

= X2 =

S), which then dimerise to give derivatives of tetrathiafulvene. Thus it is possible that the reverse of this process might be occurring in similar carbenes.

= = = Bertrand's carbenes = = =

In Bertrand's persistent carbenes, the unsaturated carbon is bonded to a phosphorus and a silicon. However, these compounds seem to exhibit some alkynic properties, and when published the exact carbenic nature of these red oils was in debate.

= = = Other nucleophilic carbenes = = =

One stable N-heterocyclic carbene has a structure analogous to borazine with one boron atom replaced by a methylene group. This results in a planar 6-electron compound.

= = = Cyclopropenylidenes = = =

Another family of carbenes is based on a cyclopropenylidene core, a three-carbon ring with a double bond between the two atoms adjacent to the carbenic one. This family is exemplified by bis(diisopropylamino) cyclopropenylidene.

= = = Triplet state carbenes = = =

In 2001, Hideo Tomioka and his associates were able to produce a comparatively stable triplet carbene (bis(9-anthryl) carbene, with a half-life of 19 minutes), by taking advantage of resonance.

In 2006 a triplet carbene was reported with a half-life of 40 minutes. This carbene is prepared by a photochemical decomposition of a diazomethane with expulsion of nitrogen gas at a wavelength of 300 nanometers in benzene.

Exposure to oxygen (diradical) converts this carbene to the corresponding benzophenone and the diphenylmethane compound is formed when it is trapped by 1,4-cyclohexadiene. As with the other carbenes this species contains large bulky substituents, namely bromine and the trifluoromethyl groups, that shield the carbene and prevent or slow down the process of dimerisation to a 1,1,2,2-tetra(phenyl) alkene.

Based on computer simulations, the distance of the divalent carbon atom to its neighbours is claimed to be 138 picometers with a bond angle of 158.8° . The planes of the phenyl groups are almost at right angles to each other (the dihedral angle being 85.7°).

= = Mesoionic carbenes = =

Mesoionic carbenes (MICs) are similar to N-heterocyclic carbenes (NHCs) except that canonical resonance structures with the carbene depicted cannot be drawn without adding additional charges. Mesoionic carbenes are also referred to as abnormal N-heterocyclic carbenes (aNHC) or remote N-heterocyclic carbenes (rNHC). A variety of free carbenes can be isolated and are stable at room temperature. Other free carbenes are not stable and are susceptible to intermolecular decomposition pathways.

= = Chemical properties = =

= = = Basicity and nucleophilicity = = =

The imidazol-2-ylidenes are strong bases, having a pK_a of ca. 24 for the conjugate

acid in dimethyl sulfoxide (DMSO) :

However , further work showed that diaminocarbenes will deprotonate the DMSO solvent , with the resulting anion reacting with the resulting amidinium salt .

Reaction of imidazol @-@ 2 @-@ ylidenes with 1 @-@ bromohexane gave 90 % of the 2 @-@ substituted adduct , with only 10 % of the corresponding alkene , indicating that these molecules are also reasonably nucleophilic .

pKa values for the conjugate acids of several NHC families have been examined in aqueous solution. pKa values of triazolium ions lie in the range 16 @-@ 5 - 17 @-@ 8 , around 3 pKa units more acidic than related imidazolium ions .

== Dimerisation ==

At one time , stable carbenes were thought to reversibly dimerise through the so @-@ called Wanzlick equilibrium . However , imidazol @-@ 2 @-@ ylidenes and triazol @-@ 5 @-@ ylidenes are thermodynamically stable and do not dimerise , and have been stored in solution in the absence of water and air for years . This is presumably due to the aromatic nature of these carbenes , which is lost upon dimerisation . In fact imidazol @-@ 2 @-@ ylidenes are so thermodynamically stable that only in highly constrained conditions are these carbenes forced to dimerise .

Chen and Taton made a doubly tethered diimidazol @-@ 2 @-@ ylide by deprotonating the respective diimidazolium salt . Only the deprotonation of the doubly tethered diimidazolium salt with the shorter methylene bridge (-CH₂-) resulted in the dicarbene dimer :

If this dimer existed as a dicarbene , the electron lone pairs on the carbenic carbon would be forced into close proximity . Presumably the resulting repulsive electrostatic interactions would have a significant destabilising effect . To avoid this electronic interaction , the carbene units dimerise .

