4	Dipp	Br, H	223.3	-	-	60
8C5	Dipp	Ph$_2$P, H	223.5	-	-	60
8C6	Dipp	CF$_3$SO, H	231.6	-	-	60
8C7	Dipp	Me$_3$Si, H	223.7	-	-	60
9F	C$_6$H$_4$NMe$_2$	NMe$_2$	208.4	-	-	63
10C1	P(t-Bu)$_2$	Ad	222.0	-	-	65
10C2	P(t-Bu)$_2$	t-Bu	222.7	-	-	65
11E	Dipp	Ph$_2$SiCl	225.88	1.373	1.580	67
				1.380	1.540	
11C	t-Bu	Mes$_2$B	224.6	1.364	1.632	68
				1.373	1.580	
12D	p-Tol	NMe$_2$	190.0	-	-	69

Carbene	R	R', R''or X	δ C_carb	N-C or C-C	Bond order*	Ref.
13C	*[3]	H	208.7	-	-	72
15C	*i*-Pr	H	195.8	-	-	78

Table 1. Continued

Carbene	R	R', R''or X	δ C_carb	N-C or C-C	Bond order*	Ref.
16D	*[3]	H	212.6	1.364 1.357	1.632 1.672	85
17A1	Me	(CH_2)_2	215.9	-	-	90
17A2	Mes	CH_2	218.0	1.370 1.362	1.644 1.598	91
17A3	Dipp	Pyridin-2,6-diyl	217.4	1.359 1.372	1.661 1.586	93
17B	t-Bu	H	215.3	-	-	92
18B	Dipp	Ph_2Si	226.3	1.367 1.367	1.615	67
19D	*t*-Bu	Ph_2Si	212.01	-	-	101
20E	Ad	(CH)_4	229.0	1.374	1.575 1.586	104
21D	Np	(CH)_4	231.5	1.361	1.649	106
22A	P(*t*-Bu)_2	Me	235.4	1.387 1.355	1.500 1.684	110
22A	P(*t*-Bu)_2	Ad	233.8	-	-	65
22A	P(*t*-Bu)_2	t-Bu	234.1	-	-	65
24A1	Np	-	235.2	-	-	113
24A2	Np	-	235.8	-	-	113
24D	Dipp	-	-	1.379 1.377	1.546 1.557	116
24E1	Bu	MeC*HPh	223.3	-	-	121
24E2	Bn	MeC*HPh	225.1	-	-	121
24E3	Bu	Bu	225.1	-	-	120
24E4	*o*-Tol	*o*-Tol	224.5; 224,9	-	-	122
27C1	Me	H,H,H	209.7	1.389 1.355	1.489 1.684	132
27C1	Mes	H,H,Me	206.9	-	-	133
29D1	-	H	197.8	-	-	139
29D2	-	t-Bu	196.3	1,374 1,380	1,575 1,540	133
32D1	1-Ad	-	227.6	1,369 1,368	1,603 1,609	153
32D2	*t*-Bu	-	228.3	-	-	153
32D3	*t*-Am	-	230.2	-	-	153
34D	*t*-Bu	Hx	225.8	1.379	1.546	157
34E	*t*-Bu	-	230.4	1.370	1.598	160

				1.374	1.575	
34E	Mes	-	231.4	-	-	160

Table 1. Continued

Carbene	R	R', R''or X	δ C$_{carb}$	N-C or C-C	Bond order*	Ref.
36C	Ph	Ph	214.6	1.351 / 1.373	1.707 / 1.580	168
42D2	Ad	Ph, C$_6$H$_4$Br-*p*	210.6	1.346 / 1.384	1.736 / 1.517	195
42D2	Ad	Ph, C$_6$H$_4$Br-*p*	210.6	1.346 / 1.384	1.736 / 1.517	195
42D6	*t*-Bu	Ph, C$_6$H$_4$Br-*p*	207.8	1.335 / 1.388	1.799 / 1.494	196
42D17	*t*-Bu	Ph, Dipp	213.0	1.349 / 1.384	1.718 / 1.517	51
43A4	*t*-Bu	C$_6$H$_4$-*p*	202.9	1.343 / 1.385	1.753 / 1.511	202
43B1	Ad	C$_6$H$_4$-*p*	206.2	1.338 / 1.390	1.782 / 1.483	204
44D	H	Me	203.8	-	-	211
46F	Dipp	Dipp	205.99	1.347 / 1.389	1.730 / 1.489	226
48B	Dipp	H	-	1.375 / 1.361	1.569 / 1.649	228
49D	M = Li	-	212.8	-	-	230
49D	M = K	-	212.5	1.385 / 1.354	1.511 / 1.690	230
50D	-	X = H	218.34	-	-	231
51D	Dipp	Ph	*4	1.417 / 1.383	1.328 / 1.766	232
52C	Dipp	Ph, Me	202.1	1.366 / 1.405	1.620 / 1.653	243
53C	Dipp	t-Bu	194.8	1.374 / 1.408	1.575 / 1.640	244

Notes to Table 1. * The bond orders were calculated according to their linear dependence from the bond lengths of the simplest comparable compounds.[246] *[1] R = DippN = C(Me); *[2] R= Ph$_2$PCH(Mes); *[3] According to the structure; *[4] For tetraphenyl derivative δ 201.9 ppm.[232]

least 208.7 ppm for **13C**). The same can be said about the signal of the diphosphanyl substituted carbene **9F** (δ 208.4 ppm). The influence of the di-*tert*-butylphosphanyl group is close to that of the aromatic analogues (**10C1,2**). In the spectra of the biscarbenes **17A1-3, 17B** the chemical shift of C2 is a function of the substituents, and there is little mutual influence of the nuclei. The influence of the diphenylsilylene bridge in **18B** is larger and δ rises markedly (226.3 ppm).

The fused analogues of the imidazol-2-ylidenes **20E, 21B, 22A, 24A** exhibit chemical shifts in the ^{13}C NMR spectra that are almost 18 ppm deshielded (i.e. to lower field) than those of their unfused analogues (cf. **20E** and **2D2**); these fall in the range of 229-236 ppm. The chemical shifts of the carbenic carbon atoms for the phenanthrene fused compounds **24E1-4** are 223-225 ppm and therefore somewhat deshielded than those for the imidazol-2-ylidenes. In contrast, they are more shielded than those for the 2-benzimidazol-2-ylidenes (for the diadamantyl derivative **20E** the value is 229 ppm, while for the neopentyl substituted analogue **21D** the value is 231.5 ppm). This may imply an electron donating impact on the fused carbenic carbon atom. However, in the spectra of the aza-fused analogues **27C**, δ of C2 is significantly shielded (up to 209.7 ppm). Moreover, in the spectra of the diaza-fused compounds **29D1,2**, δ of C2 passes the threshold of 200 ppm (196.3, 197.8 ppm). It is likely that this outcome arises from the significant influence of the electron donating nitrogen atoms. The chemical shifts of C2 for the compounds **32D, 34D,E** are comparable to those for their mononuclear fused analogues.

In the case of the 1,2,4-triazol-5-ylidenes, an even wider variation in the structure does not substantially change the δ (C5) value (203–215 ppm). For the sterically shielded carbenes of the 1,2,4-triazole series **42D** (aryl, Mes, or Dipp in the 4-position) the signals for the C5 atoms are shifted somewhat downfield (δ 211.5-213 ppm).[51] In the case of the biscarbenes that feature five aromatic rings, **43A,B**, the C5 signals of the triazolylidene nuclei are shifted upfield (up to 203-206 ppm) versus 208 ppm for the aliphatically connected 3,3'-bridged biscarbenes. This is probably due to conjugation between the nuclei. The increased thermal and chemical stabilities of these compounds also support this idea. In the aza-annulated triazolylidene **44D** the carbenic carbon signal is strongly shifted upfield (203.8 ppm) in comparison with that of its imidazolylidene analogue **27C**.

In the case of the HBN-carbene **46F** the expected upfield shift of the signal for the C2 atom (δ 206 ppm) was observed, in comparison with the same signal for its neutral analogues. The signal for the phosphanide carbene **49D**, even in complexes with lithium and potassium cations, was found to be in the range of 212–213 ppm.

In the spectra of the imidazolium-4-ides **51D** the C4 signals were found to be in the same range as those for C5 of 1,2,3-triazolium-5-ides **52C** (201 − 202 ppm).[232,243]

3.2. Structures

The bond lengths at the carbenic carbon atoms of the imidazol-2-ylidenes (Table 1) do not differ significantly for open and sterically shielded aryl substituted structures (the bond orders at the carbene carbon atom *p* are 1.55–1.64). With the introduction of the electron withdrawing benzoyl group (**8C1**), the order at one of the bonds increased to 1.71. In the case of the adamantyl- and aryl- substituted carbenes **1D2,3** and **1E1,2**, the angle at the C2 atom increased by almost one degree with respect to those for other derivatives. For the 1,3-di-(1-adamantyl)benzimidazol-2-ylidene **20E**, the bond angle at the carbenic carbon atom increased by 1.6° relative to that of the imidazol-2-ylidene **1D2**. This increase occurs in concert with an increase in the chemical shift of the C2 atom in the ^{13}C NMR spectra. As in the Dipp-substituted imidazol-2-ylidenes, in the Dbep-substituted carbenes the *N*-aromatic nuclei are located in an almost perpendicular fashion with respect to the imidazole nucleus.

The structural characteristics of the 30-n,π electron compound **34E** are similar to those of the 1,3-di-(1-adamantyl)benzimidazol-2-ylidene **20E**, despite the considerable chain conjugation in the planar aromatic system.

In the case of the 1,2,4-triazol-5-ylidenes and their conjugated analogues, the bond length N1-C5 is shorter and C5-N4 is longer for the N1-alkyl substituted carbenes relative to those for the more conjugated

N1-aryl substituted analogues. This is indicative of an increased contribution of the ylidic resonance form (for compound **42D6** up to 80% (*p* to 1.80)).

In imidazolium-4-ides, the C-C5 bonds are substantially elongated (for the Dipp$_2$Ph$_2$ derivative *p* is 1.77) and the C4-N3 bonds are shortened (*p* is 1.33) due to interaction with the aromatic ring. The bond angle at the anionic carbon atom is 101.0°.

In the case of the 1,2,3-triazolium-5-ides the nature of the bonds is similar to the above. For example, the C4-C5 bond for the Dipp$_2$PhMe derivative is elongated relative to those for the imidazolium-4-ides (*p* is 1.65) and the C4-N3 bond is shortened (*p* is 1.65), thus implying a stronger interaction of these atoms than in the case of the imidazolium-4-ides. The bond angle at the anionic center is even smaller (99.7°) than those of the imidazolium-4-ides.

3.3. Basicities and electron donating properties

The *basicities* of the imidazol-2-ylidenes have been determined in several studies of individual carbenes, using indicator compounds with similar acidities (usually within two units of pK_a), NMR or spectroscopic methods (see, e.g., refs 247–249), and they fall in the range of pK_a 19.6–24.0 (in THF). For 1,3-diisopropylimidazol-2-ylidene, taking into account ionic pairs, a pK$_a$ value of 23.04 was obtained in DMSO.1,3-di-*tert*-butylimidazol-2-ylidene gave values of 22.2 in DMSO and 20.0 in THF.[248] Using the ^{1}H NMR method with comparison to fluorene, 1,3-di-(1-adamantyl)benzimidazol-2-ylidene **20E** and 1-*tert*-butyl-3,4-diphenyl-1,2,4-triazol-5-ylidene **42D6** gave indices of 23.4 and 21.6 (in benzene-d$_6$), respectively.[21]

For a series of imidazol-2-ylidenes, pK_a evaluations were carried out in aqueous media by studying the deprotonation equilibria of their respective imidazolium salts.[250,251] Specific values were obtained for the diaryl (Mes and Dipp) substituted carbenes (20.8, 21.1), along with those for the di-*tert*-butyl (25.2) and di(1-adamantyl) (25.4) derivatives.[250]

For the bridged carbene **17A** the pK_a value in water was found to be 19.9. However, upon transition to the dimethylene bridged compound, the pK_a value increased to 21.6, and for the trimethylene analogue the value was determined to be 22.3. For the 3,4-aliphatic annulated derivatives of 1,2,4-triazol-5-ylidenes the pK_as were found to be in the range of 16.8–18.5 (in H$_2$O).[252]

The basicities of a number of stable heterocyclic carbenes have been calculated[253] on the basis of their free energies in an appropriate solvent, which for imidazol-2-ylidenes in DMSO fall in the range 16.1–24.5 (*cf.* for 1,3-dimethyl-5,6-dihydro-4*H*-pyrimidin-2-ylidene, 27.9, and 3-methylthiazol-2-ylidene, 14.6).

Detailed characteristics of the basicities have been presented in a review paper.[254] Usually, basicities are changed automatically to proton affinities, although definite deviations have been observed (see, for example reference 253).

According to the calculations of the review authors, the proton affinities PA of the aromatic derivatives of imidazol-2-ylidenes differ only slightly from one another (Ph - 263.7, Mes - 274.6, Dipp - 272.5, Dbp - 274.2, Ttbp 269.8 Kcal/mol, calculated at the level DFT/B3LYP5/3-21G/RHF). There is some reduction for the phenyl and tris-*tert*-butylphenyl derivatives as such systems have substantial differences in their steric buried volumes. The steric influence of the substituents in these cases has been transferred to the proton affinities of the system: the effects of the *tert*-butyl groups acting through the aromatic nucleus are conspicuous when they are located in *ortho*-positions. The reduction of the PA for the diphenyl derivative, with respect to the Mes and Dipp-substituted imidazol-2-ylidenes, is apparently due to electronic factors (the absence of donor alkyl groups).

The PA of 1,3-dimethylimidazol-2-ylidene is significantly less than that of its 1,3-di-(1-adamantyl) analogue (265.0 versus 277.2 Kcal/mol), due to an increase of the electron donating effect of the alkyl group in the

latter. Overall, for carbenes with a considerable steric effect (Dbp, Dbmp, Dbep, etc.) the proton accepting properties are probably close to those for the related Mes- and Dipp-substituted compounds.

Benzimidazol-2-ylidenes are slightly inferior to imidazol-2-ylidenes in terms of their PAs (for the 1,3-dimethyl derivative the PA value is 264.2, while that for the 1,3-di-(1-adamantyl) derivative is 274.9 Kcal/mol). The 1,2,4-triazol-5-ylidenes are significantly more proton accepting (for the aromatic derivative of 1-*tert*-butyl-3,4-diphenyl-1,2,4-triazol-5-ylidene the PA value is 265.3 Kcal/mol, while that for 1,4-dimethyl-1,2,4-triazol-5-ylidene is 250.3 Kcal/mol).

The previously unknown 1,2,3,5-tetramesitylimidazolium-4-ide has a very high PA (300.3 Kcal/mol), which distinguishes it from all other carbene bases that have been studied. The 1,2,3-triazolium-5-ides have significantly smaller proton affinities, although they are still higher than those for normal carbenes of the imidazole and 1,2,4-triazole series (for 1-(1-adamantyl)-3-methyl-4-phenyl-1,2,3-triazolium-5-ides the PA is 276.4 Kcal/mol).
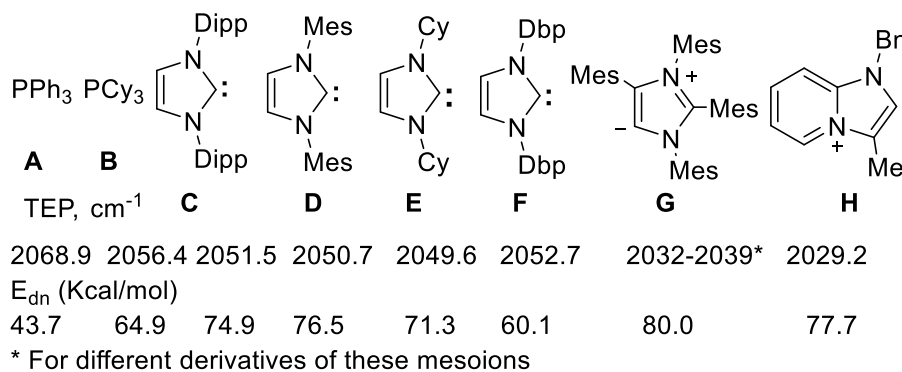
σ-*Electron donating* carbene properties are usually evaluated with respect to metal atoms. It must be kept in mind that the interaction with metals is energetically different than that with a proton (Bronsted basicity). However, both properties (basicity and electron donation) are manifestations of Lewis basicity, i.e. the electron donating properties of an unshared electron pair. Although there is no fundamental difference between basicity and electron donating properties, the concrete expression of the latter depends on the specific object of the donation. Here, the nature of the metal and the structure of the compound have important implications. In early work, Tolman proposed a method to estimate electron donating properties according to the infrared frequencies of carbonyl absorption for complexes of donors with tricarbonylnickel $LNi(CO)_3$ (Tolman's electronic parameter, TEP).[255] Subsequently, this process was repeated with rhodium and iridium complexes of the type $LM(CO)_2Cl$, which can be related back to the TEP according to linear equations of the type, *e.g.*, TEP = $0.722\nu_{av}(CO)[Ir]$ + 593 cm^{-1},[254] where $\nu_{av}(CO)[Ir]$ is a corresponding frequency for the related Ir complex. In this type of assessment, steric interactions of the carbene with the carbonyl groups can have a definite contribution which then reduces the electron donation. The TEP indices for a large group of carbenes have been discussed in some detail.[254]

The value of the TEP should harmonize with the interaction energy between the electron donor and $Ni(CO)_3$ (E_{dn}), both of which are easy to calculate theoretically. The E_{dn} indices for a selected group of carbenes were calculated by the authors of this article (at the DFT/B3LYP/3-21G/RHF level) and are given in Scheme 54. The results suggest a substantially greater electron donating effect for the heterocyclic imidazol-2-ylidenes with respect to phosphines, for the imidazol-2-ylidenes towards the 1,2,4-triazol-5-ylidenes, for the imidazolium-4-ides relative to the 1,2,4-triazolium-5-ides and for the imidazolium-4-ides compared with neutral carbenes. The strongest electron donating carbenes should be the HBN-carbenes with exocyclic anionic centers. However, despite the correspondence of E_{dn} with the TEP in many cases, the moderate E_{dn} value calculated for the structure **54H** draws attention since its TEP index was the lowest found experimentally (2029.2 cm^{-1}).[256] The high value of E_{dn} calculated for the yet unknown mesoion **54G** (80.0 Kcal / mol) is also noteworthy (Scheme 54).

The theoretically estimated stabilities, nucleophilicities, electrophilicities and redox indices of a number of heterocyclic carbenes have been reported[257,258] and show that mesoionic (abnormal) carbenes are generally less stable and more nucleophilic than conventional carbenes. Furthermore, the annulated and carbonylated carbenes are less nucleophilic and more electrophilic than the normal ones.

In addition to the σ-electron donating ability of carbenes, the ability to form double bonds with metals and other electrophiles is a characteristic that depends on the carbene's ability to accept π-electron density (its π-electron withdrawing properties). As a criterion of the π-electron accepting properties, the

measurement of the chemical shifts of hetero groups bonded to the carbene (^{31}P and [77]Se) have been proposed;[259-266] these have been found to correlate, one with the other, moderately well (R^2 = 0.9051). However, the correlation coefficient with the electron donating indices TEP is worse (R^2 = 0.833).[262] An improved correlation of σ-electron donation with the NMR coupling constant $^1J_{CSe}$ has been reported.[262] However, the data for this index are considerably scarcer than those for the chemical shifts of ^{31}P and [77]Se. Obviously, the chemical shift of ^{77}Se, as well as other NMR indices, are under the influence not only of electronic but also anisotropic shielding effects.

	A	B	C	D	E	F	G	H
TEP, cm⁻¹	2068.9	2056.4	2051.5	2050.7	2049.6	2052.7	2032-2039*	2029.2
E_{dn} (Kcal/mol)	43.7	64.9	74.9	76.5	71.3	60.1	80.0	77.7

* For different derivatives of these mesoions

Scheme 54. Electron donating properties of stable carbenes and their analogues.

3.4. Hyperbasic and hypernucleophilic carbenes (HBNC)

As noted above, the introduction of anionic centers into the conjugated molecule results in fundamental changes in the properties of the carbene. A significant increase in their basicities and nucleophilicities is observed due to charge transfer along the chain of conjugation. These have been termed "hyperbasic and hypernucleophilic" carbenes (HBNC).[21,212] The anionic centers can be either exocyclic or endocyclic.

According to DFT calculations (carried out at the B3LYP5/6-31G/RHF level), the proton affinities PA for carbene systems with exocyclic anionic centers range in value from 330 to 460 Kcal/mol, and the affinities for copper (I) and potassium cations are 220-424 and 92-230 Kcal/mol, respectively (Scheme 55). These are significantly larger than the respective values for the neutral carbenes (230-285, 149-170, and 26-34 Kcal/mol).[21,212]

Obviously, anionic compounds cannot exist without a cation (although they can be involved in zwitterionic complexes). Closest to the anionic carbene state are carbene complexes formed with alkali metal cations, those in which the interaction of the carbene center with the metal atom are smallest (e.g., potassium, cesium, etc.). It has been found, however, that the interaction with alkali metal cations is quite significant, although not so large as the interaction with transition metal atoms. As a consequence of the forgoing, the hydroxyl form of carbene **55E1** is less protonophilic (PA 258.3 Kcal/mol) than even the primordial diphenyl substituted carbene of this series (PA 265.5 Kcal/mol).

On the other hand, the potassium-oxide carbene **55E2** is more protonophilic than all of the known neutral nucleophilic carbenes (PA 286.3 Kcal/mol). Furthermore, the oxide **55E3** is significantly more protonophilic than the former (PA 330.5 Kcal/mol). The *ortho*-substituted compounds **55F,G** are, again, even more protonophilic (PA 352 and 422 Kcal/mol). Considering that proton affinities and basicities typically change symbatically, it can be assumed that the same conclusions can be reached about the basicities of these systems.

The HBN-properties are particularly pronounced for the oxido-, sulfido-, and phosphido-containing aromatic derivatives of carbenes. However, they are also characteristic of nitrogen- and carbon-containing, and related, anionic conjugated carbene systems.

