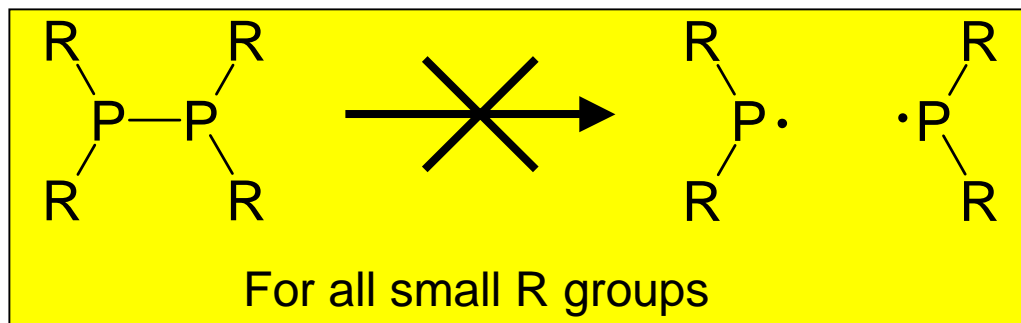


# Chem 59-651 Bulky Groups and Drastic Changes

Sterically demanding substituents can also be used to change the thermodynamic stabilities of systems in even more extreme ways. For example, diphosphines generally have relatively strong P-P bonds (200 kJ/mol) that remain intact in all phases.

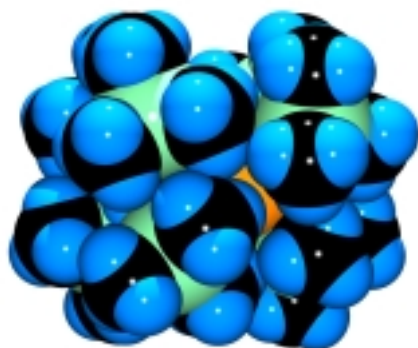


R = Me



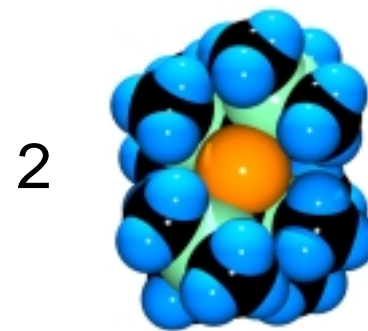
However, the disyl-substituted derivative cleaves spontaneously when it is not in the solid state.

(Hinchley, JACS, 2001, 123, 9045)



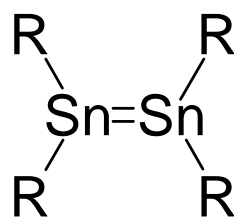
R = CH(SiMe<sub>3</sub>)<sub>2</sub>

Melt, Solution or Gas Phase

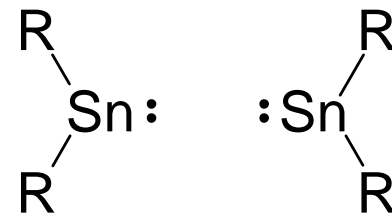


Stable Free Radicals

Some multiple bonds can also be fragmented into carbenoids in a similar way. (Lappert, JCS, Dalton., 1986, 1551 and 2387)



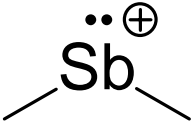
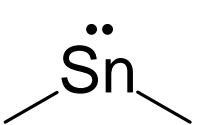
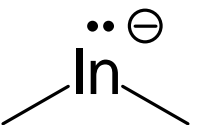
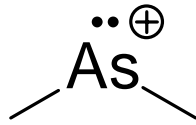
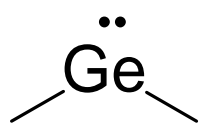
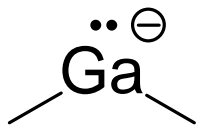
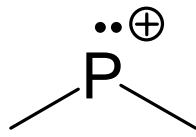
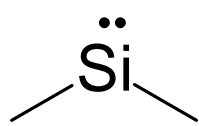
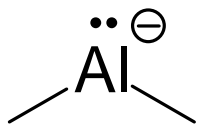
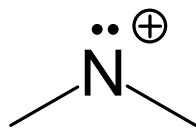
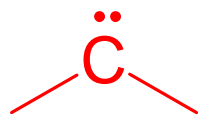
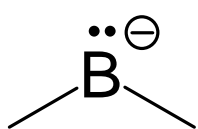
Solution or Gas Phase





# Carbenes, Carbenoids and Related Species

An important class of compounds that were also considered to be “non-existent”, or at least transient, for many years are carbenes and the various unsaturated species related to them. An understanding of the behaviour of such “building block” molecules allows us to understand many other aspects of the chemistry of the main group elements. Also, from a fundamental point of view, an examination of carbenoids allows us to explore other methods of stabilizing reactive species.