On the other hand , heteroamino carbenes (e.g. R₂N @-@ C : -OR or R₂N @-@ C : -SR) and non @-@ aromatic carbenes such as diaminocarbenes (e.g. R₂N @-@ C : -NR₂) have been shown to dimerise , albeit quite slowly . This has been presumed to be due to the high barrier to singlet state dimerisation :

Diaminocarbenes do not truly dimerise , but rather form the dimer by reaction via formamidinium salts , a protonated precursor species . Accordingly , this reaction can be acid catalysed . This reaction occurs because unlike imidazolium based carbenes , there is no loss of aromaticity in protonation of the carbene .

Unlike the dimerisation of triplet state carbenes , these singlet state carbenes do not approach head to head (" least motion ") , but rather the carbene lone pair attacks the empty carbon p @-@ orbital (" non @-@ least motion ") . Carbene dimerisation can be catalyzed by both acids and metals .

== Reactivity ==

The chemistry of stable carbenes has not been fully explored . However , Enders et al. have performed a range of organic reactions involving a triazol @-@ 5 @-@ ylide . These reactions are outlined below and may be considered as a model for other carbenes .

These carbenes tend to behave in a nucleophilic fashion (e and f) , performing insertion reactions (b) , addition reactions (c) , [2 + 1] cycloadditions (d , g and h) , [4 + 1] cycloadditions (a) as well as simple deprotonations . The insertion reactions (b) probably proceed via deprotonation , resulting in the generation of a nucleophile (? XR) which can attack the generated salt giving the impression of a H @-@ X insertion .

The reported stable isothiazole carbene (2) derived from an isothiazolium perchlorate (1) was questioned , who were only able to isolate 2 @-@ imino @-@ 2H @-@ thiete (4) . The intermediate 3 was proposed through a rearrangement reaction . This carbene is no longer considered stable .

== Carbene complexation ==

Imidazol-2-ylidenes, triazol-5-ylidenes (and less so, diaminocarbenes) have been shown to coordinate to a plethora of elements, from alkali metals, main group elements, transition metals and even lanthanides and actinides. A periodic table of elements gives some idea of the complexes which have been prepared, and in many cases these have been identified by single crystal X-ray crystallography. Stable carbenes are believed to behave in a similar fashion to organophosphines in their coordination properties to metals. These ligands are said to be good π donors through the carbenic lone pair, but poor π acceptors due to internal ligand back donation from the nitrogen atoms adjacent to the carbene centre, and so are able to coordinate to even relatively electron deficient metals. Enders and Hermann have shown that these carbenes are suitable replacements for phosphine ligands in several catalytic cycles. Whilst they have found that these ligands do not activate the metal catalyst as much as phosphine ligands they often result in more robust catalysts. Several catalytic systems have been looked into by Hermann and Enders, using catalysts containing imidazole and triazole carbene ligands, with moderate success. Grubbs has reported replacing a phosphine ligand (PCy_3) with an imidazol-2-ylidene in the olefin metathesis catalyst $\text{RuCl}_2(\text{PCy}_3)_2\text{CHPh}$, and noted increased ring closing metathesis as well as exhibiting "a remarkable air and water stability". Molecules containing two and three carbene moieties have been prepared as potential bidentate and tridentate carbene ligands.

Legend

Carbene complex with element known

No carbene complex with element known

=== Carbenes in organometallic chemistry & catalysis ===

Carbenes can be stabilised as organometallic species. These transition metal carbene complexes fall into two categories:

Fischer carbenes in which carbenes are tethered to a metal and an electron withdrawing group (usually a carbonyl),

Schrock carbenes; in which carbenes are tethered to a metal and an electron donating group. The reactions that such carbenes participate in are very different from those in which organic carbenes participate.

=== Triplet state carbene chemistry ===

Persistent triplet state carbenes are likely to have very similar reactivity as other non persistent triplet state carbenes.

=== Physical properties ===

Those carbenes that have been isolated to date tend to be colorless solids with low melting points. These carbenes tend to sublime at low temperatures under high vacuum.