462 (399, 230)
A

432 (346)
B

409 (287)
C

337 (221, 77)
D

258
E1

286
E2

330 (220)
E3

352 (276, 92)
F

422
G
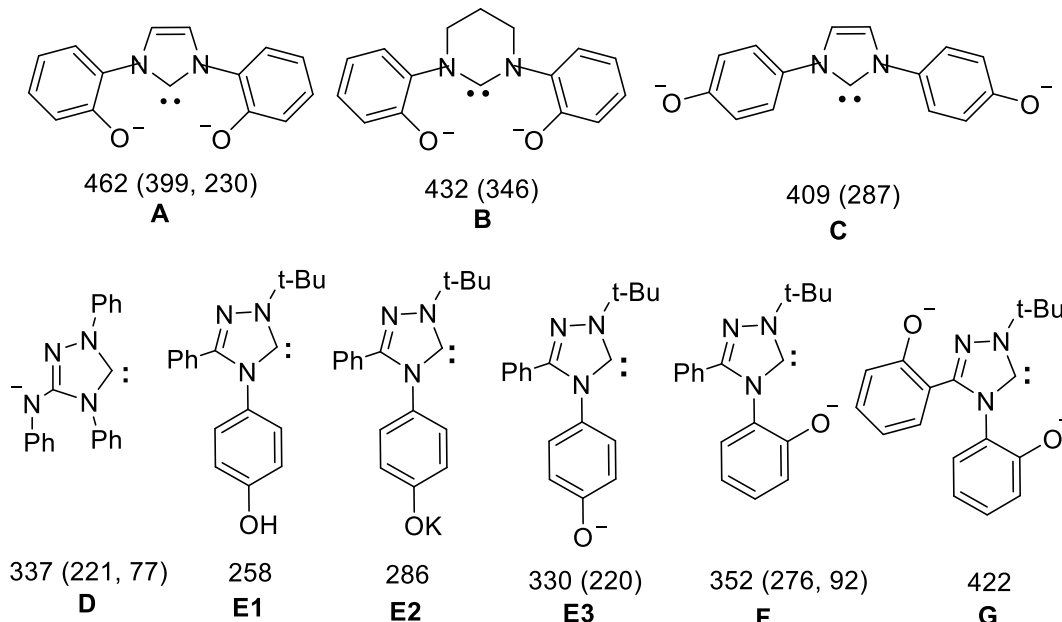
Scheme 55. Calculated H⁺, Cu⁺ and K⁺ affinities for oxide containing HBN-carbenes.

In the case of the latter, a change of the most basic reaction center is possible. Typically, hyperbasic systems are formulated with alkali metal cations and anions of the type **56A-G,** most of which are yet unknown (Scheme 56).[212] In all of the structures the basicity of the carbene center is significantly increased with respect to that in the non-anionic (for anion protonated) carbenes (in brackets), due to the transfer of electron density from the anion center (by 75-120 Kcal/mol, calculated at the DFT/B3LYP5/3-21G/RHF level).

A
(260.2)

B
(272.5)

C
(270.6)

D
(278.0)

E
(272.5)

F
(265.7)

G
(258.8)
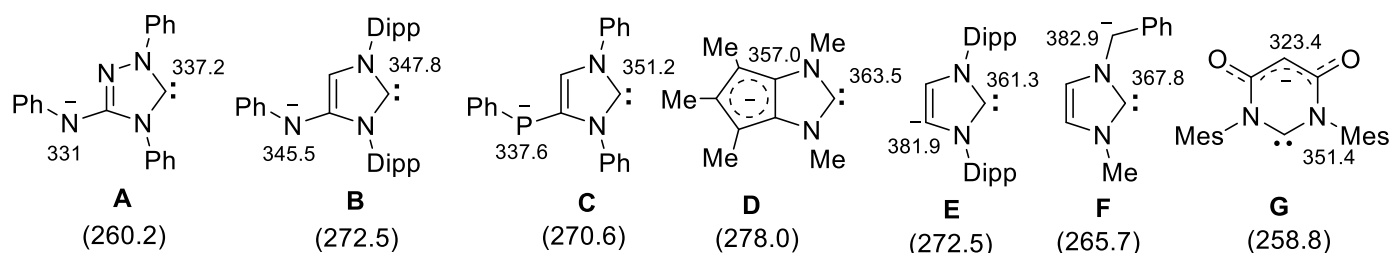
Proton affinities of the related non-anionic carbenes are indicated in brackets

Scheme 56. Proton affinities of HBN-carbenes and their exocyclic centers.

In compound **56A** the proton affinities of the basic centers are close to each other (N$_{an}$ and C5 331.0 and 337.2 Kcal/mol, respectively). In the case of the isolated imidazolylidene analogue **56B** of Danopoulos (without the crystallization solvent THF),[226] the PAs are even closer (345.5 and 347.8 Kcal/mol, respectively), but the carbene centers are the more basic in both compounds. In such cases, the direction of the interaction with electrophiles depends on the hardnesses of the reaction centers and may vary for different partners.

In the phosphide anion **56C** the difference between the carbenic and anionic centers becomes more substantial (13.6 *vs.* 6.2 Kcal/mol), relative to that in **56A**. In the hypothetical Arduengo bicyclic system **56D**

the basic centers are closer in their PAs (C2 363.5, C_{an} 357.0 Kcal/mol) than those of the known complexes **56E** (C_{an} 381.9 and C2 361.3 Kcal/mol)**.** In the case of the yet unknown anionic carbene **56F** the larger PA relates to the exocyclic carbon atoms (C_{an} 382.9, C2 367.8 Kcal/mol). In comparison, the anionic azine system **56G** has a larger PA for the carbene atom C2 (PA 351,4 Kcal/mol) than that for the atom C5 (323.4 Kcal/mol). In the case of complexes with alkali metal cations, the PA values are reduced significantly. Nevertheless, these complexes remain the more basic in comparison with neutral carbenes. For example, in the case of the 4-Li derivative of the imidazol-2-ylidene **56E** the value of the PA (at C2) is 284.9 Kcal/mol while that for the 4-K-derivative is 293.3 Kcal/mol.

3.5. Steric properties

Steric factors can have a significant impact on the reactivities of carbenes and their indices, such as the TEP and E_{dn}. On the basis of the above data (Scheme 51) it is clear that the value of E_{dn} is significantly reduced for compound **54F** in comparison with that of **54D**, and even that of **54C**.

Recently the steric influence of carbenes has been estimated using the criterion of ''percent buried volume'' (%V_{bur}),[267] which is defined as the percentage of the total volume of a sphere occupied by a ligand. It is generally considered to be a more reliable method than use of the Tolman cone angle (the cone angle is such that the metal is at the vertex and the atoms are at the perimeter of the cone).

For large structures such as **2E**, the values of the %V_{bur} for complexes of the type LAuCl are in the range of 50-53%.[50] The values for complexes of Mes and Dipp-substituted imidazol-2-ylidenes are significantly lower (36.5 and 44.5 %, respectively). New types of sterically complicated carbenes, ones that contain 2,6-dialkyl-4-methoxyphenyl substituents, are used frequently in catalytic studies, *e.g.*, palladium complex catalysis of the Buchwald-Hartwig[268,269] and Kumada reactions.[53] However, the individual carbenes have not yet been isolated. Catalytic applications of these highly sterically shielded compounds are described.[270,271]

The electron donating and steric properties of some related carbenes with branched aromatic groups have been compared (IPr, IPr[OMe], IPr*, IPr*[OMe]).[264] It was found that the introduction of a *p*-methoxy-group to the 2,6-diisopropylphenyl system (IPr[OMe], IPr*[OMe]) leads to a marked increase in the Tolman donating ability of the ligand. However, the buried volumes are somewhat smaller (by 2-3%) with respect to those for the compounds IPr and IPr*. On the basis of ^{77}Se chemical shifts in the NMR spectra of the respective selenones, it was found that the π-accepting properties of the carbenes with aromatic branched fragments (IPr*, IPr*[OMe]) are markedly increased in relation to those of the Dipp-substituted carbenes (IPr, IPr[OMe]). Furthermore, the methoxy-substituted carbenes were found to be slightly less electron accepting, than the related IPr and IPr* compounds. These properties are important from the standpoint of the catalysis of organic reactions such as Buchwald-Hartwig, arylthiol arylation, etc.[272,273] In the case of the imidazolylidene, IPent with 2,6-di-(3-amyl)phenyl substituents, synthesized by Nolan *et al*.,[274] the %V_{bur} is almost the same (about 49%) as that for IPr*.

Another sterically shielded carbene, namely the 1,3-di-(2,6-dinaphthohydryl-4-methylphenyl) substituted imidazol-2-ylidene, has been used *in situ* for the preparation of silver, copper, rhodium and palladium complexes.[275] The %V_{bur} values for the AgCl and CuCl complexes, which are normally close in value to those of the related AuCl complexes, reach 57.1 and 57.4%, respectively.

4. Transformations of Individual Carbenes

It is clear from the previous section that structural features have a definite influence on the reactivities of carbenes. In the present paper, the focus of the work concerns those transformations that, according to the authors, have previously been inadequately represented in the literature. This comment includes rearrangements, autotransformations, ring expansions, insertions, the formation of organic complexes, reactions with multiple bonds, and complexes with non-metals,[19,32,33] all of which are important from the standpoint of organic synthesis.

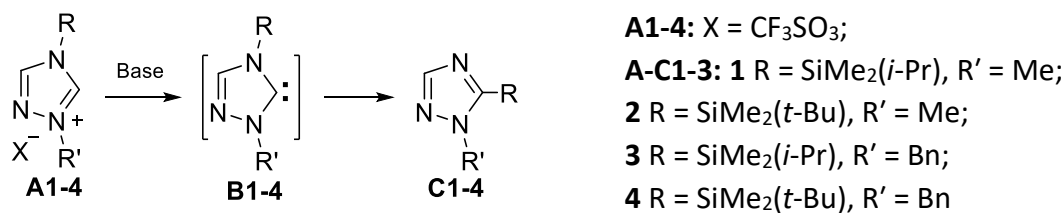## 4.1. Rearrangements and autotransformations

Rearrangements that involve the migrations of groups and atoms in carbenes are related to the most important carbene properties. Autotransformations are cascade (tandem) transformations that take place, between heterocyclic carbenes and the products of their thermal decomposition, *in situ* without the participation of other reagents. Thermolysis reactions can be carried out by heating or under mild conditions (at room or low temperatures). In the simplest cases, these consist of proton migrations, which are particularly easy in the case of simple carbenes, and which occur even at low temperatures. Autotransformations of heterocyclic carbenes, and their aromatic derivatives, were only discovered in the 1990s.[276-278] Several of the studies showed that some heterocyclic carbenes become unstable upon heating.[103,168,279] Interestingly, reactions of this type have not been studied until recently.

4.1.1. Migrations of atoms and groups in stable carbenes. The simplest example of such a migration involving heterocyclic carbenes is the 1,2H-shift reaction to imidazol-2-ylidenes that has been known since the beginning of the 1990s.[19,32,33,280-284] The unimolecular concerted mechanism for this reaction was found to take place only with carbenes of low stabilities.[281,285,286] This prompted a search for an alternative intermolecular mechanism. The intermolecular proton transfer mechanism was found to be the best option for heteroaromatic carbenes,[287-289] where the intramolecular reaction was found to be energetically unfavorable. The migration of protons results in the aromatization of heterocycles such as imidazoles (Scheme 57) or thiazoles. Theoretical calculations revealed that the activation energy of the reaction is quite large (E_a 40-47 Kcal/mol), despite the fact that the process is exothermic (ΔH −26 to −29 Kcal/mol). Mayer *et al*. obtained similar values for thiazol-2-ylidene (E_a 42 and ΔH −34 Kcal/mol). However, quantum mechanical tunneling was found to reduce the enthalpy of the process significantly (for thiazol-2-ylidene by a factor of about 10^5 at 60K).[290]
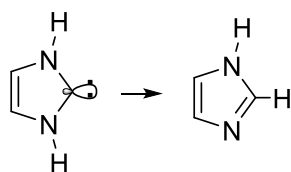
Scheme 57. Proton migration in imidazol-2-ylidenes.

　　The migration of trimethylsilyl groups in a number of stable carbenes was discovered by Bertrand *et al*.[291] These authors showed that the deprotonation of trimethylsilyl substituted 1,2,4-triazolium salts **58A1-4** (Scheme 58) with different bases through the intermediate triazolylidenes **58B1-4** resulted in the formation of 3-trimethylsilyltriazoles **58C1-4** in yields of 42–81%.

A1-4: X = CF$_3$SO$_3$;
A-C1-3: 1 R = SiMe$_2$(*i*-Pr), R′ = Me;
2 R = SiMe$_2$(*t*-Bu), R′ = Me;
3 R = SiMe$_2$(*i*-Pr), R′ = Bn;
4 R = SiMe$_2$(*t*-Bu), R′ = Bn

**Scheme 58.** Silyl migrations in 1,2,4-triazol-5-ylidenes.

It was found that the addition of strong bases, in less than equimolar amounts, resulted in an interaction of the carbene with the unreacted salt. This was accompanied by the migration of a trimethylsilyl group onto the carbene carbon atom, thereby forming triazoles. A similar result was observed when Enders' carbene was reacted with the trimethylsilyl substituted salt. In an excess of 1-benzyltriazole, the *N*-methyl-*N*′-trimethylsilyl substituted salt resulted in the formation of a 1-methyltrimethylsilyl substituted triazole and a triazolium salt, i.e. an exchange of alkyl and silyl substituents had taken place. Deprotonation of the mixture of triazolium salts (Me-, Bn-, R-, R′- substituted, where R = SiMe$_2$*i*-Pr; R′ = SiMe$_2$*t*-Bu) with potassium hydride resulted in a mixture of triazoles with the same substituents. This confirmed the mechanism of the reaction as a rearrangement (autotransformation) of the intermediate carbene (Scheme 58).

The migration of a methyl group was also observed in the recently discovered mesoionic 1,2,3-triazolium-5-ide carbenes. In addition, the reaction of the Dipp-Ph-Me substituted **59B**, that was obtained from the salt **59A**, took place quite readily at 50 °C in benzene solution and resulted in the formation of the triazole **59C** (Scheme 59).[246] However, the methyl group could be replaced with an aromatic group thereby stabilizing the system. In fact, the transformation of the Mes$_2$Ph substituted carbene did not take place under these conditions even after 12 hours. Furthermore, dimerization was not observed under these conditions.[246] In contrast to the 1,2,3-triazolium-5-ides, the imidazolium-4-ides are considerably more stable. However, only their aromatic derivatives have been studied.
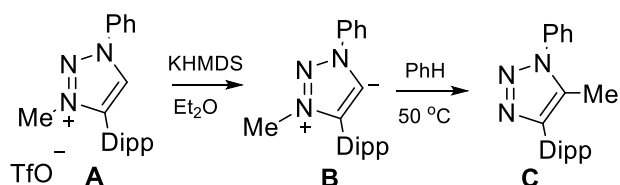
Scheme 59. Rearrangement (methyl migration) of 1,2,3-triazolium-5-ides.

Denk *et al.*[292,293] discovered an intermolecular H-D exchange between 1,3-di-*tert*-butylimidazol-2-ylidene and DMSO-d_6.[294,295] The deoxygenating properties of these carbenes had been reported previously. For example, deoxygenation of DMSO by short lived carbenes had been described.[294] Wishing to examine the deoxygenation of DMSO by stable carbenes at elevated temperatures, the authors found that the ^{13}C NMR signals of the C4 and 5 atoms gradually disappeared after dissolution in DMSO-d_6; 4,5-dideuterium-1,3-di-*tert*-butylimidazol-2-ylidene was isolated (Scheme 60).
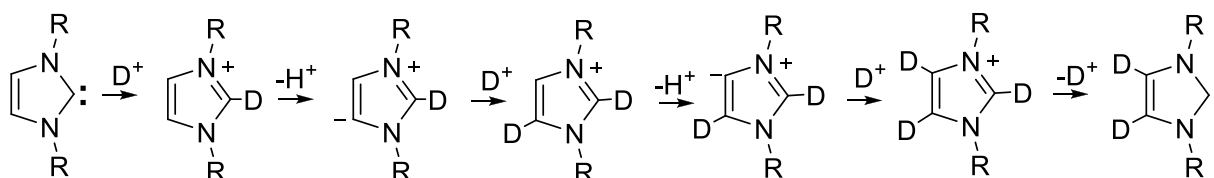
Scheme 60. Deuteration of imidazol-2-ylidenes in deuterated solvents (e.g., DMSO-d_6).

The proton/deuterium exchange that took place in the imidazol-2-ylidene at positions 4 and 5 could occur by a mechanism similar to that found for the related reactions of carbenes with CCl$_4$ (in the latter case proton/ Cl$^+$ exchange).[57] The method for the preparation of stable imidazol-2-ylidenes reported by Arduengo[41] was used for the synthesis of the bisdibenzotropylidene substituted carbene **61B** (Scheme 61) starting from the corresponding amine.[296] However, the deprotonation of salt **61A** resulted in a rearrangement of the carbene **61B** to the imidazole **61C** in 44% yield. The reaction mechanism involves a 1,2-alkyl shift and isomerization of the tropylidene radical (from a *5-* to a *10*-substituted isomer). It is assumed that this rearrangement occurs because of the addition of the carbene to a double bond of the dibenzotropylidene ring. This results in the rearrangement of the cyclopropane adduct first formed to the imidazole **61C**. Unfortunately, the isolation of the pure carbene **61B** failed in this case.
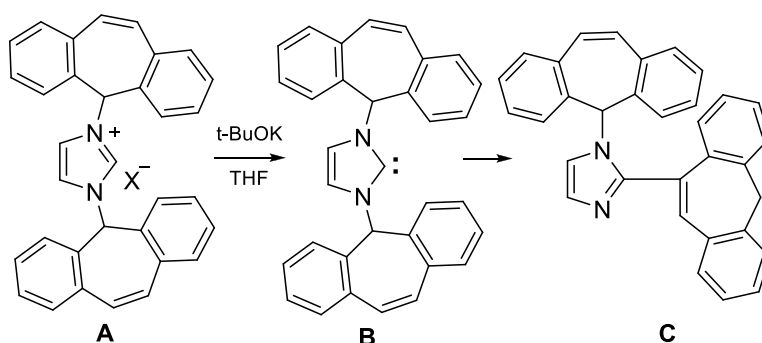
Scheme 61. Rearrangement of tropylidene derivatives of imidazol-2-ylidenes.

The sterically shielded 1-alkyl-3-phosphanylbenzimidazol-2-ylidenes **62A** undergo rearrangement upon heating to form the corresponding 2-phosphanylbenzimidazoles **62B** (Scheme 62).[65,110] As a consequence, it was demonstrated that the intermediates in the electrophilic substitution reactions of azoles are carbenic in nature. Previously, cyclic ylide structures had been assigned to such intermediates on the basis of the resonance possible for these carbenes.[297] The reaction of phosphanylated imidazoles and 1,2,4-triazol-5-ylidenes **62C** to phosphanylazoles **62D** proceeds similarly.[65,200,201] Thus, although in mainstream heterocyclic chemistry the *N*-substituent migration involves a carbene carbon atom, shifts to the 4 and 5 positions of the imidazol-2-ylidene nucleus are also possible.

A, B R = t-Bu, i-Pr$_2$N; R' = Me, i-Pr; **C, D:** R = t-Bu, R' = Me (**1**), Et (**2**), i-Pr (**3**)
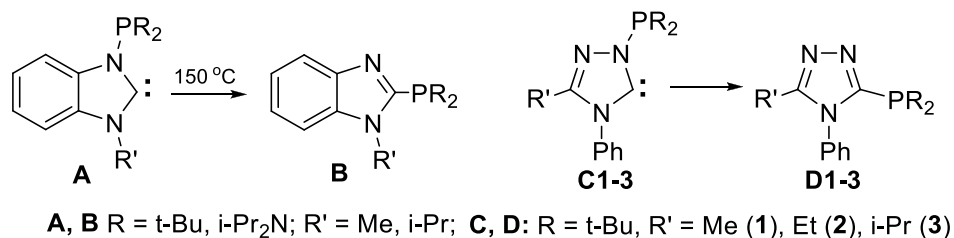
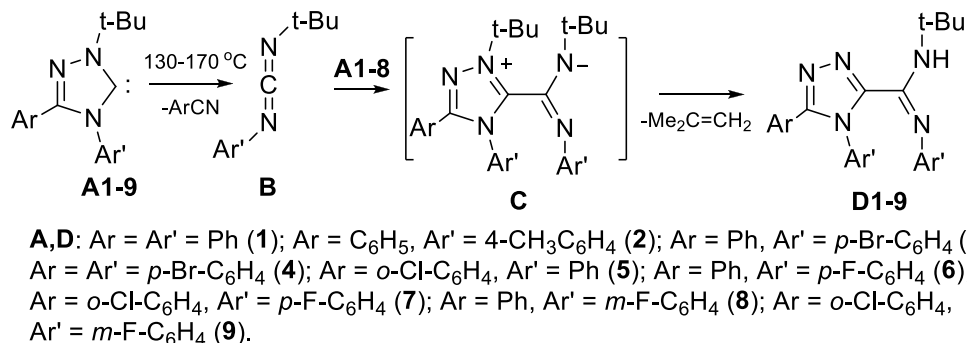**Scheme 62.** Rearrangement of *N*-phosphanylazolylidenes.

4.1.2. Other autotransformations. In several early studies, instability was noted for the aryl substituted 1,2,4-triazol-5-ylidenes upon heating.[168] However, the processes that take place at elevated temperatures in the absence of other reactants have not been studied.

Subsequently, it was discovered that heating 1-alkyl-3,4-diaryl substituted 1,2,4-triazol-5-ylidenes **63A** in organic solvents (decane or 1,3,5-triethylbenzene), at temperatures close to their melting points, resulted in autotransformation to give 5-amidino-1,2,4-triazoles **63D** in yields of 41–81% (Scheme 63).[196,218] The reaction involves decomposition of the carbene 1,2,4-triazole ring to a nitrile and an alkylarylcarbodiimide **63B**. This is followed by further reaction of the latter with the remaining carbene (the induced tandem reaction).