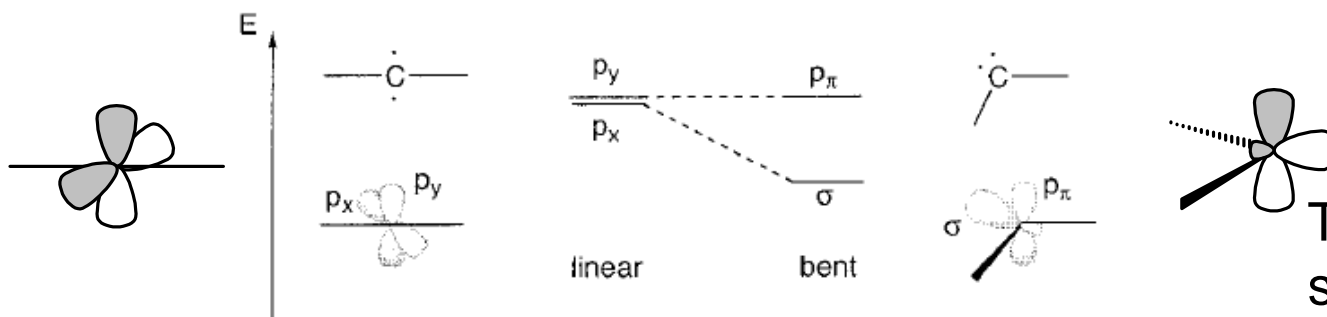
Carbenes, and the isovalent carbenoids from groups 13, 14 and 15 are compounds that contain di-coordinate atoms and bear a pair of electrons for a total of 6 valence electrons.

Such compounds are also often called “ylidenes”.

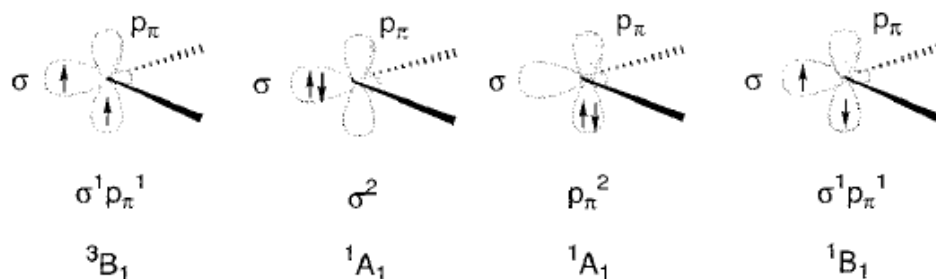
The parent molecule of the family is  $\text{CH}_2$  - methylene.



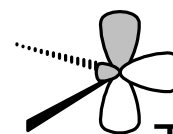
The structure, stability and reactivity of carbenes is very dependent on the electron configuration of the carbenic atom. The major division that is used to classify carbenes is whether the two non-bonding electrons are paired (singlet) or unpaired (triplet). Although in theory there could be 4 possible electron configurations (Figure 3) (Bertrand, *Chem. Rev.*, 2000, 100, 39) in practice only the first three configurations are ever observed for ground state species.