One of the more useful physical properties is the diagnostic chemical shift of the carbenic carbon atom in the ^{13}C NMR spectrum. Typically this peak is in the range between 200 and 300 ppm, where few other peaks appear in the ^{13}C NMR spectrum. An example is shown on the left for a cyclic diaminocarbene which has a carbenic peak at 238 ppm.

Upon coordination to metal centers, the ^{13}C carbene resonance usually shifts highfield, depending on the Lewis acidity of the complex fragment. Based on this observation, Huynh et al. developed a new methodology to determine ligand donor strengths by ^{13}C NMR analysis of trans π -palladium(II)-carbene complexes. The use of a ^{13}C labeled N heterocyclic carbene ligand also allows for the study of mixed carbene π -phosphine complexes, which undergo trans π -cis π isomerization due to the trans effect.

=== Applications ===

NHCs are widely used as ancillary ligand in organometallic chemistry . One practical application is the ruthenium π -allyl based Grubbs ' catalyst and NHC π -allyl Palladium Complexes for cross π -allyl coupling reactions . NHC π -allyl metal complexes , specifically Ag (I) -NHC complexes have been widely tested for their biological applications .

= = Preparation methods = =

NHCs are often strongly basic (the pKa value of the conjugate acid of an imidazol π -allyl ylide was measured at ca . 24) and react with oxygen . Clearly these reactions are performed using air π -allyl free techniques , avoiding compounds of even moderate acidity . Although imidazolium salts are stable to nucleophilic addition , other non π -allyl aromatic salts are not (i.e. formamidinium salts) .

In these cases , strong unhindered nucleophiles are avoided whether they are generated in situ or are present as an impurity in other reagents (e.g. , LiOH in BuLi) .

Several approaches have been developed in order to prepare stable carbenes , these are outlined below .

= = = Deprotonation = = =

Deprotonation of carbene precursor salts with strong bases has proved a reliable route to almost all stable carbenes :

Imidazol π -allyl ylidenes and dihydroimidazol π -allyl ylidenes , e.g. Imes , have been prepared by the deprotonation of the respective imidazolium and dihydroimidazolium salts . The acyclic carbenes and the tetrahydropyrimidinyl based carbenes were prepared by deprotonation using strong homogeneous bases .

Several bases and reaction conditions have been employed with varying success . The degree of success has been principally dependent on the nature of the precursor being deprotonated . The major drawback with this method of preparation is the problem of isolation of the free carbene from the metals ions used in their preparation .

= = = Metal hydride bases = = =

One might believe that sodium or potassium hydride would be the ideal base for deprotonating these precursor salts . The hydride should react irreversibly with the loss of hydrogen to give the desired carbene , with the inorganic by π -allyl products and excess hydride being removed by filtration . In practice this reaction is often too slow , requiring the addition of DMSO or t π -allyl BuOH . These reagents generate soluble catalysts , which increase the rate of reaction of this heterogeneous system , via the generation of tert π -allyl butoxide or dimsyl anion . However , these catalysts have proved ineffective for the preparation of non π -allyl imidazolium adducts as they tend to act as nucleophiles towards the precursor salts and in so doing are destroyed . The presence of hydroxide ions as an impurity in the metal hydride could also destroy non π -allyl aromatic salts .

Deprotonation with sodium or potassium hydride in a mixture of liquid ammonia / THF at -40 ° C has been reported for imidazole π -allyl based carbenes . Arduengo and co π -allyl workers managed to prepare a dihydroimidazol π -allyl ylide using NaH . However , this method has not been applied to the preparation of diaminocarbenes . In some cases , potassium tert π -allyl butoxide can be employed without the addition of a metal hydride .

= = = Alkylolithiums = = =

The use of alkylolithiums as strong bases has not been extensively studied , and have been unreliable for deprotonation of precursor salts . With non π -allyl aromatic salts , n π -allyl BuLi and PhLi can act as nucleophiles whilst t π -allyl BuLi can on occasion act as a source of hydride ,

reducing the salt with the generation of isobutene :

===== Amides bases =====

Lithium amides like the diisopropylamide (LDA) and the (tetramethylpiperidide (LiTMP)) generally work well for the deprotonation of all types of salts , providing that not too much LiOH is present in the n -butyllithium used to make the lithium amide . Titration of lithium amide can be used to determine the amount of hydroxide in solution . The deprotonation of precursor salts with metal hexamethyldisilazides works very cleanly for the deprotonation of all types of salts , except for unhindered formamidinium salts , where this base can act as a nucleophile to give a triaminomethane adduct .