The intermediate products of the reaction are the zwitterionic compounds **63C**, which further eliminate isobutene to form the final products, the 5-amidino-1,2,4-triazoles **63D**. The reaction was found to take place via a slow first step followed by a rapid second stage. As a consequence, there was no accumulation of carbodiimide.

The first example of a tandem reaction for stable carbenes was probably carried out by Arduengo *et al.*[57] The interaction of 1,3-dimesitylimidazol-2-ylidene with CCl_4 in THF at room temperature (Scheme 6) was found to form 4,5-dichloro-1,3-dimesitylimidazol-2-ylidene **6G** and chloroform. The subsequent conversion of **6G** with carbon tetrachloride results in the formation of 2,4,5-trichloroimidazolium chloride and an adduct of carbene **6G** with dichlorocarbene. However, this reaction is not an autotransformation because it occurs with the participation of CCl_4.

A,D: Ar = Ar' = Ph (**1**); Ar = C_6H_5, Ar' = 4-$CH_3C_6H_4$ (**2**); Ar = Ph, Ar' = *p*-Br-C_6H_4 (**3**);
Ar = Ar' = *p*-Br-C_6H_4 (**4**); Ar = *o*-Cl-C_6H_4, Ar' = Ph (**5**); Ar = Ph, Ar' = *p*-F-C_6H_4 (**6**);
Ar = *o*-Cl-C_6H_4, Ar' = *p*-F-C_6H_4 (**7**); Ar = Ph, Ar' = *m*-F-C_6H_4 (**8**); Ar = *o*-Cl-C_6H_4,
Ar' = *m*-F-C_6H_4 (**9**).

Scheme 63. Tandem induced autotransformation of 1-tert-butyl-3,4-diaryl-1,2,4-triazol-5-ylidene.

Similar conversions take place with the tetrazol-5-ylidenes, but proceed more rapidly than the reactions of the 1,2,4-triazol-5-ylidenes. Deprotonation of the 1,4-disubstituted tetrazolium salts **64A,D**, using sodium hydride or hydroxide (Scheme 64), resulted in the formation of the unstable carbenes **64B,E**. In the subsequent decomposition, the carbodiimides **64C,F** were formed, thus proving the low stabilities of the intermediate 1,4-disubstituted tetrazol-5-ylidenes under these reaction conditions.[298] Given that tetrazol-5-ylidene is one of the most aromatic of this type of heterocyclic carbene,[299] the instability of **64B** may be a consequence of the presence of intermediates that may be formed during the synthesis of tetrazol-5-ylidenes from the corresponding tetrazolium salts.
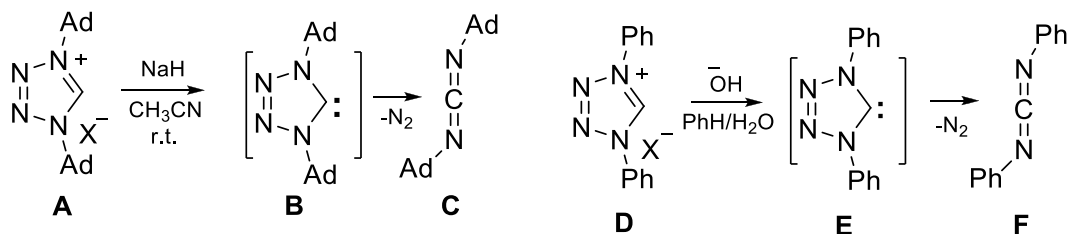
Scheme 64. Formation and cleavage of tetrazol-5-ylidenes.

Scheme 65 shows the calculated bond energies that were obtained from DFT calculations (at the B3LYP5/RHF/6-311G (d, p) level) for a series of tetrazol-5-ylidene derivatives. In the case of the singlet carbene **65A**, the cyclic bonds are strong enough to avoid the instability problem. In the case of the triplet carbene **65B**, which could be formed during reactions, the cyclic bonds are weakened. However, the bond energy of N1-N2 in the anionic tetrazol-5-ylidene **65C**, which is formed by the transfer of a hydride ion from the nucleophile (metal hydride) to the carbene, is significantly smaller. As a consequence, rapid decomposition of the intermediate was possible, thus converting the anion into the carbodiimide and nitrogen. In contrast, the tetrazolylidenes themselves are probably stable, and two types of isomeric compounds have been obtained in complexes, namely, normal **65D** and mesoionic **65E**.[300] To the best of our knowledge, comparable studies of carbenes of other azole series have not yet been undertaken.
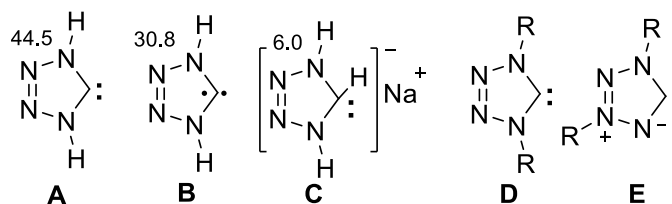
Scheme 65. Calculated bond energies (Kcal/mol) for different types of tetrazol-5-ylidene derivatives.

Recently, a related decomposition was detected for a non-aromatic 1,3-*p*-tolyl-4,5-dihydroimidazol-2-ylidene at 110 °C in toluene. This compound eliminated ethylene (from the ethylene moiety of the ring), and the resulting carbodiimide (di-*p*-tolyl substituted) added to a second equivalent of the unreacted carbene, forming the zwitterion **66C** (Scheme 66).[301] This reaction resembles the above-described autotransformation reaction (Scheme 63); the only difference is that here the stable tolyl groups in the adduct are not cleaved, and hence the zwitterion **66C** is the final product.

$$Tol = p\text{-}C_6H_4CH_3$$
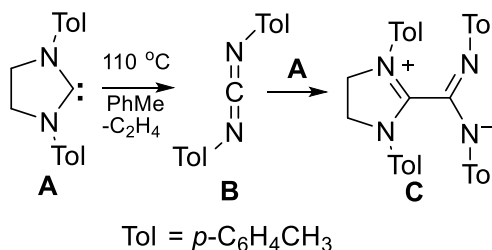
Scheme 66. Tandem autotransformation of 1,3-ditolyl-4,5-dihydroimidazol-2-ylidene.

4.1.3. Ring expansions of heterocyclic carbenes. The reactions of mono- and di-substituted silanes with aliphatically substituted imidazol-2-ylidenes **67A** resulted in ring expansion to give the six-membered carbene sila-containing diazines **67C** (Scheme 67). [302] In the course of the reaction, the carbene was inserted into the Si-H bond of the silane (intermediate **67B**). This was followed by reduction of the heterocyclic carbene by the silyl moiety at the 2-position, thus moving the hydride anion from silicon to the carbon atom. The outcome was confirmed by deuteration of the carbon atoms with $R'R''SiD_2$ and also by calculation.[303]

The ring expansion of imidazol-2-ylidenes is also effected by other Lewis acids, particularly boranes[304] and aminoboranes.[305,306] These result in the formation of borazines of types **67D,E**, along with boroxoles **68B** (Scheme 68). [307] A beryllium analogue[308] of the silazines **67C**, compound **67F** (Scheme 67), is also known. Compounds of this type (and their precursor borane carbene complexes) are promising reduction catalysts of the FLP-type.
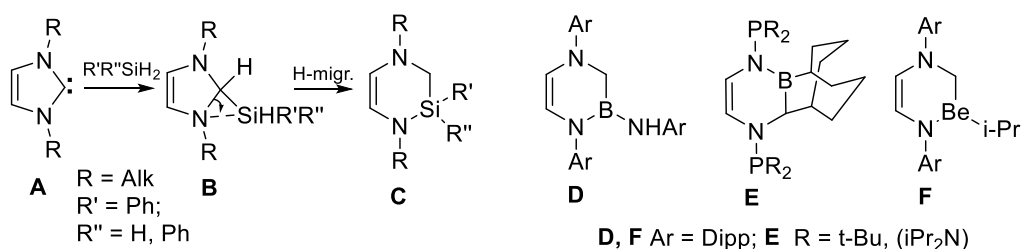
Scheme 67. Ring expansion of imidazol-2-ylidenes with silanes.
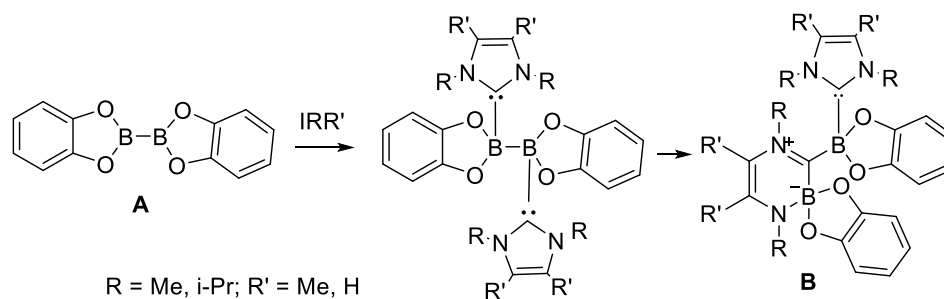
Scheme 68. Transformation of carbene-boroxole complexes.

The benzimidazol-2-ylidene related derivatives of the indazol-3-ylidene **69A**, and their mesoionic pyrazol-3-ylidenes, have not yet been isolated in a pure state. However, if the process is carried out *in situ* by refluxing in a variety of solvents, they can be converted by ring expansion into the 9-amino derivatives of acridine **69D** (Scheme 69).[309,310]
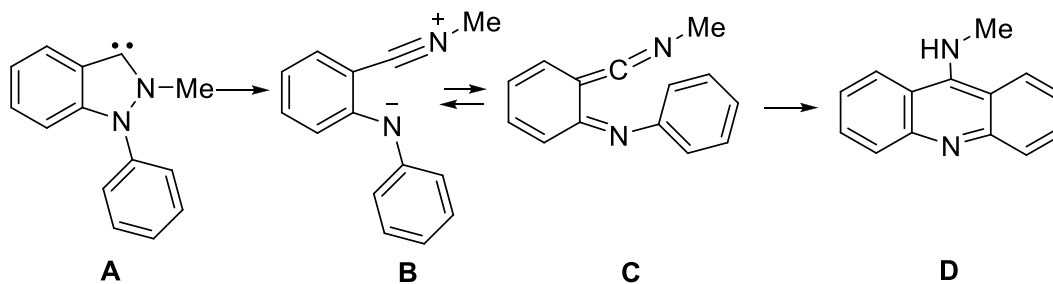
Scheme 69. Rearrangement of indazol-3-ylidenes into 10-aminoacridines.

In carbene chemistry, the reconstruction processes for heterocyclic or aliphatic moieties (proton migrations, rearrangements, cleavages, and ring expansions) play a particularly important role. The most stable species are the imidazol-2-ylidenes, for which decomposition does not occur even at elevated temperatures (for the 1,3-diadamantyl derivative the temperature is 240 °C). In the case of fused rings (**24D**, at 300 °C) and the conjugated biscarbenes chemical behavior upon heating is similar (the melting points for 1,1'-diadamantyl- and 1,1'-di-*tert*-butyl-substituted bistriazolylidenes **43A1,2** are 208-210 and 196-197 °C, respectively, without the autotransformation inherent to *tert*-butyl-substituted mononuclear systems).

4.1.4. Dimerization reactions and cross-couplings. On the basis of thermodynamic and kinetic data, the dimerization (coupling) of many types of carbenes without sterically shielding groups was found to be preferred under normal conditions. Theoretical data have received extensive experimental confirmation, starting with Wanzlick's work.[7,311] Nevertheless, it has long been debated whether dimerization is a catalyzed process (e.g., with acids) or if it occurs spontaneously without a catalyst. Lemal's data[312-314] provides evidence in favor of a catalytic reaction. According to this theory, impurities of protic substances (e.g. azolium salts in the case of Hahn's dimerization of 1,3-diisobutylbenzimidazol-2-ylidene,[107] Arduengo's 3-substituted thiazol-2-ylidenes,[315] Alder's diaminocarbenes,[316,317] and others) may well be present in the reaction mixtures when carbene dimerizations occur. According to Lemal the pure dimers do not dissociate. However, Denk's experiments[318] give reason to acknowledge the possibility of a cross-dissociation occurring in the dimer forming reaction. On the other hand, Taton and Chen have shown[319] that dimerization is observed for the cyclic bisimidazole-2-ylidenes with two linkers of three methylene units, while for the analogue with four methylene links only the biscarbene was detected.

Recently Bertrand *et al.* have developed a new method to accomplish certain carbene couplings. These authors successfully conducted cross-coupling reactions between the aromatic 1,2-bis(diisopropylamino)-cyclopropenylidene and a number of non-aromatic carbenes (pyrrolidin-2-ylidenes, 3,5-dioxo-4*H*-pyrimidin-2-ylidenes, and 1,5-dioxo-2,4-benzodiazepin-3-ylidenes) (Scheme 70). In the first two cases, the initial coupling products of type **70B** rearranged, via a ring expansion, into the azetidinylallenes **70D,E**[320] while in the last case the olefin **70F** was formed.

The results of these experiments have established that a prerequisite for dimerization is an adequate difference in the HOMO and LUMO energies of the reactive carbenes. Thus far, comparable experiments with heteroaromatic carbenes of the azole series have not yet been carried out.
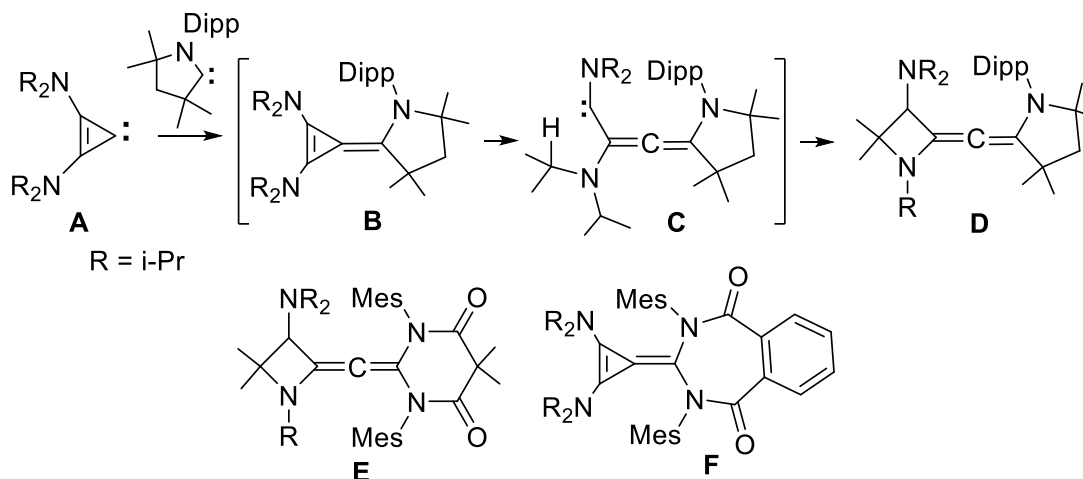
Scheme 70. Couplings of different stable carbenes and their accompanying reactions.

Bielawski *et al*. used the dimerization process of benzimidazole-type carbenes for the preparation of polymeric biscarbenes **71A** (Scheme 71).[321] The biscarbene polymers were combined with dimers, thereby forming shorter mixed polymers **71B** that confirmed the possibility of the dissociation of Denk's dimers.[318] Taking into account the potential use of conjugated polymers as photosensitive materials in solar cells, the utilization of benzimidazol-2-ylidene dimers, as structural fragments of polymers with both electron donating and electron withdrawing substituents, was studied to try to control their properties.[322] By varying the substituents on the 5- and 6-positions of the nucleus, the absorption bands were found to undergo a shift to the visible region (up to 444 nm), thereby signaling a change in their redox potentials. The structure of the dimer is characterized by the presence of almost planar rings. However, with the addition of halogen and methoxy substituents both rings become twisted by 16-17°.
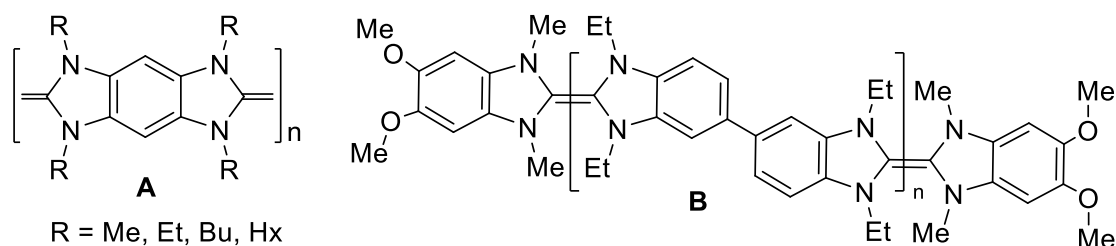
Scheme 71. Polymers based on biscarbenes.

4.2. X-H insertion reactions
4.2.1. Insertions into polar X-H bonds. One of the characteristic properties of the heterocyclic carbenes relates to their reactions with substances that contain mobile protons, XH. [7,9,168,198] As such, these reagents can act as alcohols, thiols or amines. However, such insertion products are generally labile and upon heating transform back into the original carbenes. For this reason the generation of carbenes in liquid ammonia by Herrmann *et al*. allowed isolation of the carbenes but not of the insertion products, aminoazolines.[90] The stabilities of the insertion products can vary depending on the type of X-H bond, on the heterocycle, and on the steric conditions around the carbenoid center. As an example, 5-methoxy-1,3,4-triphenyl-5*H*-1,2,4-triazoline **36B** is relatively stable, and decomposes to a carbene and methanol only when heated at 80 °C for 24 hours (Scheme 36).[168] On the other hand, 1,3-dimethyl-2-(*N*-morpholinyl)-2*H*-benzimidazoline sublimes

when heated, which may be due to its reversible cleavage into the carbene and the amine.[198] The reactions with alcohols have been used to protect carbenic centers and to produce high quality carbenes.[103,104,195-199]

The role of product insertion in the hydrolysis of carbenes is described in the following references.[33,198] However, it has been noted that imidazol-2-ylidenes and diaminocarbenes fail to react with such nucleophiles (in this case NH_3). This is in contrast to pyrrolidin-2-ylidenes, aminoalkylcarbenes and 3,5-dioxo-4*H*-pyrimidin-2-ylidenes, all of which react even at low temperature (–78 °C). [323] The possibility of a reaction occurring between aromatic carbenes and ammonia was confirmed by calculating the enthalpies of the reactions, which were confirmed to be negative. The calculated activation energies, even for diaminocarbenes, were significantly reduced compared to those for pyrrolidin-2-ylidenes and aminoalkylcarbenes (from approximately 33 to 21 Kcal/mol). However, as for the C-H bond insertion reactions, the energetically unfavorable proton loss from the amine molecule must be compensated for by the formation of new bonds via a concerted reaction mechanism. The final result of the reaction in ammonia (return of the heteroaromatic carbene upon heating or even at room temperature when dry) is due to the equilibrium nature of the reaction and an insufficient C-N bond strength.

4.2.2. Hydrogen bonds of carbenes. In the presence of steric hindrances, or if the proton donor is highly acidic, the insertion reaction becomes unprofitable and the H-carbene complexes that are formed can be of the azolium or carbene type. For example, with 2,6-di-*tert*-butyl-4-cresol,[324] 1,3-dimesitylimidazol-2-ylidene forms the azolium phenoxide structure **72A**, and with less acidic alcohols and diphenylamine the carbene complexes **72B**, **72C** are formed (Scheme 72).[325] According to X-ray diffraction studies the C···H distances are 2.801(4) and 2.832(2) Å, in **72A** and **72B**, respectively. They are considerably shorter than those of known systems with C-H...O bonds, including the related H-complexes of some C-H acids with dioxane (2.94 − 3.02 Å).[325] The length of the C...H bond in structure **72C** is 2.30(1) Å, while the N...C distance is 3.196(2) Å.
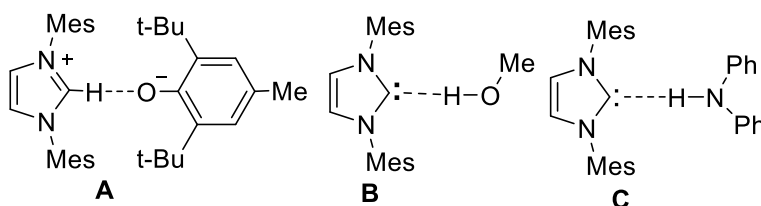
Scheme 72. Hydrogen bonds of 1,3-dimesitylimidazol-2-ylidene.

Confirmation of the carbenic nature of the complexes with methanol and diphenylamine (**72B** and **72C**) is provided by the presence of δ_c ^{13}C NMR signals at 210 and 215 ppm, respectively, which are close to those of the pure carbene (δ_c 220 ppm).

Depending on the substituents at the nitrogen atoms of the carbene, a shift of the hydrogen bound proton has been observed. Thus, TEMPO-H is bound to 1,3-dimesitylimidazol-2-ylidene by a hydrogen bond (**73A**), and the corresponding Dipp-substituted analogue transfers the proton of TEMPO-H to form a complex of an imidazolium salt with the respective *N*-oxide (**73B**) (Scheme 73).[326]
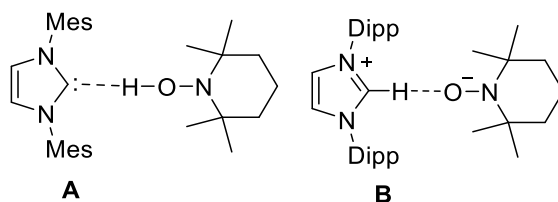
Scheme 73. Hydrogen bonds of imidazol-2-ylidenes with TEMPO-H.

4.2.3. Insertions into C-H bonds. Reference was made earlier[8] to the absence of reactions between stable carbenes and C-H bonds. Enders *et al*. assumed that the formation of such products falls outside the temperature limits of carbene stability (> 150 °C).[327] Nevertheless, it should be noted that carbene insertions have been carried out with the C-H bonds of malononitrile and other CH-acids from carbene dimers.[7] Obviously, these reactions take place via carbenoid mechanisms and can therefore differ significantly from the reactions of individual free carbenes.