**Figure 2.** Relationship between the carbene bond angle and the nature of the frontier orbitals.



**Figure 3.** Electronic configurations of carbenes.

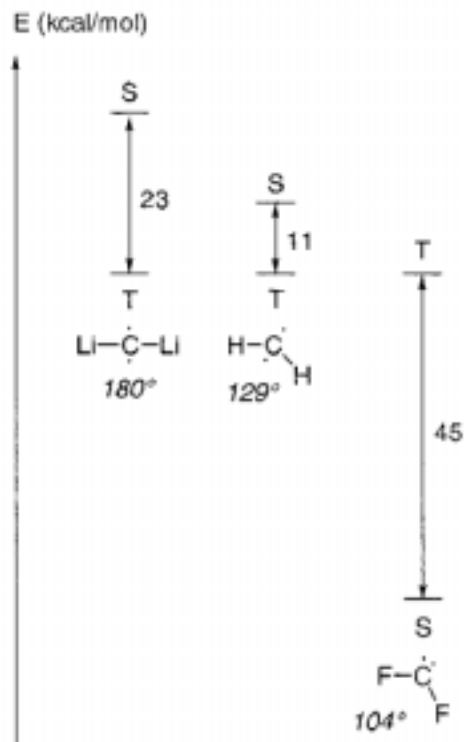


The vast majority of stable carbenes are of the singlet ( $\sigma^2$ ) type.

The relative stability of the singlet and triplet states depends on the energy difference between the  $p_\pi$  and the  $\sigma$  orbitals.



The relative stability of the  $p_\pi$  and the  $\sigma$  orbitals is determined by the nature of the substituents adjacent to the carbenic center. This means that, at least for carbon, we can control the multiplicity of the molecule by choosing appropriate substituents.



**Figure 4.** Influence of the substituents' electronegativity on the ground state carbene spin multiplicity.

Carbon and other members of the 2<sup>nd</sup> row of the periodic table are “special” because of the relatively small energy differences and size differences between the 2s and the 2p orbitals.

Because of these properties, the parent carbene  $\text{CH}_2$  has a triplet ground state (as does  $\text{NH}_2^+$ ). In practice, it is much easier to use substituents to favour singlet carbenoids than triplet ground states so both multiplicities are possible for carbon but not for most other elements.

A variety of factors must be considered to determine whether a particular group will tend to favour singlet or triplet. These include the steric properties of a substituent and the influence the group has on the electronic structure of the compound. The electronic consequences of a substituent can be subdivided into inductive effects and mesomeric (resonance) effects.

*Inductive effects can be understood in terms of the electronegativity of the atom bonded to the carbene atom.*

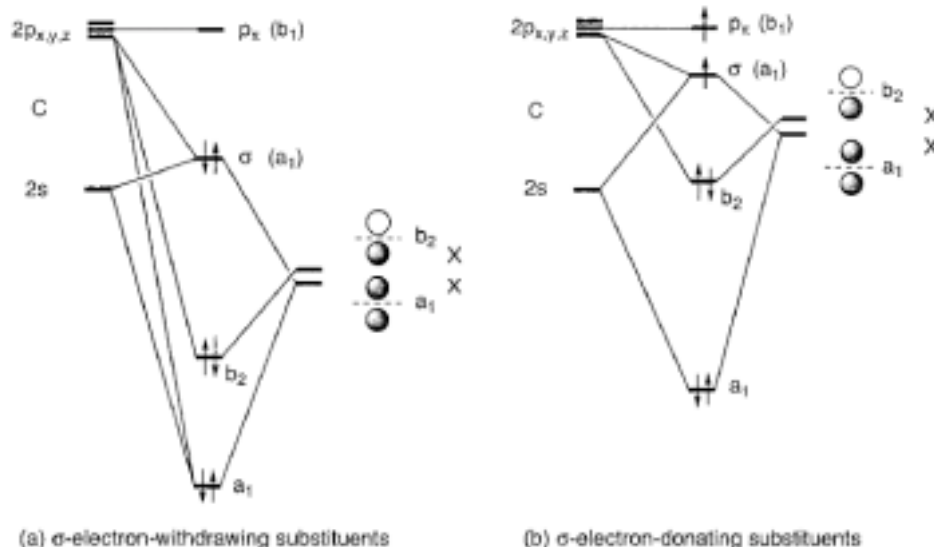
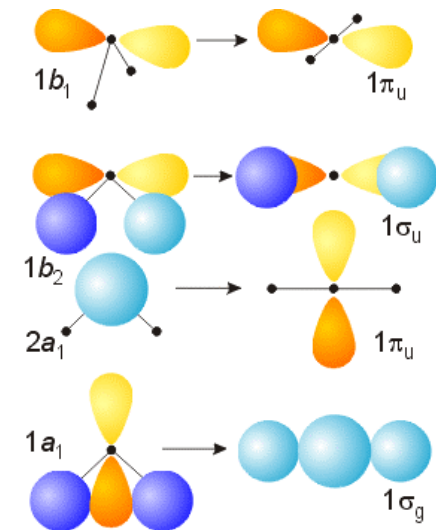
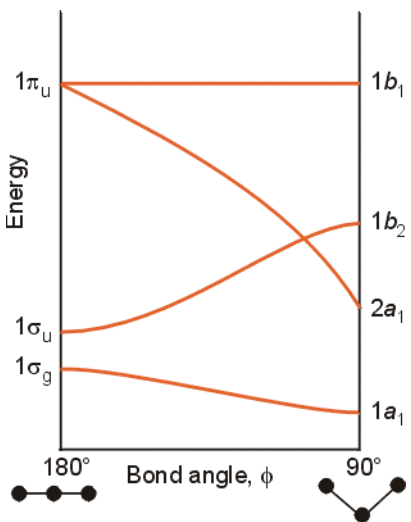