===== Metal -free carbene preparation =====

The preparation of stable carbenes free from metal cations has been keenly sought to allow further study of the carbene species in isolation from these metals . Separating a carbene from a carbene -metal complex can be problematic due to the stability of the complex . Accordingly , it is preferable to make the carbene free from these metals in the first place . Indeed , some metal ions , rather than stabilising the carbene , have been implicated in the catalytic dimerisation of unhindered examples .

Shown right is an X -ray structure showing a complex between a diaminocarbene and potassium HMDS . This complex was formed when excess KHMDS was used as a strong base to deprotonate the formamidinium salt . Removing lithium ions resulting from deprotonation with reagents such as LDA can be especially problematic . Potassium and sodium salt by -products tend to precipitate from solution and can be removed . Lithium ions may be chemically removed by binding to species such as cryptands or crown ethers .

Metal free carbenes have been prepared in several ways as outlined below :

===== Dechalcogenation =====

Another approach of preparing carbenes has relied on the desulfurisation of thioureas with potassium in THF . A contributing factor to the success of this reaction is that the byproduct , potassium sulfide , is insoluble in the solvent . The elevated temperatures suggest that this method is not suitable for the preparation of unstable dimerising carbenes . A single example of the deoxygenation of a urea with a fluorene derived carbene to give the tetramethyldiaminocarbene and fluorenone has also been reported :

The desulfurisation of thioureas with molten potassium to give imidazol -2-ylidenes or diaminocarbenes has not been widely used . The method was used to prepare dihydroimidazole carbenes .

===== Vacuum pyrolysis =====

Vacuum pyrolysis , with the removal of neutral volatile by -products (CH₃OH , CHCl₃) , has been used to prepare dihydroimidazole and triazole based carbenes :

Historically the removal of chloroform by vacuum pyrolysis of d adducts was used by Wanzlick in his early attempts to prepare dihydroimidazol -2-ylidenes but this method is not widely used . The Enders laboratory has used vacuum pyrolysis of a c adduct to generate a triazolium -5-ylidene c .

===== Bis (trimethylsilyl) mercury =====

Bis (trimethylsilyl) mercury (CH₃)₃Si -Hg -Si (CH₃)₃ reacts with chloro -iminium and chloro -amidinium salts to give a metal -free carbene and elemental mercury

. For example , $(\text{CH}_3)_3\text{Si}-\text{Hg}-\text{Si}(\text{CH}_3)_3 + \text{R}_2\text{N}=\text{C}(\text{Cl})-\text{NR}_2 + \text{Cl}^- \rightarrow \text{R}_2\text{N}-\text{C}(\text{Cl})-\text{NR}_2 + \text{Hg}(\text{l}) + (\text{CH}_3)_3\text{Si}-\text{Cl}$

=== Photochemical decomposition ===

Persistent triplet state carbenes have been prepared by photochemical decomposition of a diazomethane product via the expulsion of nitrogen gas , at a wavelength of 300 nm in benzene .

=== Purification ===

Stable carbenes are very reactive , and so the minimum amount of handling is desirable using air-free techniques . However , provided rigorously dry , relatively non-acidic and air-free materials are used , stable carbenes are reasonably robust to handling per se . By way of example , a stable carbene prepared from potassium hydride can be filtered through a dry celite pad to remove excess KH (and resulting salts) from the reaction . On a relatively small scale , a suspension containing a stable carbene in solution can be allowed to settle and the supernatant solution pushed through a dried membrane syringe filter . Stable carbenes are readily soluble in non-polar solvents such as hexane , and so typically recrystallisation of stable carbenes can be difficult , due to the unavailability of suitable non-acidic polar solvents . Air-free sublimation as shown right can be an effective method of purification , although temperatures below 60°C under high vacuum are preferable as these carbenes are relatively volatile and also could begin to decompose at these higher temperatures . Indeed , sublimation in some cases can give single crystals suitable for X-ray analysis . However , strong complexation to metal ions like lithium will in most cases prevent sublimation .