It was later found[104,195,279,328] that benzimidazol-2-ylidene **20E**, 1,3,4,5-tetraphenyl substituted imidazol-2-ylidene, and the soluble 1,2,4-triazol-5-ylidenes **42D** are all easily inserted (at room temperature) into a C-H bond of acetonitrile thereby producing the corresponding azolines **74A-C** (Scheme 74). Dibenzyl- and dimethyl-substituted benzimidazol-2-ylidenes react *in situ* in a similar fashion. The reactions of the sparingly soluble 1,2,4-triazol-5-ylidenes proceed slowly (but more easily when heated to 100 °C). The formation of sparingly soluble analogues of the 1,2,4-triazol-5-ylidenes **42D** and the bis-1,2,4-triazol-5-ylidenes **43A,B** became the basis for the preparation of highly pure samples of these carbenes when solutions of the triazolium salts **42A** in acetonitrile were treated with sodium hydride.
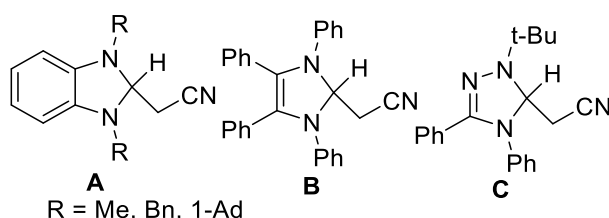
Scheme 74. Insertion products of azolylidenes into the C-H bond of acetonitrile.

On the other hand, 1,3-di(1-adamantyl)imidazol-2-ylidene failed to give an insertion product and only a weakly bound carbene-acetonitrile solvated complex was isolated.[329] The reverse decomposition reaction of 1,3-di(1-adamantyl)-2-benzimidazoline **20D** was used for the preparation of the first representative carbenes of the benzimidazole series **20E** (Scheme 20).[103,104]

Subsequently, the insertion reactions of 4,5-dihydroimidazol-2-ylidenes into the C-H bonds of acetylene, dimethyl sulfone, acetonitrile, and chloroform were studied.[329] In the case of acetylene two types of products were isolated, namely the heteryl- and diheteryl- substituted azolines **75A,B**. The reactions of dimethylsulfone and acetonitrile resulted in the formation of the compounds **75C,D** (Scheme 75).
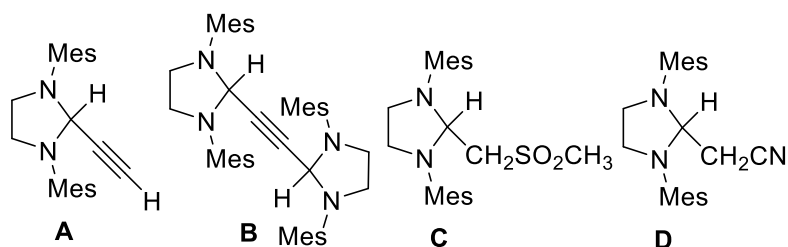
Scheme 75. Insertion products of 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene into C-H bonds.

Thus, the reactions of compounds with a mobile proton CH are very characteristic for carbenes, and take place with compounds that have slightly acidic C-H bonds. For comparison, the reaction of the 1,3-dimethyl-1,3-diadamantylamidinium salt **76A** (related to azolium compounds) with sodium hydride in acetonitrile formally gives the insertion product of the carbene into a C-H bond of acetonitrile **76B** (Scheme 76).[330]
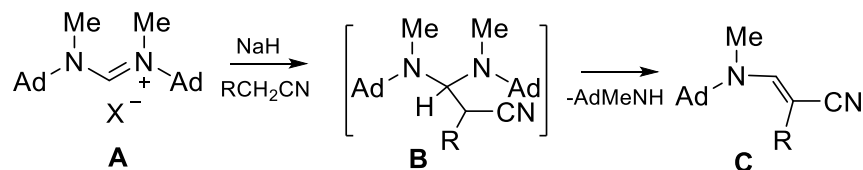
Scheme 76. Carbenoid Hofmann cleavage in amidinium systems.

The absence of any *meso*-substitution of the protons (to deuterium) in the reaction of the salts **76A** with deuteroacetonitrile has shown that compounds **76B** are generated via deprotonation of acetonitrile and addition of the $^-CH_2CN$ anion to the amidinium cation. The resulting adducts **76B** undergo an unusual (carbenoid) Hofmann cleavage in non-aqueous media to form the β-aminoacrylonitriles **76C**.

The insertion of carbenes into the C-H bonds of aldehyde groups occurs with both aliphatic and aromatic aldehydes, e.g., propionaldehyde and benzaldehyde (Scheme 77).[331] The reaction proceeds in THF solution at room temperature if left for 60 hours and results in the formation of the racemic products **77B,C**. Attempts to obtain the enol form by silylation of the product with *N,O*-bistrimethylsilylacetamide (BSA) was only successful with the propionaldehyde adduct. Furthermore, this approach afforded the *Z*-enol isomer after participation of the alkyl group. In the case of the product from the benzaldehyde reaction, the keto-form was favoured over the enol form by 11.7 and 13.1 Kcal/mol (*E*- and *Z*-forms, respectively).

Scheme 77. Insertion of 1,3,4-triphenyl-1,2,4-triazol-5-ylidene into the C-H bonds of aldehydes.

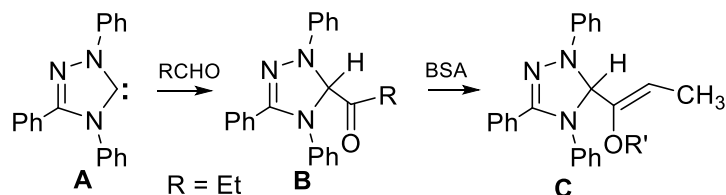**4.2.4. Carbenoid properties of carbene insertion products.** By increasing the degree of ionization of the C-C bond in the insertion product its carbenoid properties are increased due to the interaction of the anion with the *meso*-proton. An example of such a reaction is the interaction of azolium carboxylates with sulfur at room temperature,[332] in which the formation of a complex acetic acid-acetate anion is postulated (the authors explain this by the existence of an equilibrium between the acetate salts and the free carbenes in ionic liquids). According to the authors of this review, this behavior is observed during the reaction of acetates in common organic solvents and is connected with the carbenoid reaction.

Another example of carbenoid promotion is provided by the carbene reduction that occurs upon heating azolium formates.[32,333] Similarly to the hydroxyazolines,[33] azolium formates **78A** are capable of reducing the salts **78A** to form the 2*H*-azolines **78C** (Scheme 78). The sensitivity of the reaction to moisture, which reduces the yields of the azolines **78C**, confirms the mechanism of the carbene reaction.
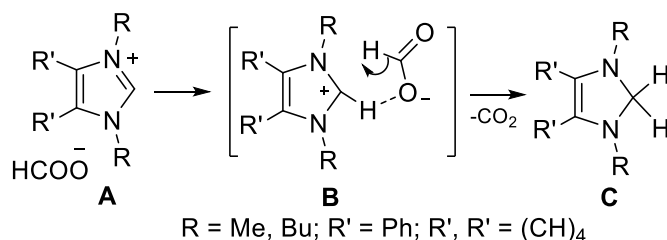
Scheme 78. Carbenoid decomposition of azolium formats.

The C-C bond of the covalent products of carbene C-H-insertions is weaker than those found in alkanes, albeit to a lesser degree than those in the ionic compounds. The C-C bond is, however, stronger than the C-O and C-N-bonds of the OH- and NH-insertion products (Scheme 79). The consequence of these weakened bonds is evident not only in the above-mentioned decomposition of cyanomethylazolines to carbenes but also in the carbenoid properties of the cyanomethylazoline **79A**, the reactions of which were carried out under the influence of metal salts to give the carbene complexes **79B,C** (Scheme 79).[216,334,335]

(i) - CuCl/MeCN, -MeCN; (ii) - CuI/MeCN, -MeCN
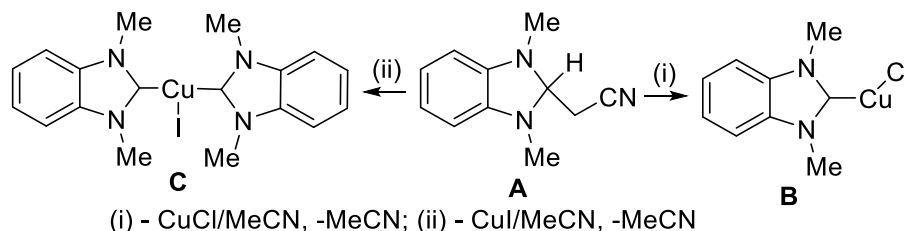
Scheme 79. Carbenoid reactions of 2-cyanomethyl-2*H*-benzimidazoline with copper(I) salts.

4.3. Alkylation and arylation of carbenes

The methylation of a stable carbene was first reported by Enders *et al*. It involved the reaction of 1,3,4-triphenyl-1,2,4-triazol-5-ylidene with trimethyloxonium tetrafluoroborate and gave the anticipated salt.[327] An analogous reaction was used subsequently by Arduengo; 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and methyl iodide were combined, followed by deprotonation of the intermediate salt to form methylene-imidazolidine.[57] In this study it was also shown that 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene **80A**, which results from the combination of the unchlorinated analogue and CCl$_4$, reacts further with CCl$_4$ by removal of two chlorine atoms thus forming the salt **80B**. The generated dichlorocarbene adds to the heterocyclic compound to afford 2-(dichloromethylen)imidazoline **80C** (Scheme 80). Aryl- and arylmethoxy-substituted methylenimidazolines, analogous to **80C** (R = Ar, R '= H, OMe), were obtained via the reaction of the carbene with benzyl halides and methoxybenzyl chloride, respectively.[336-338]
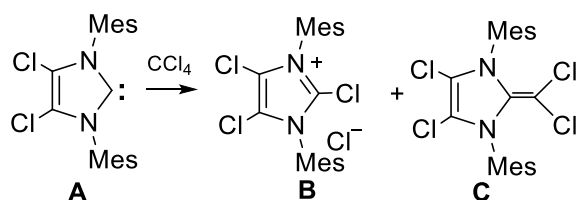
Scheme 80. Carbene-carbene coupling upon chlorination of imidazol-2-ylidenes with CCl$_4$.

Aromatic carbenes have been aralkylated using diphenylmethyl salts, stabilized in the *p*-positions with dimethylamino groups, or arylated by quinoids **81B** (deprotonation products of similar salts) thus forming the desired azolium salts **81C, E** (Scheme 81).[337] According to kinetic data collected, the reactivity of carbene **81A** is slightly inferior to that of its 4,5-dihydro analogue, but significantly higher than that of triazolylidene **81D**. The reactivity of the latter is even smaller than that of DBU, but significantly higher than that of triphenylphosphine. Note also, that if this was not the case, it would suggest that deprotonation of the alkylating reagent by the carbene had taken place.

An unusual feature was found when the reactivities of the 1,3-diarylimidazol-2-ylidene **81A** and its 4,5-dihydro analogue, in the arylation reactions by quinoids and diarylmethyl salts, were compared with the azolium methylide arylation at the terminal atom of the olefinic bond.[336] Although the reactivity of carbene **81A** is inferior to that of its 4,5-dihydro analogue by about 2.5 times, the aromatic azolium methylide is three orders of magnitude more reactive than its 4,5-dihydro analogue.
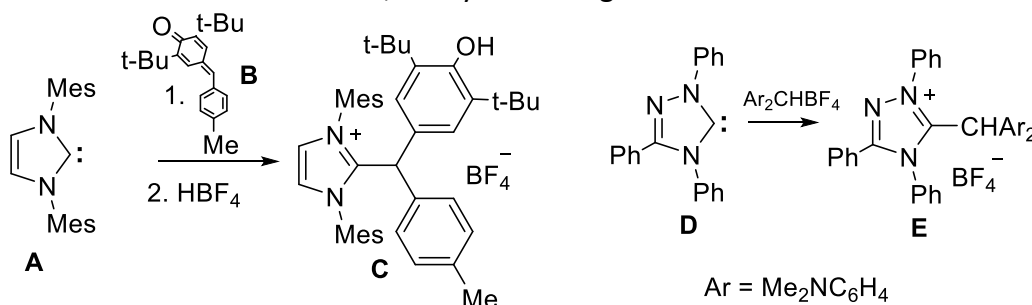
Scheme 81. Alkylation of carbenes with quinoids and carbenium salts.

In the case of the 4-nitro-substituted azolium phenylmethylide, the difference in reactivity was maintained (by approximately two orders of magnitude); moreover, the reactivity of the 1,3,4-triphenyl-1,2,4-triazolium phenylmethylide is almost an order of magnitude higher than that for the 4,5-dihydroimidazolium phenylmethylide. In our opinion, this effect can be explained by the stronger stabilization of the ylide state in the aromatic structures than that in their non-aromatic analogues.

The alkylation of carbenes **82A** has been carried out using activated unsaturated ketones, *e.g.*, tetrakis(trifluoromethyl)cyclopentanone (Scheme 82). Two types of products were obtained, after bond formation at either a carbon atom (**82B**) or the oxygen atom of the ketone (**82C**), thereby forming zwitterionic complexes.[339] In the case of the dimesityl and Dipp derivatives **82A1** and **82A2** only products with the carbon product **82B1,2** were observed. For the more sterically shielded carbene **82A3**, the trifluoromethyl group partly migrated to the 4-position of the cyclopentadiene ring thus forming the stable derivative **82D3** along with the O-connected zwitterionic compound **82C3**.
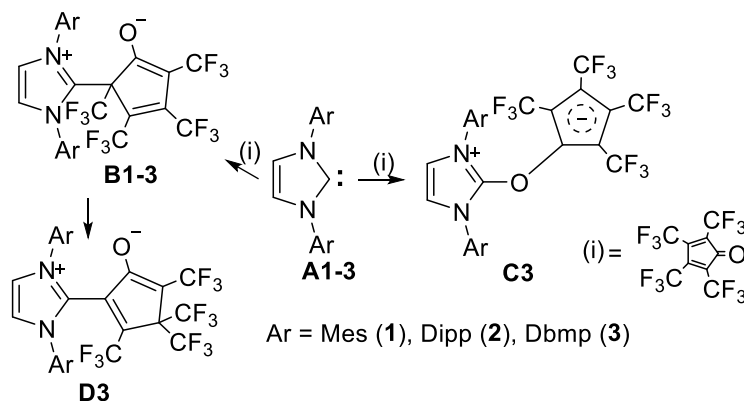
Scheme 82. Additions of tetrakis(trifluoromethyl)cyclopentanone to imidazol-2-ylidenes.

The first example of the arylation of an imidazol-2-ylidene was reported by Kuhn *et al.*[340] These authors carried out the reaction with pentafluoropyridine and obtained the salt product after substitution at the 4-position of the pyridine nucleus. The arylations of carbenes with less active aryl halides were easily carried out using palladium(0) complexes as catalysts (Scheme 83).[341] The resulting 2-aryl substituted salts **83B** have been used to prepare sterically shielded complexes of mesoionic carbenes **83C**.
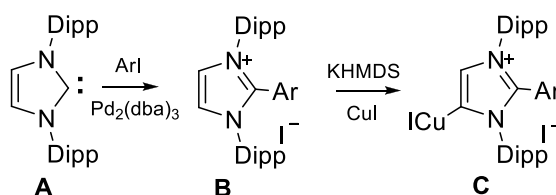
Scheme 83. Catalytic arylation of imidazol-2-ylidenes.

4.4. Reactions with activated multiple bonds
4.4.1. Reactions with olefins. Nucleophilic heteroaromatic carbenes of the azole series, thanks to their electron donating nature, do not react with non-activated olefins such as cyclohexene (effective traps of electrophilic carbenes). However, it has been reported that the benzothiazol-2-ylidenes do form adducts with substrates containing electron deficient multiple bonds **84A** (Scheme 84).[342]

R = Mes, R' = H; R = i-Pr, R' = Me
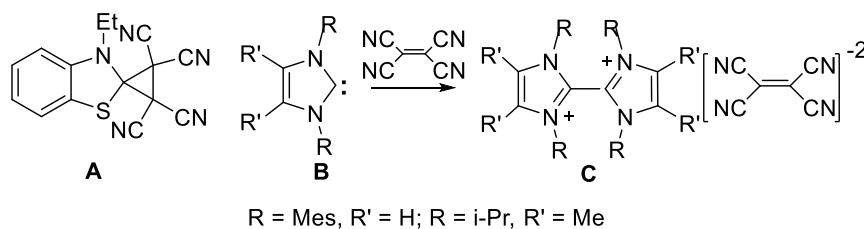
Scheme 84. Carbene adduct **A** and reaction of imidazol-2-ylidenes with tetracyanoethylene.

Recently, transformations of this type have been studied for the imidazol-2-ylidenes **84B** (R = iPr, Mes).[343] In this case the transfer of two electrons (one electron from each of the carbene molecules) to an electron acceptor were carried out thereby forming the bis-salts **84C**. Although the authors (JACC) invoked a possible

radical cation intermediate, recent results clearly show that this cation is not involved,[344] The reactions of NHCs with TCNE gave a variety of cyclized products that were isolated and characterized, including X-ray crystal structures. Formation of **84C** was probably due to hydrolysis although this needs to be reinvestigated.

Carbene adducts with multiple bonds are only obtained if the electrophile is sufficiently strong, contains electron withdrawing substituents and competitive with carbene, otherwise carbene can form the self-condensation products.

In early work, W.M. Jones *et al*. observed the *in situ* transformation of cyclopropenylidene **85B** (Scheme 85) with fumaric esters, thereby forming the corresponding cyclopropenylidene succinic esters **85D**.[345]
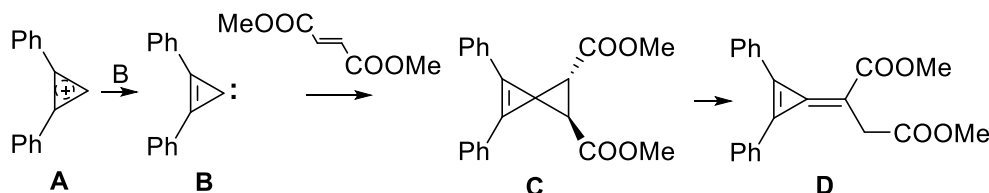
Scheme 85. *In situ* reaction of 2,3-diphenylcyclopropenylidene **B** with fumaric esters.

Enders *et al*. obtained several transformation products of 1,2,4-triazol-5-ylidenes **86A** with maleic and fumaric esters, acrylonitrile, nitrostyrene and maleimides (*N*-Me, Bu, Ph) (Scheme 86).[327] According to the authors, the first step in the reaction involves a hypothetical spirocyclic compound **86B** that is formed and subsequently converted into the carbanion **86C**. Finally, a 1,2-*H* shift of the proton generates the respective azolinylidene substituted alkanes **86D**.

R, R' = COOMe (**1**), R, R' = CONR"CO, R" = Me (**2**), R" = Bu (**3**), R" = Ph (**4**);
R = H, R' = C$_6$H$_4$NO$_2$-*p* (**5**); R = H, R' = COOMe (**6**).
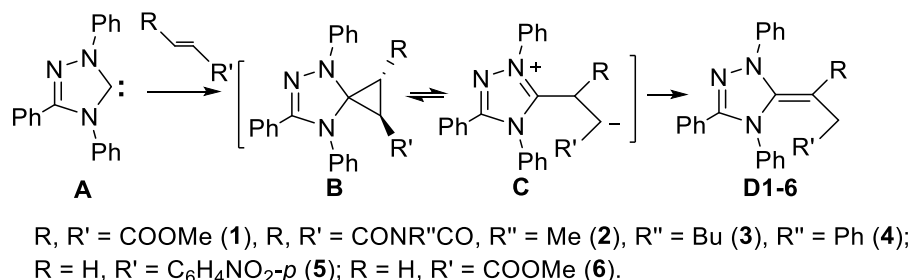
Scheme 86. Reaction of 1,3,4-triphenyl-1,2,4-triazol-5-ylidene with activated olefins.

The results of the reactions of N-phenylmaleimide with two carbenes, namely 1,3-di-(1-adamantyl) benzimidazol-2-ylidene **20E** and 1-adamantyl-3,4-di(4-bromophenyl)-1,2,4-triazol-5-ylidene **42D3** have been compared.[346] The first compound reacts to give predominantly the oligomeric structure, while the second one undergoes addition and a proton shift to give a product of the type **86D**. The cause of such a change in the latter case may be the larger contribution of the cyclopropane structure **86B** in the equilibrium **86B** ⇌ **86C**. This, in turn, is likely to be connected with the larger electron deficiency of the triazole ring compared to that of benzimidazole. Decreasing the carbanion **86C** content in the mixture tends to reduce the possibility of the chain growth by the addition of new maleimide molecules and, consequently, causes the transformation of the anion **86C** to the olefin **86D**.

It is noteworthy that, in contrast to the three-membered heterocyclic adducts which cannot be isolated, the phosphanylsilylcarbenes form stable derivatives of cyclopropanes.[347] This is apparently due to the more pronounced electrophilic nature of the carbene.

Carbanion formation in a chain reaction is also confirmed by dimer formation, which in turn is a consequence of the nucleophilic attack of the carbanion on a second olefin molecule. Thus, carbene initiated growth of the alkane chain is possible in the reaction products. This was confirmed by Matsuoka *et al.*,[348,349] who studied a reaction which underwent an unusual catalytic dimerization (tail-to-tail) upon heating methyl methacrylate **87A** (Scheme 87). Related olefins were also activated by electron withdrawing groups in the presence of carbenes, e.g., **86A** (10 mol%).
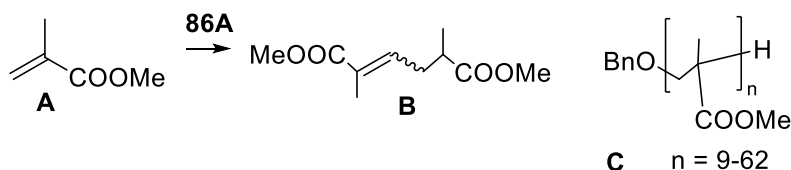
Scheme 87. Unusual carbene catalyzed dimerization (tail-to-tail) of methyl methacrylate.