Figure 5. Perturbation orbital diagrams showing the influence of the inductive effects.

*Resonance effects are best understood in terms of the  $\pi$ -acidity or basicity of the substituent adjacent to the carbenic center.*

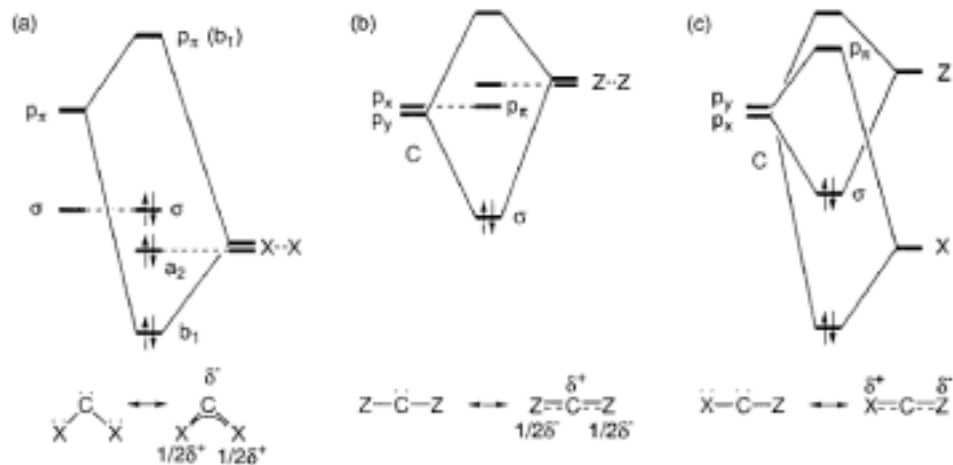
The classes of substituent are thus generally divided into the categories of:

$\pi$ -donors (X), such as  $\text{PnR}_2$ ,  $\text{ChR}$ , halogens, etc.

or

$\pi$ -acceptors (Z), such as  $\text{PnR}_3^+$ ,  $\text{SiR}_3$ ,  $\text{BR}_2$ , metals etc.

*Mesomeric effects generally favour singlet species.*



X:  $\pi$ -electron-donating substituents; Z:  $\pi$ -electron-withdrawing substituents

**Figure 6.** Perturbation orbital diagrams showing the influence of the mesomeric effects.

# Chem 59-651 Carbenes: Overall Electronic Substituent Effects

The total electronic contribution for a given substituent is often summarized using the following convention:  $+I$  = inductive donor,  $-I$  = inductive acceptor,  $+M$  = mesomeric donor,  $-M$  = mesomeric acceptor.

Pauling suggested in 1980 (*J.C.S., Chem. Comm.*, 1980, 688) that substituents with opposing effects would stabilize singlet carbenes because it would populate the vacant orbital while avoiding the build-up of excessive charge at the carbon atom. This is known as “Push-Pull” substitution and it can be done in a variety of ways.