The direction of the reaction differs from that of the known Rauhut-Courier reaction (head to tail) which is attributable to the nucleophilic properties of the olefinic carbon atom adjacent to the R-intermediate of type **86C**. Further attack on a second olefin molecule forms the dimeric olefin **87B**.

In the presence of carbenes (10 mol%) and alcohols in dimethylformamide, acrylates are capable of polymerizing under mild conditions (at room temperature) to form **87C**.[350] Previously, it had been shown that alcohols could add to activated olefins without polymerization.[351] When the ratio of carbene to methyl methacrylate is 1:2, two molecules of the substrate join and the cyclization to the zwitterion **88F** occurs via the intermediates **88B-E** (Scheme 88).[352]

R = i-Pr, t-Bu
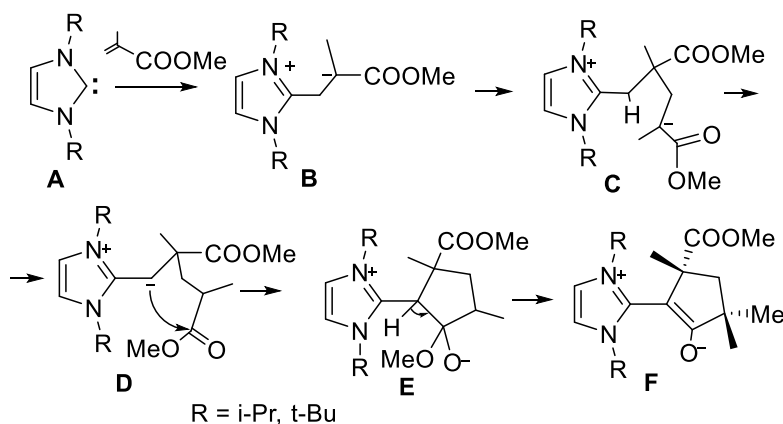
Scheme 88. Cycloaddition of methyl methacrylate with imidazol-2-ylidenes.

4.4.2. Reactions with acetylenes. The transformations of heteroaromatic carbenes with acetylene derivatives also require activation of the triple bond by electron withdrawing substituents. The usual cycloaddition to the ethyne bond is observed, via a characteristic transcarbenation reaction with terminal transfer of the carbene center in the intermediate. Subsequent stabilization occurs by intramolecular cyclization or secondary addition of the respective electrophilic reagent in the reaction mixture (e.g., **89B**, see also refs 7,32) (Scheme 89).
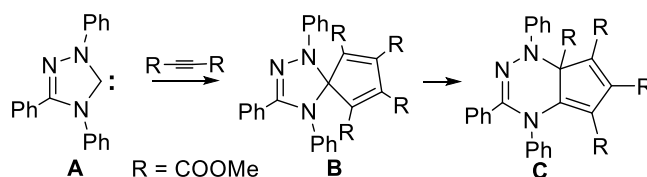
Scheme 89. Cycloaddition of 1,3,4-triphenyl-1,2,4-triazol-5-ylidenes with an activated acetylene.

The reactions of stable 1,2,4-triazol-5-ylidenes **89A** with acetylenedicarboxylate esters[327] also begin by cycloaddition of the reagent and formation of the spiro-adducts **89B** followed by their rearrangement upon heating to form the fused 1,2,4-triazine derivatives **89C**.

Carbenes with different levels of steric shielding revealed unusual behavior with respect to their reactions with dimesitylboryl acetylene **90A** (Scheme 90).[353] If 1,3-dimethylimidazol-2-ylidene (IMe) forms the complexed borane, the zwitterionic product **90B** as a result of the reaction at the boron centre. The dimesityl substituted carbene reacts at the terminal carbon atom of the acetylene to form a new bora-allene zwitterion **90C**. However, in the case of the Dipp-substituted imidazol-2-ylidenes (IPr), cyclization is observed along with insertion of a central nucleophilic carbon of the bora-allene into the C-H bond of one of the borane mesityl groups thereby forming the boracyclic derivative **90D**.
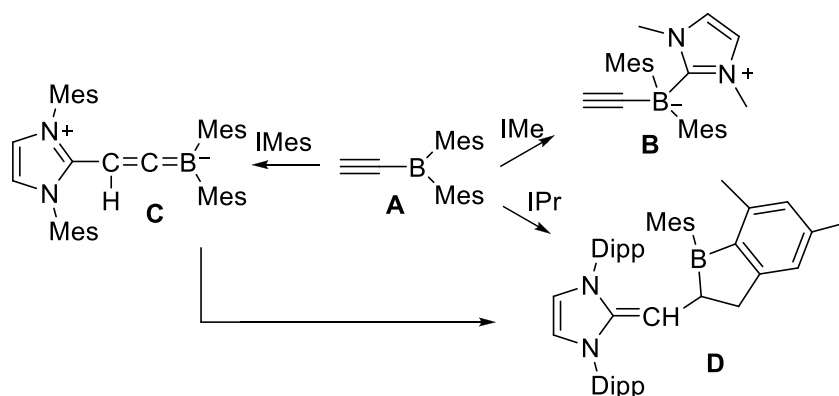
Scheme 90. Addition of dimesitylborylacetylene to imidazol-2-ylidenes.

4.4.3. Reactions with allenes and fullerenes. The highly electrophilic allene **91A** reacts readily with the carbene **91B** at −78 °C to form the adduct **91C** (Scheme 91).[354] Due to the conjugation in the fluorene fragment, the electron transfer is carried out from the carbene to the aromatic ring, and the resulting polar system is blue in color. However, with the Dipp-substituted carbene this reaction is not observed due to the extremely high steric hindrances that are encountered on approach to the reaction center.

In the presence of diphenyl disulfide, the reaction does proceed with the participation of the disulfide to form the more complicated salt system **92A**. Unlike the allene **92A**, fullerene C_{60} reacts with the Dipp-substituted carbene IPr in *o*-dichlorobenzene at room temperature thereby forming an adduct with a C-C single bond (1.502 Å) (Scheme 92).[355] Furthermore, a charge transfer takes place in the molecule, from the carbene to the fullerene, and hence the structure of the molecule is zwitterionic. Rapid rotation of the fullerene fragment occurs around the imidazolium stator (around the C-C bond) even in the solid state.[356]

Compounds of the type **91C**, **92B** are typically FLP-adducts and are promising catalysts for reduction processes.[357]
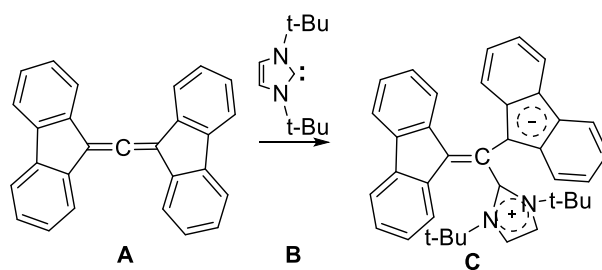
Scheme 91. Addition of 1,3-di-*tert*-butylimidazol-2-ylidene to an allene.
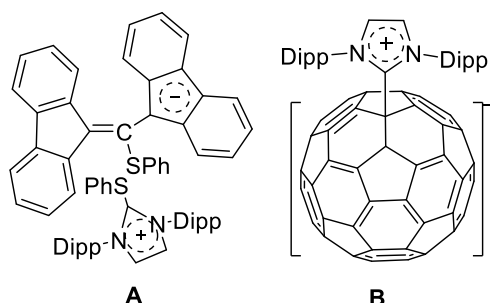
Scheme 92. Adducts of Dipp-substituted imidazol-2-ylidene with allenes (in the presence of diphenyl disulfide) and fullerene.

4.4.4. Reactions with CX$_2$ (X = O, S). It has long been known that carbenes add CS$_2$,[7] as was first shown for an individual compound by Enders.[168] The reaction of carbene **93A** with CO$_2$ was carried out by Kuhn *et al*., forming the adduct **93B** (Scheme 93).[358] In both cases, zwitterionic compounds were obtained. Subsequently, CO$_2$ complexation by carbenes has been the subject of several studies.[359-361] The *in situ* methylation of 1-methylimidazole with dimethyl carbonate (DMC) leads directly to the imidazolium-2-carboxylate **93B** (R = Me).[362] The imidazole is first *N*-alkylated by DMC. The acidic hydrogen of the resulting cation is abstracted by the methyl carbonate anion, leading to the heterocarbene and HOC(O)OMe which is unstable and breaks down to MeOH and CO$_2$. Nucleophilic attack on CO$_2$ by the carbene gives the observed product. Given the reversibility of the addition, the reaction deserves attention as a way of separating CO$_2$ from the air (for imidazol-2-ylidenes this proceeds efficiently even in the solid state).[363]

Subsequently, it has been shown that instead of using the carbene, its 4-lithium derivative **93C** can be selectively directed to undergo carboxylation at the 4-position of the nucleus to give the carbene salt **93D**.[364] As expected, reaction at both centers is not observed due to passivation of the nucleus by the carboxyl group. Treatment of the lithium salts **93D** with water afforded the zwitterions **93E**.
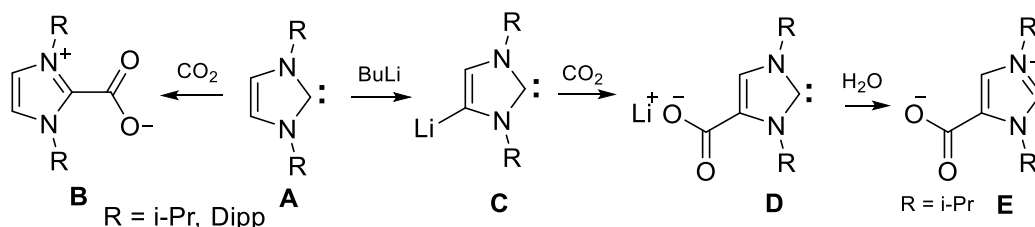
Scheme 93. Carboxylation of imidazol-2-ylidenes with CO$_2$.

4.4.5. Reactions with azides. Organic azides, as well as diazo compounds, as stabilized forms of nitrenes exhibit predominantly electrophilic properties. Their reactions with stable nucleophilic carbenes have predictably led to addition products; the imidazol-2-ylidenes **94A** react with azides to give the corresponding triazenes **94B** in high yields (Scheme 94).[365]

R = Mes, i-Pr, Me; R' = Ph, Bn,
Alk, Ad, PhCO, Ts
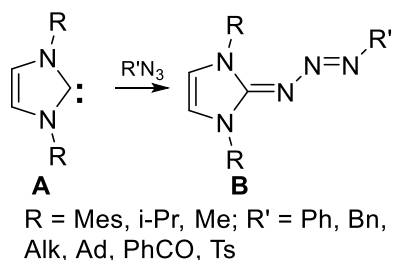
Scheme 94. Addition of imidazol-2-ylidenes with alkyl azides.

Similar conjugated compounds have been prepared from a series of benzimidazoles. These compounds contain donating substituents on the azole nucleus and accepting substituents on the aromatic nucleus of the azide **95A1-13** (Scheme 95).[366] Thus, electron transfer is carried out in the resulting triazenes, from a donor to an acceptor moiety along the conjugated chain in the products **95B1-13**. The yields are close to quantitative.

A1-13　Ar = C$_6$H$_4$R''-*p*　**B1-13**
A, B: **1-9** R = t-Bu; **1** R' = H, R'' = H; **2** R' =H, R'' = OMe; **3** R' = H, R'' = NO$_2$;
4 R' = OMe, R'' = H; **5** R' = OMe, R'' = OMe; **6** R' = OMe, R'' = NO$_2$;
7 R' = F, R'' = H; **8** R' = F, R'' = OMe; **9** R' = F, R'' = NO$_2$; **10-13** R = Me;
10 R' = H, R'' = H; **11** R' = H, R'' = NO$_2$; **12** R' = OMe, R'' = H;
13 R' = OMe, R'' = NO$_2$.
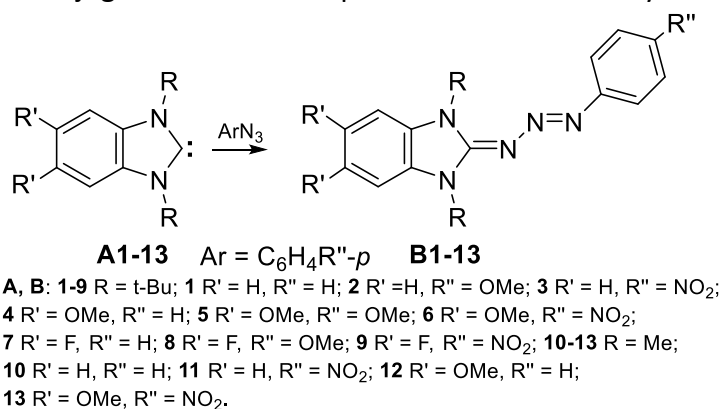
Scheme 95. Addition of benzimidazol-2-ylidenes with aryl azides.

When heated in DMSO or toluene, the triazenes **96A** undergo decomposition into nitrogen and the corresponding imines **96B** (Scheme 96). These can be considered as adducts of carbenes and the appropriate nitrenes.
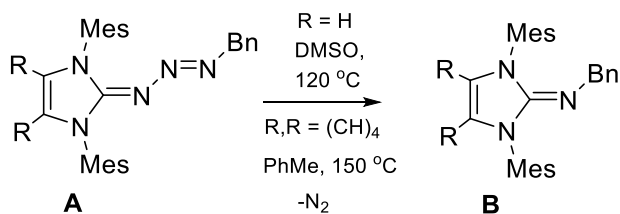
Scheme 96. Decomposition of carbene-azide adducts.

4.4.6. Reactions with diazoalkanes. It has been found that the reaction of 1,3-dimesitylimidazol-2-ylidene with 9-diazofluorene leads to the conjugated azine **97A**.[367] Analogues with donor and acceptor moieties on the molecule have also been obtained.[369] The azine fragment, depending on its substituents, can act as a conductor or breaker of the conjugation.[369] Diphenylmethylenetriazolylidenazine **97C** was prepared from the triazolylidene **97B** and diphenyldiazomethane (Scheme 97).[196]

A similar reaction was carried out for the related biscarbenes and produced a similar result (**97D**).[216] Note that decomposition of the diazo-compound, followed by addition of the intermediate diphenylcarbene to the heteroaromatic carbene, does not take place. This is due to the high stability of the diazo compound under the reaction conditions and the high reactivity of the carbene.

B,C Ar = C_6H_4Br-*p*; **D** Ar = Ph
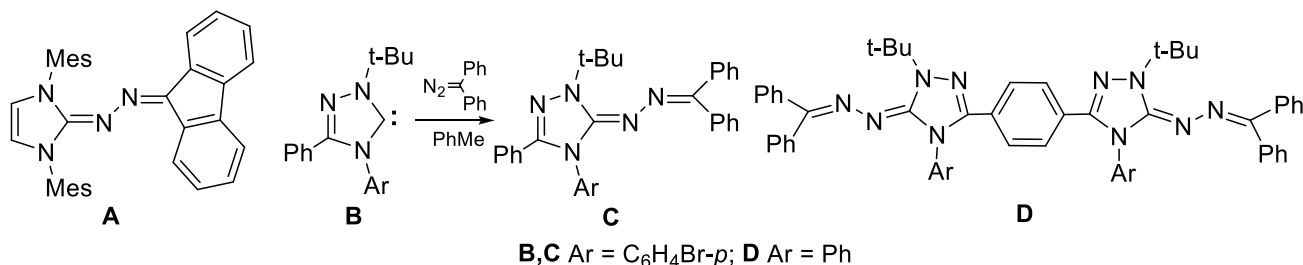
Scheme 97. Addition of azolylidenes with diazo compounds.

4.4.7. Reactions with N₂O and NO. Nitrous oxide N_2O is a polar compound and a mild oxidant. It can be viewed as a stable form of a nitrenium zwitterion. Being a strong electrophile it reacts readily with the carbenes **98A** to form the zwitterionic compounds **98B** (Scheme 98).[370]

Upon heating in toluene the adduct **98B** (Mes) decomposes to form the corresponding imidazolone **98C** and nitrogen, as a result, the oxidizing action of the reagent (N_2O) is carried out. The activation of N_2O by a carbene leads to a substantial change in its properties. For example, with electrophiles, the adduct **98B** reacts at the oxygen atom, and insertion of a nickel compound into the N-N bond has also been observed.[371–373]

A, B, C Ar = Mes; **D** R = Mes, Dipp; **E** R = R' = Me, R" = i-Pr (**1**);
R = Mes, R' = H, R" = Tol (**2**), R = Dipp, R' = H, R" = Tol (**3**)
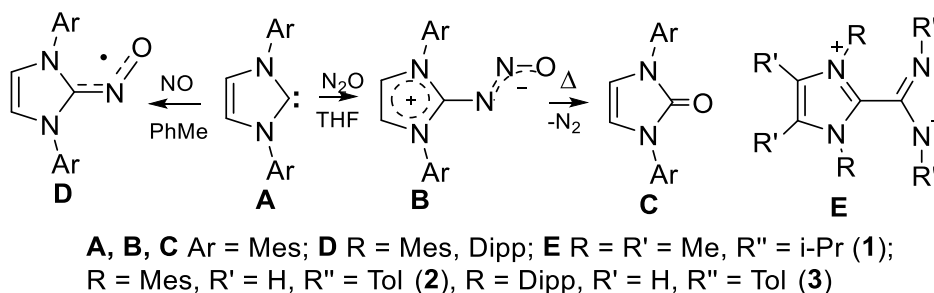
Scheme 98. Reactions of imidazol-2-ylidenes with N_2O and NO.

In contrast, the reaction of imidazol-2-ylidenes with NO gives the stable radical **98D**.[374] Thermal decomposition of the radical leads to imidazolones of the type **98C** and the initial carbene **98A**.

4.4.8. Reactions with carbodiimides. The zwitterionic adduct **98D1** was obtained from the reaction of 1,3-diisopropylimidazol-2-ylidene with diisopropylcarbodiimide.[375] The analogous zwitterions **98D2,3** were synthesized from ditolylcarbodiimide at room temperature.[301] This reaction is one step in the more complicated decomposition process involving 1,3-ditolyl-4,5-dihydroimidazol-2-ylidene, which proceeds upon heating at 110 °C (Scheme 66).

Carbenes of the 1,2,4-triazole series also react with a variety of carbodiimides, and the nature of the carbodiimide significantly influences the reaction pathway.[196] As was shown above, in the tandem autotransformation of carbenes, interaction with alkylarylcarbodiimides forms amidinotriazoles. This reaction occurs not only in the tandem transformation of stable 1,2,4-triazol-5-ylidenes (the *in situ* reaction), but also with previously isolated *tert*-butylarylcarbodiimides. The reaction results in the formation of amidinotriazoles **63C1,2** in 47–50% yields.

In the reaction with diphenylcarbodiimide **99B**, the formation of the spiro-compound **99D** was observed (Scheme 99). The process likely proceeds via the zwitterionic intermediate **99C**, an intermediate similar to that observed in the tandem transformation of **63C**. In the next step, a second molecule of carbodiimide **99B** reacts rapidly at the nitrogen atom of compound **99C**, thereby forming the triazolo-spiro-imidazolidine **99D**. This type of transformation is a well known interaction of carbenes with isocyanates and isothiocyanates.[7,169,327] However, in the case of carbodiimides similar transformations had not been observed earlier.

The reactions with aliphatic carbodiimides are slower than those with alkylarylcarbodiimides. For example, the reaction of carbene **99A** with dicyclohexylcarbodiimide (DCC) was not observed at temperatures below 100 °C. However, the more nucleophilic imidazol-2-ylidenes do react with the related diisopropylcarbodiimide, which results in the formation of the stable zwitterionic compounds **98D**.[358]
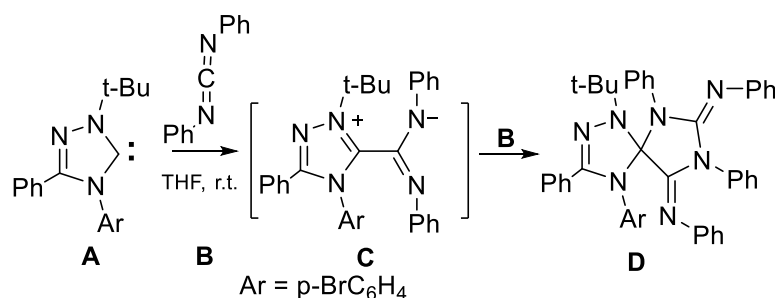
Scheme 99. Cycloaddition of 1-alkyl-3,4-diaryl-1,2,4-triazol-5-ylidenes to diphenylcarbodiimide.

The reactivities of carbenes with carbodiimides can be explained by the electronic influence of the substituents of the carbodiimide molecule on its central carbon atom. According to DFT calculations (B3LYP5/3-21G/RHF), the positive charge on the central carbon atom in the series diphenylcarbodiimide **100A**, *tert*-butylphenylcarbodiimide **100B**, and dicyclohexylcarbodiimide **100C** decreases in the order: 0.846, 0.805 and 0.783 (Scheme 100). A similar comment can be made about the chemical hardnesses of these molecules: (η = 6.45, 6.12, 5.73 eV, respectively).

In the case of diphenylcarbodiimide, the electron withdrawing phenyl substituents significantly enhance the electrophilicity of the molecule. This makes it possible not only to react quickly with the carbene molecule, but also to interact with the zwitterionic compound (**99C**) eventually forming the spiro-adduct **99D**.

tert-Butylphenylcarbodiimide is less electrophilic, hence only one molecule of the carbodiimide reacts with the carbene. The electrophilicity of dicyclohexylcarbodiimide is the smallest calculated and reaction with the carbene is not observed even under forcing conditions (100 °C).

The adducts of carbenes and azolides, such as phosphabenzimidazolide **100D**, which serve as active carbenoids,[376] participate in a similar reaction with di-*tert*-butylcarbodiimide.
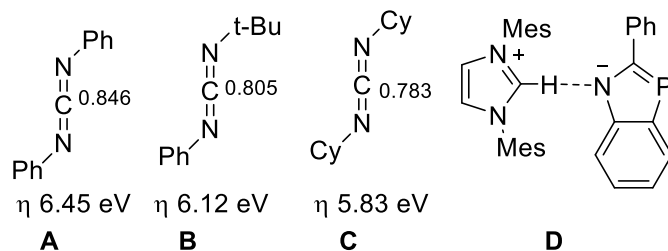
Scheme 100. Calculated carbon charges and chemical hardnesses for carbodiimides and a carbene-phosphazole adduct.

4.5. Carbenes in the synthesis of zwitterionic and ionic compounds

Since they have both basic and nucleophilic properties, azolylidenes are capable of forming polarized products (zwitterionic or ionic compounds) with electrophiles, due to a shift of the electron density (electron transfer) from the carbene to the electrophilic part of the molecule or the breakaway of an acidic proton(s) by the carbene.

4.5.1. Reactions with esters. *Interaction with a malonic ester (a carbene version of the Claisen reaction).* Given the presence of α-protons in the ester molecule, insertion reactions into the C-H bond of the substrate might be expected. However, it was found that the stable carbenes **101A** reacted instead with an ester function of the malonic substrate thereby forming the heterocyclic zwitterionic compounds **101C** (Scheme 101).[197] Removal of the alcohol, formed during the reaction, by means of a nitrogen gas flow, promoted product formation.

Initially the carbene nucleophilically attacks the ester carbonyl group to form the zwitterionic intermediate **101B**. This is stabilized by removal of the alcohol molecule and subsequently forms the anion-conjugated zwitterionic product **101C**. The observed reaction is a carbene version of the Claisen reaction (leading to the condensation of two carbon compounds with the participation of an ester group). As in the traditional Claisen reaction, the carbene can be regarded as being analogous to an anionic methylene group that has been formed by deprotonation of the appropriate azolium salt.

A, C Ar =Ph, Ar' = p-BrC$_6$H$_4$ (**1**); Ar = Ar' = Ph (**2**);
Ar =Ph, Ar' = p-FC$_6$H$_4$ (**3**); Ar = o-ClC$_6$H$_4$, Ar' = p-FC$_6$H$_4$ (**4**)
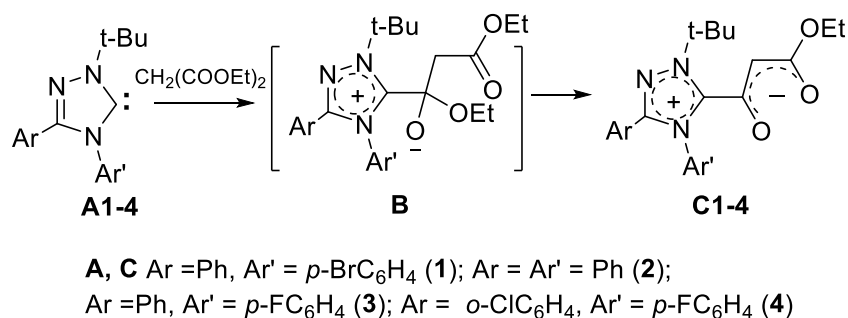
Scheme 101. Carbene version of the Claisen reaction with a malonic ester.

Deesterification reactions. In the absence of α-protons, esters react in a different fashion. Thus, when carbene **102A** is heated with methyl benzoate in toluene solution, deprotonation of the methyl ester group occurs to form the triazolium benzoate **102C** (deesterification). This is accompanied by the elimination of ethylene (Scheme 102).[218] In contrast to the ester saponification reaction, this transformation takes place in

non-aqueous media. The reaction with diethyl oxalate also proceeds extremely quickly (within a few minutes at room temperature) to form the salt **102D**.
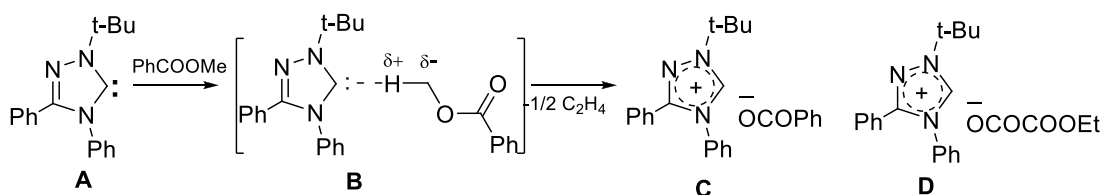
Scheme 102. Deesterification reaction by 1-*tert*-butyl-3,4-diphenyl-1,2,4-triazol-5-ylidene.

The anions of azolium perchlorates can also be replaced using a similar method. Heteroaromatic salts that would otherwise be difficult to prepare can easily be isolated.[32]
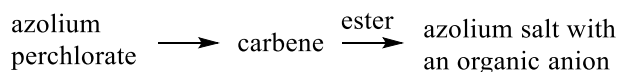
Reactions with acetoacetic ester, 1,3-dimethylbarbituric acid and malononitrile. Reaction of the carbene **103A** with the acetoacetic ester (pKa 11), 1,3-dimethylbarbituric acid (pKa 4.68) and malononitrile (pKa 11-12) produces the organic salts **103A1-3** as a result of deprotonation of the substrates by the carbene (Scheme 103). The salt **103A1** was isolated as a toluene solvate.[197]
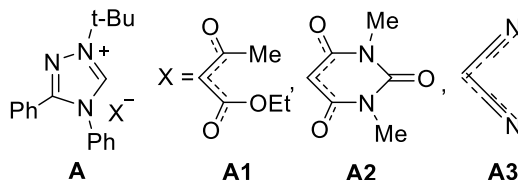
Scheme 103. Products of deprotonation of C-H acids by 1-tert-butyl-3,4-diphenyl-1,2,4-triazol-5-ylidene.

This is in contrast to the results of the interaction of dithiolenylidene dimers with malononitrile.[377] Singlet nucleophilic carbenes of the type **102A** are capable of deprotonating the above substrates to form the salts **103A**.

Some preliminary conclusions can be drawn on the basis of the observed transformation routes. These are helpful in predicting the outcomes of the reactions of carbenes with C-H acids. For example, 1,2,4-triazol-5-ylidenes give the corresponding salts when reacted with C-H acids having a pK_a less than 12 (e.g., 1,3-dimethylbarbituric acid (pK_a 4.68), malononitrile (pK_a 9) and the acetoacetic ester (pK_a 11)). The malonic ester (pK_a 12–13) also generated the corresponding salts when reacted with carbenes. Upon heating these undergo rearrangements involving the ester groups to afford zwitterionic compounds.[218] Insertion of the carbene into a C-H bond of the substrate proceeds with the less acidic acetonitrile (pK_a 25).

It should be emphasized that the nature of the transformation products greatly depends on the type and properties of the particular carbene used. For example, 1,3-di(1-adamantyl)imidazol-2-ylidene, some aromatic derivatives of the 1,2,4-triazol-5-ylidenes and conjugated biscarbenes of the type **9A** do not react with acetonitrile, at least under mild conditions. On the other hand, 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene is easily inserted into the C-H bonds of some of the compounds. Generally speaking, the more basic carbenes undergo deprotonation more easily than do their less basic analogues.

4.5.2. Formation of zwitterionic compounds in reactions with other multiple bonds and cyclic sulfoesters.

To obtain new types of zwitterionic heterocyclic compounds, it is worth focussing on the reactions of carbenes with some activated multiple bonds and cyclic ester groups. The zwitterionic compound **104B** was isolated from the reaction of the carbene **104A1** with benzylidenemalononitrile (Scheme 104). The reaction of carbenes **104A1,2** with propanesultone proceeds, with ring opening of the latter, thereby forming the zwitterionic compounds **104C1,2**.[218]
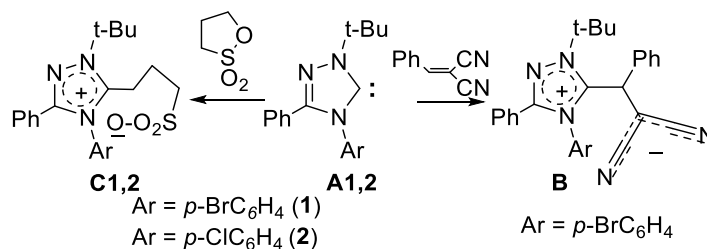
Scheme 104. Synthesis of zwitterionic compounds from 1,2,4-triazol-5-ylidenes and electrophiles.

Treatment of the *o*-dicarbethoxyvinyl substituted *N*-phenylimidazolium salt **105A** with silver oxide or carbonate resulted in a similar *in situ* reaction. Proton migration is followed by oxidation and formation of the fused ring compound **105B** (Scheme 105).[378]
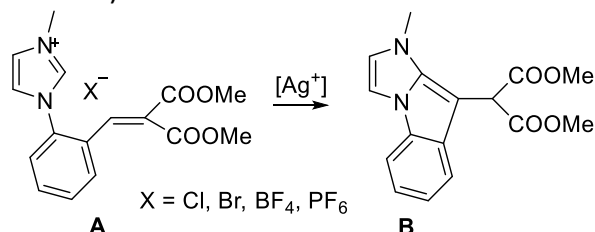
Scheme 105. Carbenoid cycloaddition in an olefinic derivative of imidazolium salts.

The reaction of stable carbenes with methylphenylketene resulted in the generation of new zwitterionic compounds, namely the azolium enolates **106B** as a mixture of two isomers (Scheme 106).[379] The latter compounds are ambident in terms of their reactivities. For example, they react with carbocations to form both azoliumketones **106C** and azoliumalkenes **106D**.
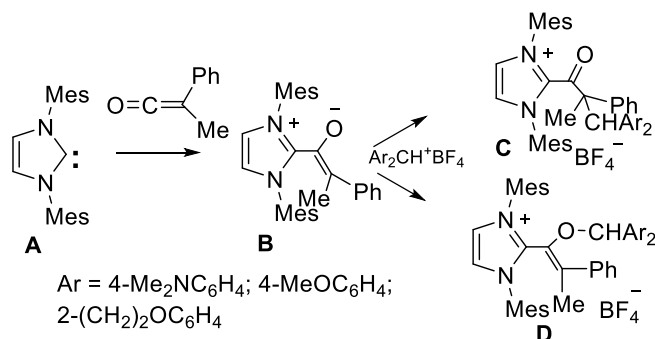
Scheme 106. Addition of methylphenylketene to imidazol-2-ylidenes.

Carbene reactions with isocyanates and isothiocyanates have been well studied for *in situ* processes and result in spirocyclic products of the type **107E** (with isocyanates) or zwitterionic compounds **107B** (with isothiocyanates)[7] (Scheme 107). For isolated carbenes the same reactivity was confirmed in the case of 1,3,4-triphenyl-1,2,4-triazol-5-ylidene.[327] Later it was found that, due to the reversible nature of the reaction of 1,3-dimesityl- or 1,3-bis-Dipp-substituted imidazol-2-ylidenes with phenylisocyanate, catalytic trimerization of the latter forms 1,3,5-triphenylisocyanuric acid **107D**.[380,381]

The reversibility of the reaction was confirmed by the transformation of zwitterion **107B** with sulfur, which resulted in the formation of the imidazole-2-thione **107C**. Similarly, carbenes are known to cause polymerization of lactides and other related electrophiles.[21,381]

Recently, the possibility of carrying out three-component reactions involving carbenes, methyl methacrylate and isocyanates or isothiocyanates has been explored.[382] However, these reactions often take place with ambiguous mechanisms.
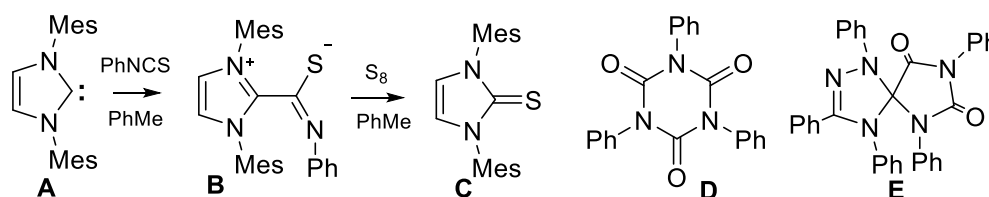
Scheme 107. Addition of isocyanates and isothiocyanates to 1,3-dimesitylimidazol-2-ylidene.

In this section, some of the major types of heteroaromatic carbene transformations have been discussed. These include autotransformations, from a simple proton to group migrations and more complicated reconstructions of the molecule. Induced tandem autotransformations of 1,2,4-triazol-5-ylidenes with a labile alkyl group at the 1-position result in the formation of amidinotriazoles. The reactions with compounds that contain mobile protons often result in the insertion of a carbene into an X-H or C-H bond of the substrate molecule. In some cases, H-bonded complexes are formed, and in the case of compounds that contain multiple bonds (acetylenes, azides, carbodiimides) new heterocyclic compounds have been obtained. From the standpoint of the preparation of zwitterionic and ionic compounds, the utility of carbenes is evident from the examples of ester reactions. Among these, there is a carbene version of the Claisen reaction (the interaction of carbenes with malonic esters), and the various reactions with cyclic esters and arylidene-malononitrile.

4.6. Reactions with non-metals and some nucleophiles

The interactions of carbenes with active non-metals (halogens, oxygen, sulfur) have been well studied by *in situ* processes[7] and subsequently used for transformations of individual carbenes.[9]

Reactions with halogens form either halogenazolium salts or carbene complexes with halogens.[383,384] The structure of a reaction product with iodine proved to be a carbene complex with an extended I-I bond.[383] Chlorination of imidazol-2-ylidenes was carried out using dichloroethane, and the resulting products were identified L Cl$_2$ although the exact structures were not determined.[384] However, the complexes did exhibit chlorinating action, indicative of their containing a reactive Cl-Cl bond. Similar chlorinated complexes from the reaction of 4,5-dichloroimidazol-2-ylidenes and CCl$_4$ were determined to be the 2,4,5-trichloroimidazolium salts.[57]

The reactions of carbenes with chalcogens have resulted in the formation of azolchalcogenones (for a recent report of fused carbenes, see, e.g., reference 385). The oxidation of even relatively stable carbenes

with triplet oxygen occurs rapidly. For example, passing anhydrous oxygen through a THF solution of 1-*tert*-butyl-3-phenyl-4-(*p*-bromophenyl)-1,2,4-triazol-5-ylidene **42D6** causes the oxidation to proceed over an 8 h period (24 h in the case of toluene) at room temperature; the corresponding triazolone is formed. In the case of some carbene complexes of copper(I), the oxidation process is even faster due to the catalytic action of the metal.[386] Even dimethylformamide transfers its oxygen atom to the carbene ligand of the complex under mild conditions.

Singlet oxygen $^1O_2$ can be generated by UV irradiation of triplet $^3O_2$ in the presence of *meso*-tetraphenyl-porphyrin. The interaction of imidazol-2-ylidenes with $^1O_2$ in deuterobenzene results in the formation of two products, namely the diimine **108C** and the imidazolium carboxylate **108D**.[387] Both result from the decomposition of the intermediate peroxide **108B** (Scheme 108).

R = t-Bu
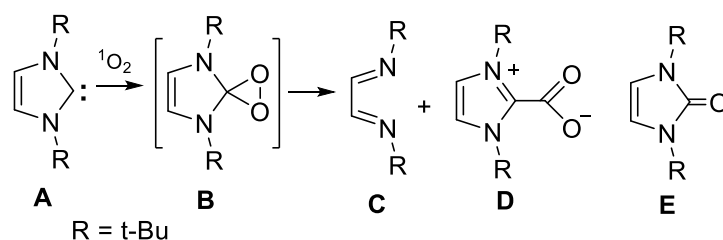
Scheme 108. Oxidation of imidazol-2-ylidenes with singlet oxygen.

The oxidation of the above-mentioned carbene with $^1O_2$ also proceeds easily in the presence of diphenyl sulfoxide. However, diimine formation is significantly suppressed, such that the imidazolone **108E** and diphenyl sulfone become the major products of the reaction.

The interaction of carbene compounds with sulfur, selenium or tellurium normally proceeds readily at room temperature, even in the case of the dimesityl substituted carbenes.[57] The reaction of 1,3-diadamantyl-benzimidazol-2-ylidene with sulfur[104] also results in the formation of an azolethione in high yield. Additionally, a quite labile, deeply colored reaction product was isolated (probably a hypervalent compound of sulfur). The latter was easily oxidized and hydrolyzed thus forming the expected azolethione. In contrast, selenium does not react with the carbene under these conditions; steric hinderence blocks the approach of molecular selenium to the reaction center. These observations may shed light on why the thione yields are sometimes decreased in these reactions; it may be due to an unusual reaction pathway involving hypervalent sulfur compounds.

The reactions of carbenes with chalcogens are sometimes used in organic synthesis. For example, the *in situ* reactions of *N*-substituted imidazoles and benzimidazoles **109A1-3** with epichlorohydrin and sulfur take place via cyclization of the intermediate cations **109C,H** thus forming the thiirane derivatives of azolones **109I** in high yields (Scheme 109).[388] Isolation of the stable *N*-glycidylazolium salts **109C** and the related *N*-glycidylazinium (pyridinium and quinolinium) salts is an argument in favor of the reaction route (a) that involves the salts **109C** and carbenes **109D** (Scheme 109).[388,389] There is a second possible route (b) which proceeds via the intermediate chlorohydrin derivatives **109B,G**.
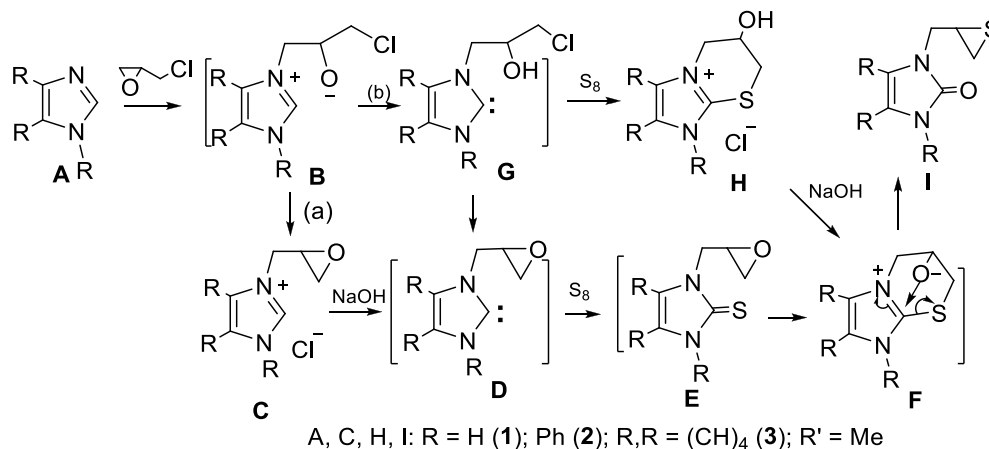
Scheme 109. Carbenic transformation of imidazoles with epichlorohydrine and sulfur.

In contrast to the transformations of halogens and chalcogens, the reactions of nonmetals such as hydrogen and phosphorus have only recently attracted attention. Highly active, non-aromatic carbenes (for example, the pyrrolidin-2-ylidenes reported by Bertrand *et al.*) serve as activators of hydrogen, thus allowing the reduction reaction to run more easily. However, imidazol-2-ylidenes and 1,2,4-triazol-5-ylidenes do not react with hydrogen.

Reactions with white phosphorus proceed more easily. As in the case of the non-aromatic carbenes (the pyrrolidinylidenes of Bertrand *et al.*, or the 4,5-dihydroimidazol-2-ylidenes), the aromatic imidazol-2-ylidenes react with phosphorus to form stabilized phosphorous units, ranging in size from 2 to 12 phosphorus atoms (see, e.g., **110A** [323,390]). The first products are formed by reaction of the carbene with the simple molecule, P_4 **110B**. Heating produces more complicated compounds such as **110C** (Scheme 110).

An adduct of a carbene and PCl_3 has been reduced using potassium graphite KC_8 to give a compound with two phosphorus atoms.[323]

Phosphorus atoms are liable to oxidation with triplet oxygen. Thus, a product with two phosphorus atoms such as RI=P-P=IR (where IR represents the 1,3-R_2-imidazol-2-ylidenes) can be oxidized to the tetraoxide RI=P(O_2)-P(O_2)=IR either with cooling or at room temperature.[391,392]
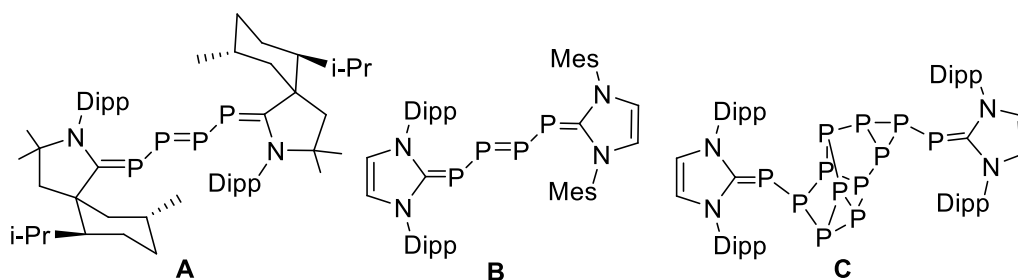
Scheme 110. Adducts of carbenes and phosphorus.

Nucleophiles, such as carbon(II) monoxide and isonitriles, do not react with aromatic nucleophilic carbenes. However, they do react readily with more electrophilic non-aromatic carbenes, even at ambient temperature and pressure.[323,393]

Generally speaking, the outcomes of these reactions are dependent upon thermodynamic factors. For example, if the reaction enthalpies for aromatic carbenes are close to zero or positive, then for the more

electrophilic carbenes, these values are significantly negative. However, the absence of products for the reactions of carbon(II) monoxide with diaminocarbenes (which react readily with isonitriles) cannot be explained by this reasoning. The authors believe that the ketene formed initially undergoes further reaction with the diaminocarbene. However, it has proven impossible to isolate any reaction products.

5. Catalytic Properties of Carbenes and their Complexes with Transition Metals

The favourable catalytic properties of transition metal carbene complexes were reported in the literature long before the first syntheses of stable carbenes.[21,394–396] Catalysis by carbenes had long been known and exploited. However, they were usually generated *in situ* which generally did not produce pure, isolable carbenes.[24] In the case of the thiazol-2-ylidenes and the benzothiazol-2-ylidenes, the formation of carbene dimers resulted in the catalytic effect, and had been utilized, e.g., for benzoin condensation. As a result of the syntheses of individual carbenes (Bertrand, Arduengo *et al.*) new catalysts became available.[21,23,24,26,28-30] It became possible to use the pure carbenes as catalysts and to prepare pure complex compounds for catalysis using individual carbenes.

The present section will focus briefly on some of the well-known catalytic transformations, for which new and unusual properties have been revealed. Their effectiveness as catalysts for possible use in industry will be discussed. The use of pure individual carbenes is of particular importance, since their level of efficiency exceeds those of their *in situ* generated analogues. To evaluate the effectiveness of catalysis, the indices TON (turnover number) and TOF (turnover frequency) have been used in many studies.[21] TON represents the number of cycles of catalytic transformation and is equal to the ratio of the number of moles of the product to the number of moles of the catalyst. Overall, it is a measure of catalyst activity. TOF corresponds to the value of TON for a certain period of time, usually 1 hour (measured in h^{-1}) and is a measure of catalyst performance. It is often convenient to compare the relative efficiency values, RTON (relative TON), taking the lowest value per unit.

5.1. Catalysis by carbenes

The present section focuses on only two types of reactions: 1) the transesterification reaction and 2) the benzoin condensation reaction, for which high catalytic efficiencies were achieved.

5.1.1. The transesterification reaction. The transesterification reaction is an important method of fine organic synthesis, which finds multiple uses in industry. In addition to the synthesis of drugs, this reaction can be utilized for the industrial synthesis of biodiesel fuels. Transesterification reactions can be catalyzed by both acids and bases. However, it is best to use basic catalysis, since this limits the corrosion of equipment in industrial applications.

$$\text{RCOOR' + R''OH} \xrightarrow{\text{cat}} \text{RCOOR'' + R'OH}$$
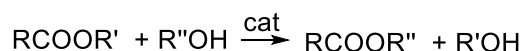
Stable carbenes are highly basic catalysts and have been used to catalyze the reaction of methyl benzoate in an excess of ethanol to form ethyl benzoate.[397,398] The carbene was combined with stoichiometric amounts of the required reagents in the presence of molecular sieves.[399–401] In the first case, catalysis with imidazol-2-ylidenes in the presence of primary alcohols, resulted values for TON and TOF of 17-19 and 1 h^{-1}. In a subsequent set of reactions, the values obtained were 20-60 and 30-220 h^{-1}, respectively. Very efficient

transesterification takes place with vinyl ethers (TON to 200 and TOF to 2300 h^{-1}) but proceeds irreversibly due to the release of acetaldehyde.

Important results were obtained recently for the transesterification of ethyl benzoate in methanol using carbene catalysis.[402,403] The carbenes were added either in a pure individual form (**111A,I**) (Scheme 111) or generated *in situ* via the reaction of potassium alkoxides with organic perchlorate salts (methanol –substrate ratio of 1:9). The catalyst loading in most cases was 0.04 mol%. The study showed that the catalytic efficiency depended greatly on the type of carbene that was used. In the case of the triazolylidenes **111A,B**, the lowest values were obtained (TON 175-255, TOF 44-64 h^{-1}, RTON 1.0-1.5). For benzyl- and methyl-substituted imidazol-2-ylidenes and benzimidazol-2-ylidenes **111C-E**, the TON was almost an order of magnitude higher (TON 1625-1800, TOF 406-450 h^{-1}, RTON 9.3-10.3). The efficiencies of the diaminocarbenes **111F,G** and cycloheptadienylidene **111H** (TON 2100-2250, 525-553 TOF h^{-1}, RTON 12.0-12.9) were even higher, particularly, in the case of the adamantyl derivatives of benzimidazol-2-ylidene and the imidazol-2-ylidenes **111I-K** (TON 2338-2350, TOF 584-588 h^{-1}, RTON 13.3-13.4).

Biscarbenes of the 1,2,4-triazole series **112A** were also less efficient (per nucleus), being similar to their monocarbene analogues. However, they were 1,8 times more effective (Scheme 112) than the monocarbene **111A**. A significant increase in the catalytic efficiency was observed in the case of the bisimidazol-2-ylidenes **112B,C**. Moreover, the system with a xylylene bridge **112C** is almost twice as effective (TON 2175, TOF 544 h^{-1}, RTON 6,2), than that with an aliphatic bridge **112B** (TON 1300, TOF 325 h^{-1}, RTON 3.7). The efficiencies of the polycarbenes with a xylylene bridge **112D,E** (TON 2100-2350, 525-588 TOF h^{-1}, RTON 6.0-6.7) were close to that of the biscarbene **112C**, which also contains the same structural moiety. Overall, however, the simplest polymer with a xylylene bridge **112F** turned out to be the most effective (TON 2350, TOF 588 h^{-1}, RTON 13.4).

A	**B**	**C**	**D**	**E**	**F**
RTON 1.0	RTON 1.5	RTON 9.3	RTON 10.0	RTON 10.3	RTON 12.0
TON 175	TON 255	TON 1625	TON 1750	TON 1800	TON 2100
TOF 44	TOF 64	TOF 406	TOF 438	TOF 450	TOF 525

G	**H**	**I**	**J**	**K**
RTON 12.6	RTON 12.9	RTON 13.3	RTON 13.3	RTON 13.4
TON 2213	TON 2250	TON 2338 (2600)	TON 2338 (3500)	TON 2350 (4300)
TOF 553	TOF 563	TOF 584 (650)	TOF 584 (875)	TOF 588 (1075)
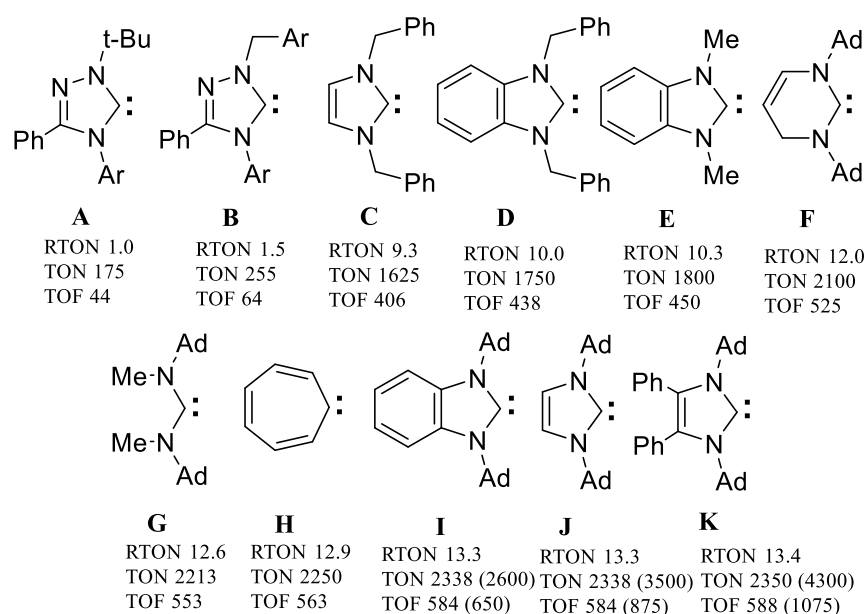
Scheme 111. Catalytic efficiencies of monocarbenes in the transesterification reaction of ethyl benzoate in methanol.

t-Bu, N—N   t-Bu
:N—X—N:

Ph **A** Ph
X = *p*-C$_6$H$_4$

RTON 1.8
TON 725
TOF 156

Me-N N—X—N N-Me

B X = (CH$_2$)$_4$
C X = CH$_2$C$_6$H$_4$CH$_2$-*p*

RTON 3.7   RTON 6.2
TON 1300   TON 2175
TOF 325   TOF 544

[–A-N   N–]$_n$

D A = CH$_2$C$_6$H$_4$CH$_2$-*p*

[–N N—X—N N·A–]$_n$

E A = CH$_2$C$_6$H$_4$CH$_2$-*p*, X = C$_6$H$_4$

[–N N-A–]$_n$

F A = CH$_2$C$_6$H$_4$CH$_2$-*p*
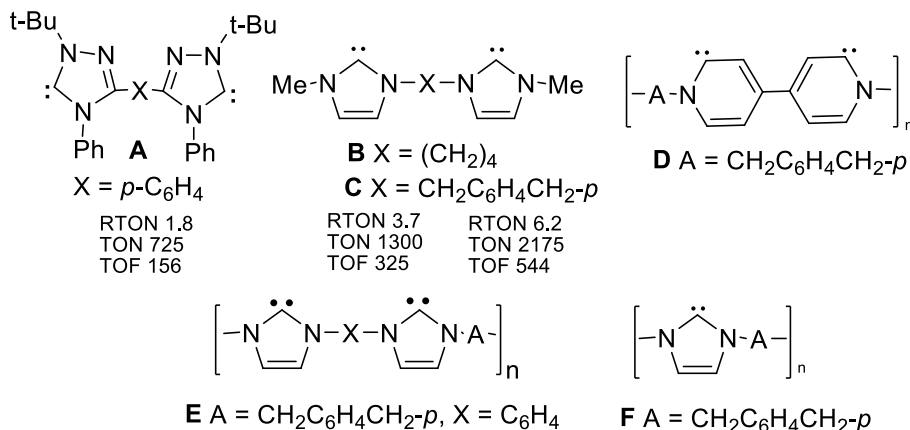
Scheme 112. Catalytic efficiencies of bis- and poly-carbenes in the transesterification reaction of ethyl benzoate in methanol.

The reverse reaction of methyl benzoate in excess ethanol in the presence of the catalyst **112F**, was less favourable thermodynamically (the molar ratio of substrate-ethanol was 1:9, the catalyst loading was 0.04 mol%). The TON reached 168 cycles, which is almost an order of magnitude higher than that for a similar reaction that was studied in the following works.[397,398]

A dilution experiment was carried out with a ratio of substrate to methanol of 1:18 and a catalyst loading of 0.01 mol%. The best catalysts, as shown by the highest efficiencies, were the carbenes **111K** and **112F** (TON 4000-4300). Using the same conditions, the carbenes **111I,J** were significantly inferior (TON 2600 and 3500, respectively). However, the use of the pure carbene **111I** (instead of the *in situ* generated product) resulted in an enhanced effect (TON 6150).

Thus, the following conclusions can be drawn:
1) The most efficient catalysts for the transesterification reaction have adamantyl and aromatic groups (even non-connected with a nucleus as in the case of the xylylenes) (**111F,G,I,J,K**, and **112F**).
2) Individual carbenes are substantially more effective than those generated *in situ* (for carbene **111I** by 2.6 times). The efficiency of catalysis is also dependent on the method used for generation of the carbene.

The efficiency was observed to increase for carbenes generated from the action of alkoxides on organic perchlorate salts. This occurs because the perchlorate anions are almost completely removed from the solution in the form of a poorly soluble potassium perchlorate.

5.1.2. Benzoin condensation. The asymmetric carbene catalysis of this reaction results in high yields and (in some cases) enhanced enantioselectivity of the benzoin derivatives.[21,24] However, the efficiencies of the currently available catalysts are insufficient. Typically, high loadings of the catalyst are used (up to 10 mol%) for this reaction. However, this approach is not appropriate for the synthesis of expensive chiral catalysts and their reaction products.

2 Ar-CHO $\xrightarrow{\text{cat}}$ Ar, Ar
O OH
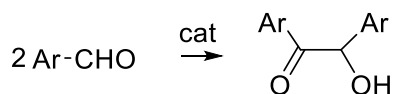
The pure carbene 1,3,4-triphenyl-1,2,4-triazole-5-ylidene **113A** reported by Enders *et al.* has been used as a catalyst in the condensation of 5-(3-trifluoromethylphenyl)furfural in tetrahydrofuran solution. Its carbenoid methoxyazoline form **113B**, and the *in situ* generated 3-benzyl-4-methyl-5-(2-hydroxyethyl)-thiazol-2-ylidene

113C (all at 5 mol%) were also tested. TON indices of 19.2, 17.8 and 17.2, respectively, were obtained (Scheme 113).[404] The reaction of furfural without a solvent was carried out with smaller loadings of Enders' carbene (1 mol%). This reaction resulted in a TON of 78 and a TOF of 156 h^{-1}.
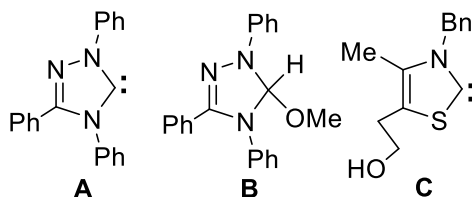
Scheme 113. Efficient catalysts of the benzoin condensation reaction.

The efficiencies of the catalysts **111I,K** generated *in situ* (two of the best for the transesterification reaction) were very moderate for the reaction of furfural (TON 10.8 and 15.4 h^{-1} when loaded at 5 mol%). However, in the case of the individual carbene **111I** the value was significantly higher (TON 62 at a loading of 1 mol%). Using a load of 0.5 mol% of catalyst the achieved TON is maximal for this reaction (120).

A possible reason for the poor catalytic efficiency of carbenes in the benzoin condensation reaction is the hypersensitivity of the carbene catalyst (or their intermediates in the catalytic cycle) to the presence of small amounts of oxygen and moisture. Their presence prevents the regeneration of the catalyst. In the transesterification reaction, the entry of the carbene into the catalytic cycle is carried out in an alcohol protected form (hydrogen carbene complexes with alcohols or alkoxyazolines are less sensitive to these agents) and hence the results are significantly better.

5.2. Catalysis by carbene complexes of transition metals

Complex carbene catalysts were used for the first time in the 1970s. Today, this type of catalysis is now widely utilized (see e.g., the following reviews [21,26,30,395,405,406]). The reaction center in the complex is an electrophilic metal atom. At the same time, the carbene has a significant impact on the state of the former by its strong electron donating effect, and its steric influence. This results in a strengthening of the metal-ligand bond compared to those in, for example, phosphine complexes. The result is a change in the characteristics of the catalyst, such as the strength of its binding to other ligands. A study of the impact of the foregoing factors, including steric influence of the carbene ligand on catalyst efficiency, is in progress. Although many of the mechanisms of the catalytic processes are well known, complete control over the efficiency of such catalysts has not yet been discovered.

Given the preceding information, it is important to consider some empirical observations from two types of reactions: 1) reduction of multiple bonds by alcohols and 2) reductive dehalogenation (hydrodehalogenation) of haloarenes. The influence of the catalyst on these transformations has been studied using the classes of carbene complexes described herein.

5.2.1. Reduction of multiple bonds with alcohols (hydrogen transfer). This reaction involves the reversible interaction of an alcohol with a multiple bond, such as is found in carbonyl compounds, imines and olefins, in order to produce the desired reduction product (alcohol, amine or alkane).[21,405] Generally the reaction takes place in the presence of a base and under catalytic promotion by a metal complex. In this process the base reacts reversibly with the alcohol to form an alkoxide. The alkoxide is the source of a hydride ion that undergoes transfer, thus transforming itself into another carbonyl compound (e.g., to acetone from isopropanol).
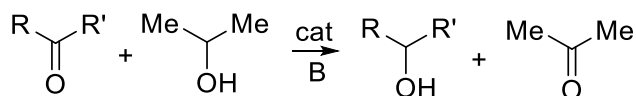
This reaction can be used for fine organic synthesis and, like many catalytic processes, potentially could be a solution for "green chemistry" problems. The reaction is also extremely important for the pharmaceutical industry. However, its utilization in asymmetric reactions has not very effective thus far.[405]

Many carbene complex catalysts have been suggested in the literature. However, the most effective of those studied so far are complexes of rhodium, iridium and ruthenium. The reaction of acetophenone with isopropanol and aldehydes in the presence of KOH proceeds more readily than the same reaction with aromatic ketones. The TON and TOF values achieved with the catalyst **114A** (R = *i*-Pr) were 890-1000 and 220-3000 h^{-1}, respectively (Scheme 114).[407] The reaction of cyclohexanone with the catalyst **114B** can produce TOF values as high as 6000 h^{-1},[408] while for the same reaction with *p*-chloroacetophenone the values can be as high as 11400 h^{-1}.[409] In the reaction of benzophenone with the same catalyst the index is substantially lower (1800 h^{-1}).

Complex **114C** catalyzes the reaction of benzophenone very effectively and achieves the greatest TON value (10580). However, the TOF is reduced to 441 h^{-1}.[410] Moreover, the reaction time is quite long (24 hours at a catalyst loading of 0.006 mol%), and a quantitative yield of the reduction product was not obtained.

Complexes **114A** (TON 4000, TOF to 24000 h^{-1})[411] and **114D** (TON to 3330, TOF to 50000 h^{-1})[412] gave the best results for TOF values. Note, however, that the structure of **114D** is ionic.
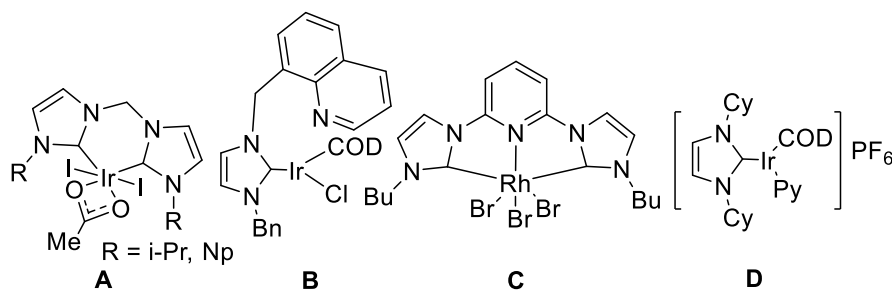
Scheme 114. Carbene complex catalysts for reduction of multiple bonds by alcohols in alkaline medium.

Three new types of transition metal carbene complexes **115A-E** have been reported, all of which display high catalytic effects for the reduction of 4-phenylbenzophenone and benzophenone (Scheme 115).[334] The chelated carbene complex of nickel **115A1** (R = 1-Ad, M = Ni) has shown high catalytic efficiency (TON 4500, TOF to 1500 h^{-1}). However, the value for its palladium analogue **115A2** is significantly higher (TON 7000, TOF of 3500 h^{-1}). A particularly high efficiency was shown by the copper biscarbene complex **115B** (TON to 50000-55000, TOF to 20000-22000 h^{-1}).

The polymeric crown-carbene complex of copper **115C** (M 43800, n_{aver} = 77; TON to 80000-85000, TOF to 28330-32000 h^{-1}), was found to have particularly high TON values. Neither of these systems was sterically shielded. Furthermore, the polymeric complex **115C** has an unusually narrow molecular-weight distribution K_n (M_w / M_n) = 1.03. The cyclic complexes **115D1** (TON to 45000, TOF to 15000 h^{-1}) and **115D2** (TON to 47000, TOF to 15667 h^{-1}) also exhibit efficiency indices that are close to those of **115B**. Note that the monocarbene copper(I) complex **115E** is significantly less efficient (TON 5300, TOF 883 h^{-1}) than the complexes **115B,C**.

The high catalytic effect for the carbene complexes of copper(I) **115B,C** could be due, at least in part, to a high degree of Cu-I ionization, which in turn could facilitate the exchange of halogen with the isopropoxide ion providing a reducing effect.[395]

A1,2

A1 R = 1-Ad, Ar = Ph, M = Ni
A2 R = t-Bu, Ar = Ph, M = Pd

R, R' = (CH)₄ **C**

D1,2

D1 X = CH₂;
D2 X = (CH₂)₃

E
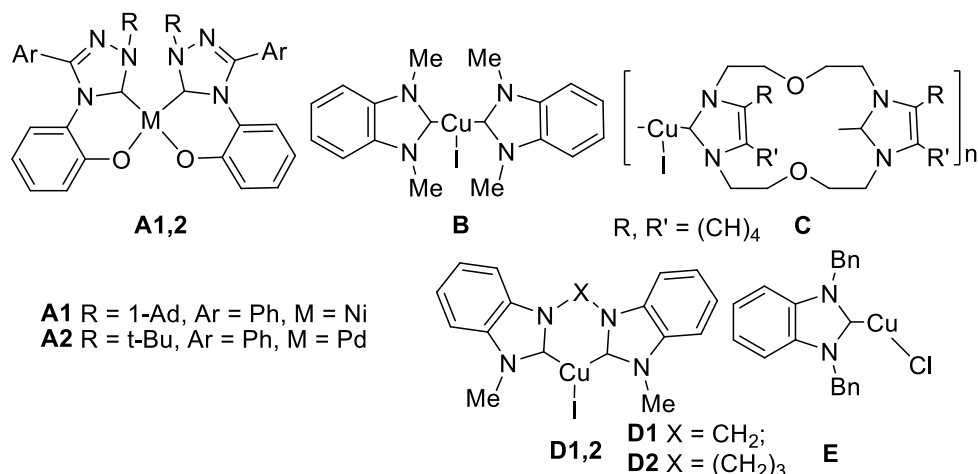
Scheme 115. New carbene complex catalysts for reduction of multiple bonds by alcohols in alkaline medium.

5.2.2. Hydrodehalogenation reactions of haloarenes. The application of this reaction is a potential solution for the environmental problems that are associated with the neutralization of haloaromatic production waste, including obsolete pesticides and used pharmaceuticals. Some of chemicals are now banned from production and use by the Stockholm convention of 22 May 2001, due to their very high toxicities (the so-called "persistent organic pollutants" - POPs). Well-known POPs of this type include such pesticides as DDT and hexachlorobenzene, dioxins (impurities to pesticides and industrial wastes), polychlorinated dibenzofurans and polychlorinated biphenyls, all of which are included on the list of the 12 most dangerous POPs.

The hydrodehalogenation reaction can be used for the effective neutralization of haloarene POPs. The reaction with metal alkoxides in alcohols in the presence of a catalyst forms metal halides and arenes. Usually a halogen atom of the haloarene interacts very strongly with the aromatic nucleus, such that replacement by other atoms or functional groups without the use of a catalyst is difficult. There are however many catalysts for the reaction. There are a number of palladium carbene complexes that are capable of achieving high yields of the desired products under relatively mild conditions (60-100 °C).
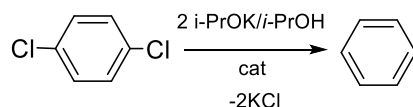
The known *in situ* methods of generating new catalysts are not particularly efficient (TON to 50, TOF to 50 h⁻¹).[413] However, individual complexes such as **116A** are able to achieve up to 200 cycles per hour at room temperature using monochlorobenzene (TON 100, TOF to 200 h⁻¹).[414] The complexes **116B1,2** undergo reaction with *p*-dichlorobenzene thus achieving similar results at 60 °C (TON of up to 200, TOF up to 110 h⁻¹)[415] (Scheme 116). The effectiveness of the catalyst **116B2** increases significantly when *p*-dichlorobenzene is exposed to microwave irradiation at 120 °C (TON 3800, TOF to 114000 h⁻¹). In fact, a quantitative yield of benzene was obtained in 2 minutes.

The carbene complexes of nickel **116C**, as well as nickel(0) complexes of the types LNi and L₂Ni (L = IMes), are not as effective as the palladium complexes. The first complex demonstrates low efficiency (TON and TOF values are 15-22, 4-44 h⁻¹, respectively) for the debromination of *p*-bromofluorobenzene and for the

dechlorination of *p*-chlorofluorobenzene.[416] The second type of complex exhibits only moderate indices of efficiency (TON 18-31, TOF 6-10 h^{-1}) for the defluorination reaction of 1-fluoronaphthalene.[417]
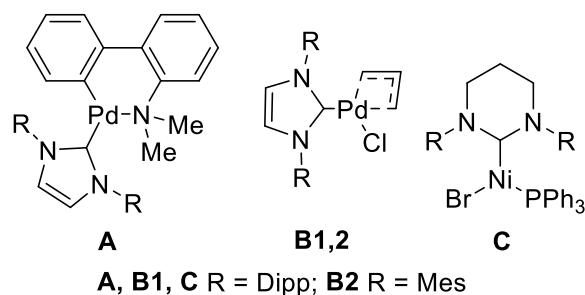
Scheme 116. Metal carbene complexes as catalysts of haloarene hydrodehalogenation.

Significantly higher TON and TOF values were obtained by using the catalyst (IPrPdCl$_2$)$_2$ **117A2** for the hydrodehalogenation reaction of 3,3',4,4'-tetrachlorobiphenyl at 80 °C in isopropanol in the presence of sodium hydroxide (10000 and 400 h^{-1}, respectively)[418] (Scheme 117). An even better result was obtained for the hydrodehalogenation of *o*-dichlorobenzene carried out under the same conditions, but with potassium *tert*-butoxide replacing the NaOH (TON 25000, TOF 1040 h^{-1}). For the reaction of 1,2,4,5-tetrachlorobenzene with potassium *tert*-butoxide it was necessary to use the high efficiency catalysts **116B1,2**, **117A1,2**, the most effective of which proved to be the **117A1**. For the reaction of potassium *tert*-butoxide and 1,2,4,5-tetrachlorobenzene with 0.02 mol% palladium, the indicated catalysts are listed on the basis of their efficiencies per one atom of chlorine (TON, TOF, h[-1]): **117A1** (19700, 821) > **116B2** (17250, 719) > **117B1** (16700, 696) > **116B1** (16550, 690) > **117A2** (14750, 615) > **117B2** (12100, 504).

It is noteworthy that the Dipp-substituted catalysts **117A1**, **117B1** (that have more steric protection) are more efficient than the mesityl-substituted compounds **117A2** and **117B2**, and the imidazolylidene catalysts **117A1,2** are more efficient than the 4,5-dihydroimidazolylidene analogues **117B1,2**.
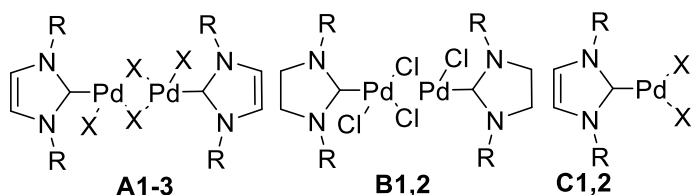
R, X: Dipp, Cl (**A1**, **B1**), Mes, Cl (**A2**, **B2**); Dipp, I (**A3**);
Dbep, Cl (**C1**), Dbep, I (**C2**); Dbep - 2,6-dibenzhydryl-4-ethylphenyl.

Scheme 117. Palladium carbene complexes for efficient catalysis of haloarene hydrodehalogenation.

The effectiveness of the 2-imidazol-2-ylidenes as catalysts was compared with that of the corresponding 1,2,4-triazol-5-ylidenes for the reaction of *p*-dichlorobenzene with potassium or sodium isopropoxides. These were generated in isopropanol by the addition of a variety of bases (NaOH, *t*-BuOK, *t*-BuONa, MeONa).[51,52,419,420] The most effective base was found to be potassium *tert*-butoxide.

Using potassium *tert*-butoxide as a reagent the following series of efficiencies was measured for the listed complexes (TON, TOF, h[-1]) (Schemes 117, 118): **118E** (160, 20) < **118A2** (220, 28) < **118D** (320, 40) ≈ **118A3** (320, 40) < **118A1** (500, 62) < **118A5** (760, 96) < **118B2** (1160, 146) < **118B1** (1320, 166) < **118A4** (1400, 176) < **118B4** (1440, 180) < **117A1** (17600, 734) < **118B3** (20000, 840) < **117A3** (44000, 1830).

It has been shown that, in general, the efficiencies of imidazol-2-ylidene catalysts with highly electron donating aromatic substituents exceed the effectiveness of the 1-alkyl-3,4-diaryl-1,2,4-triazol-5-ylidenes. Furthermore, the iodide Dipp-substituted imidazolylidene complex **117A3** is more effective than its chloride analogue **117A1**. Moreover, the iodide triazolylidene complexes **118B1**, **118B3** are superior to their chloride analogues **118B2** and **118B4**. However, it should also be noted that in the triazolylidene series, the monocarbene adamantyl substituted iodide complex **118B3** (TON 20000, TOF 840 h^{-1}) is the most effective. In turn, **118B3** is superior in terms of efficiency to its less sterically shielded analogue **118B2** and even to that of the imidazol-2-ylidene chloride complex **117A1**. The sterically open bistriazolylidene complexes **118A1-3**, and even their more hindered forms **118A4,5**, appear to be less effective. However, in the presence of 1 mol% of lithium *tert*-butoxide, the efficiencies of these complexes increase (**118B4** TON from 1140 to 8000, **117A3** TON from 44000 to 60000).

R, Ar, X: t-Bu, 4-BrC$_6$H$_4$, Cl (**A1**); t-Bu, 4-BrC$_6$H$_4$, I (**A2**);
t-Bu, 4-MeC$_6$H$_4$, I (**A3**); Ad, Mes, I (**A4**) t-Bu, Dipp, I (**A5**);
t-Bu, Dipp, I (**B1**); t-Bu, Dipp, Cl (**B2**); 1-Ad, Dipp, I (**B3**);
1-Ad, Dipp, Cl (**B4**); R, Ar: t-Bu, 4-BrC$_6$H$_4$ (**D**); t-Bu, Ph (**E**)
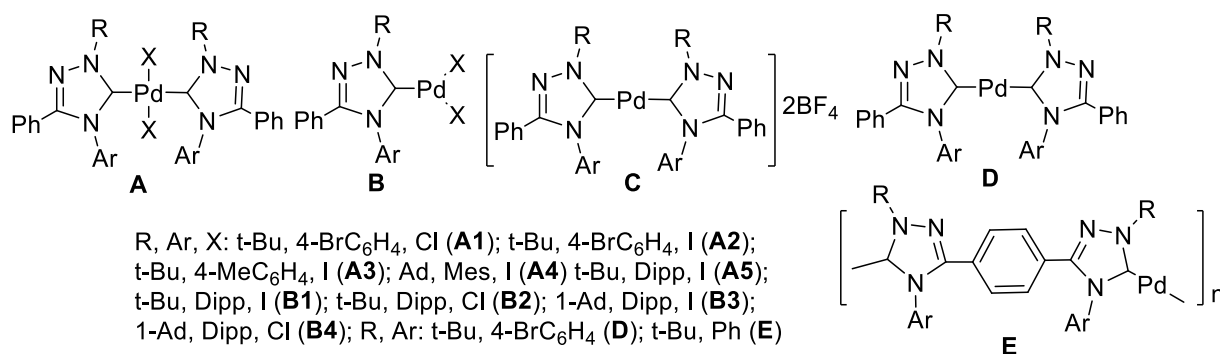
Scheme 118. Palladium 1,2,4-triazol-5-ylidene complexes for catalysis of haloarene hydrodehalogenations.

Overall, empirical observations suggest that the best catalysts in these series should be the iodide monoimidazol-2-ylidene complexes with higher steric shielding. The introduction of high volume substituents (Dbep) to the imidazol-2-ylidene complexes **117C1,2** resulted in an improvement in the efficiency of the catalysts. The reaction of *p*-dichlorobenzene, under the conditions described at 80 °C, results in high indices even for the chloride complex **117C1** (TON 140000, TOF 5833 h^{-1}), and those for its iodide analogue **117C2** are even higher (TON 180000, TOF 7500 h^{-1})[51,52,421]. The efficiencies of these catalysts were shown to be unusually high for the reaction of hexachlorobenzene under similar conditions. In the case of the chloride **117C1** the indices were TON = 210000 and TOF = 8750 h^{-1}, while for the iodide **117C2** they were 318000 and 13350 h^{-1}, respectively.

Thus, the complexes **117C1,2** are the best catalysts available today for the hydrodehalogenation reaction and offer, in principle, a viable low temperature method for the industrial neutralization of persistent organic pollutants.

6. Biological Activity of Carbene Derivatives

Carbenes themselves are likely to be toxic, taking into account those properties of their nearest analogues (carbon(II) oxide, carbon(II) thioxide and isocyanides). However, nucleophilic carbenes are readily hydrolyzable in water. Thus, it can be assumed that the actual toxicity of stable carbenes (more precisely, their hydrolysis products) may be low, except for those compounds that have increased stability in aqueous solutions. It is known that such examples are few and far between (excluding, of course, the aforementioned carbon(II) compounds).

In contrast to the individual carbenes, their metal complexes have been studied as biologically active substances for more than a decade; strong antimicrobial and antitumor properties have been found (see, e.g., the following reviews[422–424]). In the present section, some of the little-known antimicrobial properties of transition metal carbene complexes are described.

The diameter of growth delay (DGD) caused by the complexes **119A,C,D** for the bacteria *Staphylococcus aureus* is 23.6 − 27.5 mm at a concentration of 0.1%. For oxacillinum and vancomycin at a concentration of 0.01% the measured DGDs were 21 and 18 mm, respectively (Scheme 119).
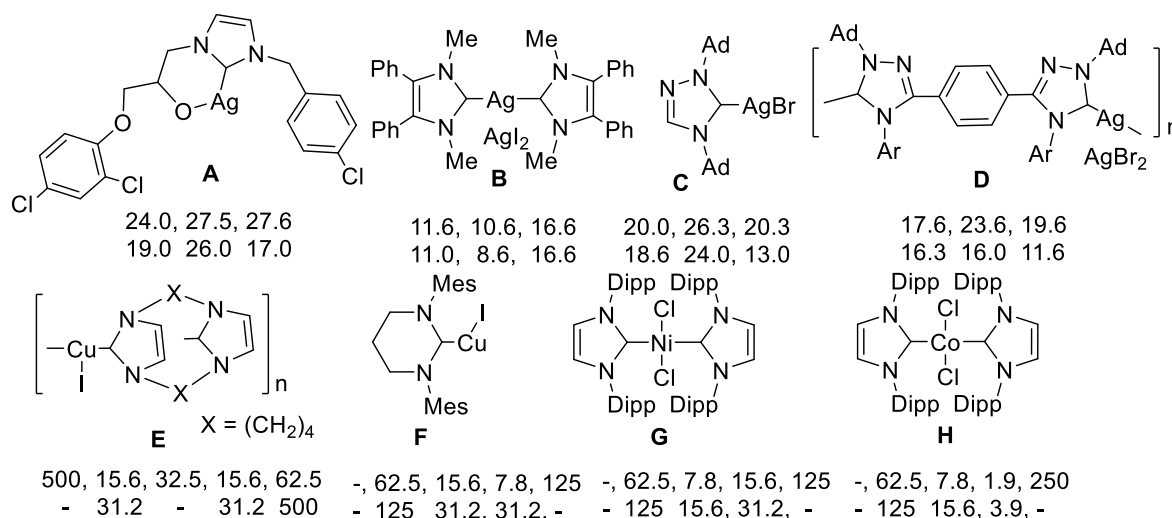
Scheme 119. Antimicrobial activity of carbene complexes of transition metals.

For compounds **119A-D**, the DGD is shown in the numerator of the scheme caption for cultures of *Escherichia coli*, *S. aureus* and *Micrococcus luteus*, respectively, at concentrations of 0.5%. The DGDs shown in the denominator are for concentrations of 0.1%. For the compounds **119E-H** the lowest inhibitory concentration (IC) is shown in the caption numerator, while the denominator lists the minimum biocidal concentration (BC) for cultures of *E coli*, *S. aureus*, *M. luteus*, *Candida tenuis* and *Aspergillus niger*, respectively. Both IC and BC are in mg/mL and (-) means that the minimum concentration was not attained.

For the cultures of *M. luteus*, the measured DGD values are 16.6 - 27.6 mm at a concentration of 0.5%. In all cases, compound **119A** is the most active (24.0, 27.5 and 27.6 mm, respectively, for the indicated cultures), although it is close in activity to **119C** (20.0, 26.3 and 20.3 mm). It was also shown that the silver carbene complexes **119A-C** exhibit a strong antibacterial effect on cultures of *S. aureus* and *M. luteus*, with **119A** being particularly effective.[425] The complex **119B** had the lowest observed activity. The DGDs for cultures of *E. coli* at a concentration of 0.5% for the compounds **119A-C** are 11.6 - 24.0 mm. The compounds do not show pronounced antifungal properties.

Typically, carbene complexes of copper show less activity towards antimicrobial compounds than do their silver analogues. However, the complex **119E** appeared to be active against cultures of *S. aureus*, *M. luteum* and *C. tenuis* (at inhibitory concentrations (IC) of 15.6, 32.5, 15.6 mg/mL). The respective biocidal concentrations (BC) were 31.2, -, 31.2 mg/mL.[426] The levels of biocidal activity for carbene complexes of copper iodide **119F**[427] and nickel chloride **119G** were similar. For the *C. tenuis* cultures, the carbene complex of cobalt **119H** appeared to be the most active (IC 1.9 mg/ mL; BC 3.9 mg/mL). However, it exhibited activities close to those for the related compounds **119E-G** on other cultures.[428]

The obtained results suggest that more significant biological effects may be achieved for carbene complexes, by varying the metal, the structure of ligand(s), and the type of complex.

7. Conclusions

The heteroaromatic carbenes of the imidazole, the 1,2,4- and the 1,2,3-triazole series and their fused analogues are the most diverse divalent carbon compounds yet known in chemical research. They can be considered to be the most accessible, since their syntheses have been well developed. However, improvement of the methods used for obtaining these compounds is continuing to provide broader practical applications for individual carbenes. The newest in this series are the mesoionic carbenes (mesoions) of which two types have been prepared, namely the imidazolium-4-ides and the 1,2,3-triazolium-5-ides. Novel syntheses of individual carbenes involve the preparation of hyperbasic and hypernucleophilic systems that exhibit high electron donating behavior. Another important development is the preparation of structures with high buried volumes (%V_{bur} > 50). This leads to a fundamental change in the properties of the carbene, namely they become more passive in reactions with electrophiles, in comparison to conventional carbenes. In some cases their complexes with transition metals can exhibit unusually high catalytic activity.

The need for practical applications of pure carbenes (instead of using reaction mixtures) is becoming more urgent. From the standpoint of organic synthesis, the *in situ* processes do not always give the same products as reactions carried out with pure compounds. In some cases, the very utilization of *in situ* processes may be problematic. For example, catalysis experiments involving the *in situ* generation of carbenes often do not give results that correspond to the maximum capabilities of these compounds. This is particularly evident in organic reactions, where it has been shown that many transformations proceed effectively only when pure carbenes are used as catalysts. Generating the required carbenes from mixtures of precarbenes has been found to be less effective in certain reactions, as in, for example, transesterification reactions and benzoin condensations. The same can be said of the carbene complexes of transition metals, in the sense that a pure compound is often more catalytically efficient than the generating mixtures (e.g., in haloarene hydrodehalogenations). Further development of the synthesis of individual carbenes should be encouraged to provide new directions for their application.

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Authors' Biographies

Prof. Nikolai Korotkikh was born in Donetsk, Ukraine, in 1951. He was educated at the Donetsk State University, Ukraine (1968–1973), obtained his Candidate of Chemistry (Ph.D.) degree in the Institute of Physical Organic & Coal Chemistry in 1982, and Doctor of Sciences degree in 1998. After defending a Doctor of Sciences thesis in 1997 he was elected to the position of Head of Department in 2000 and that he held up to 2014. In 2014 he moved to Kiev

where was elected to the position of Head of Laboratory for Chemistry of Stable Carbenes in the Institute of Organic Chemistry. Current research is connected with the synthesis, structures, reactivities, and catalytical properties of heteroaromatic carbenes, carbenoids and their analogues. Earlier works were devoted to the synthesis of heterocyclic derivatives of small rings, ring transformations of heterocycles, materials relevant to the pharmaceutical and polymer industries.

Prof. Alan H. Cowley was born in Manchester, U.K. He attended the University of Manchester from 1952 until 1958, where he received B.Sc., M.Sc. and Ph.D. degrees. After a postdoctoral sojourn at the University of Florida, he returned to the U.K. in 1960 where he was employed as a research chemist by Imperial Chemical Industries until 1962. Most of his academic career has been spent at the University of Texas at Austin where he holds the Robert A. Welch Chair in Chemistry. He has close to 500 publications, most of which are concerned with synthetic, structural, and theoretical main group chemistry. He was elected a Fellow of the Royal Society in 1988 and received an Honorary Doctorate from the University of Bordeaux I in 2003. He has served on the Board of Trustees of the Gordon Research Conferences and on several Editorial Boards, including the Journal of the American Chemical Society, Inorganic Chemistry, and Organometallics.

Dr. Jason Clyburne holds a joint appointment in Environmental Science and Chemistry at Saint Mary's University in Halifax, Nova Scotia, Canada. He obtained a BSc (Honours) from Acadia University and a PhD under the supervision of Professor Neil Burford at Dalhousie University. After a short post-doctoral project with Prof. Melbourne Schriver, he joined the research group of Prof. Alan Cowley (FRS) at the University of Texas at Austin, where he examined the coordination chemistry of main group elements. Dr. Clyburne is also an adjunct professor at Simon Fraser University. His research deals mostly with inorganic and organic materials as they apply to green chemistry, including catalysis and acid gas capture. The chemistry of N-heterocyclic carbenes and ionic liquids play key roles in his research.

Dr. Katherine Robertson obtained her PhD from Dalhousie University in 2001, working in the fields of X-ray crystallography and experimental charge density analysis under the supervision of Professors O. Knop and T. S. Cameron. Since that time she has held a variety of positions, including her current association with Dr. J. A. C. Clyburne at Saint Mary's University in Halifax, Nova Scotia.

Dr. Vagiz Saberov was born in Makeevka, Ukraine, in 1990. He studied at the Donetsk National University in Donetsk (2007 – 2012), were he received Master's Degree in organic chemistry. From 2009 he joined to the research group of Prof. N. I. Korotkih in the L.M.Litvinenko Institute of Physical Organic and Coal Chemistry (Donetsk, Ukraine). Under his supervision in 2016 he obtained his Ph.D. degree in the Institute of Organic Chemistry (Kiev, Ukraine). He is presently working on new types of carbenes, their complexes with transition metals and organocatalysis by these compounds. Also, he is an associate chemist in lab of molecular diversity at Enamine Ltd. (Kiev, Ukraine).

Dr. Nataliya V. Glinyanaya was born in Kramatorsk, Ukraine, in 1983. She was educated at the Donetsk National University, Ukraine (2001–2006) and obtained her B.Sc. and M.Sc. degrees in 2006. She obtained her Candidate of Chemistry (Ph.D.) degree in the L.M.Litvinenko Institute of Physical Organic & Coal Chemistry in

2011 under the guidance of Professor Nikolai Korotkikh. Her current research is connected with the synthesis, structures, and reactivities of heteroaromatic carbenes and their metal complexes. She has 18 publications.

Dr. Gennady Rayenko was born in Donetsk, Ukraine, in 1970. He was educated at the Donetsk State University, Ukraine (1987—1992), obtained his Candidate of Chemistry (Ph.D.) degree in the L.M.Litvinenko Institute of Physical Organic & Coal Chemistry in 2000. In 2001 he was appointed to the position of Scientific Secretary and in 2015 to the position of vice-director of the Institute that he holds up to now. Current research is concerned with the synthesis, structures, and reactivities of heteroaromatic carbenes and their analogues, chemistry of azolines.

Prof. Oles Shvaika was born in Ukraine in 1932. He completed the Lviv Polythechnical Institute, Ukraine, in 1953, obtained his Candidate of Chemistry (Ph.D.) degree at the Kharkiv State University in 1963, and Doctor of Sciences degree in 1977 at Kiev State University, became Professor in 1988. He had been Head of the Department of Azole Chemistry in the L.M.Litvinenko Institute of Physical Organic and Coal Chemistry in Donetsk for 22 years. His Doctor of Sciences thesis and major scientific works were devoted to the ring transformations of heterocyclic compounds especially azoles, azolidines and azolium salts, later to the synthesis of heterocyclic derivatives of small rings. In the 90s his interest was directed to the chemistry of heteroaromatic carbenes, electrochemical research of heteroaromatic salt association in solution, and applied chemistry concerning pharmaceutical, polymer and optical techniques.