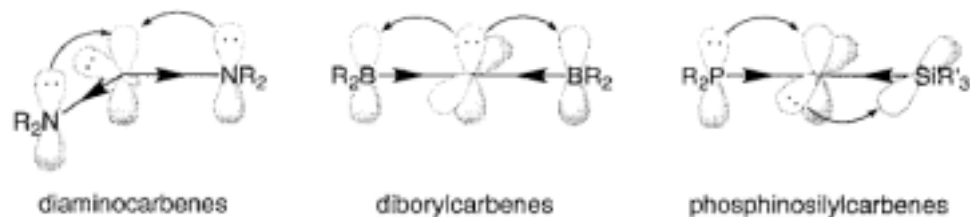
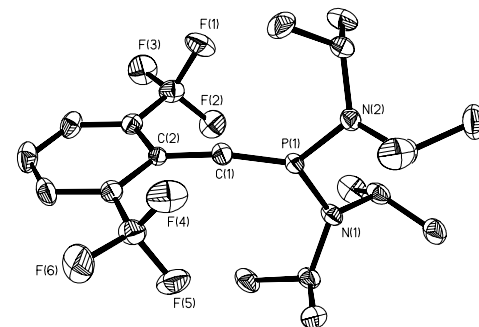
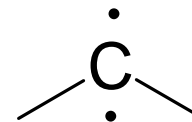


Figure 7. Electronic effects of the substituents for diamino-, phosphinosilyl-, and diboryl-carbenes.

These types of substitution patterns have allowed for the isolation of numerous stable singlet carbenes and carbenoids with a large variation in structural and reactivity characteristics.



(Bertrand, *Science*, 2000, 288, 834)

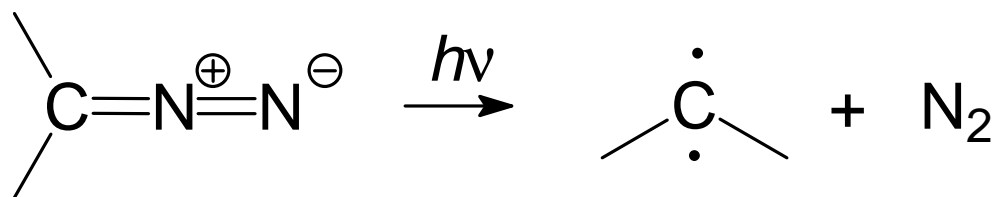


Because of their diradical nature, triplet carbenes are expected to be much more reactive than their singlet analogues - this is the case.

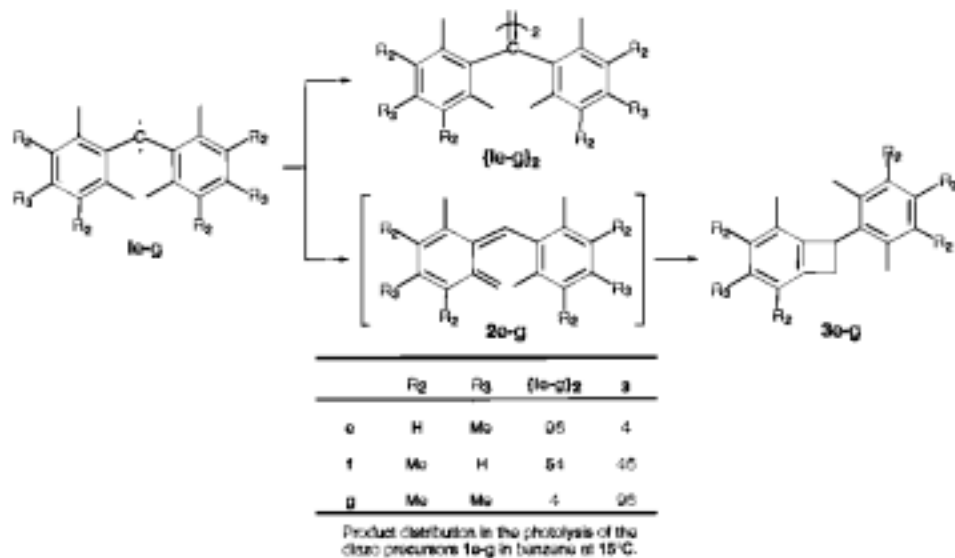
Triplet carbenes generally have half-lives in the ps or  $\mu$ s ranges and are able to react with many compounds that are often considered inert. In this context, triplet carbenes are considered exceptionally “stable” if their half-lives can be measured in the millisecond range or longer.

The rapid demise of the triplet carbenes means that they are generally studied *in situ* using kinetic and spectroscopic methods (e.g. Laser Flash Photolysis) in solution or frozen matrices, or by a variety trapping reactions/product studies.

Tomioka et al. (Tomioka, *Acc. Chem. Res.*, 1997, 30, 315) have used sterically demanding substituents to make triplet carbenes that are incredibly long-lived.







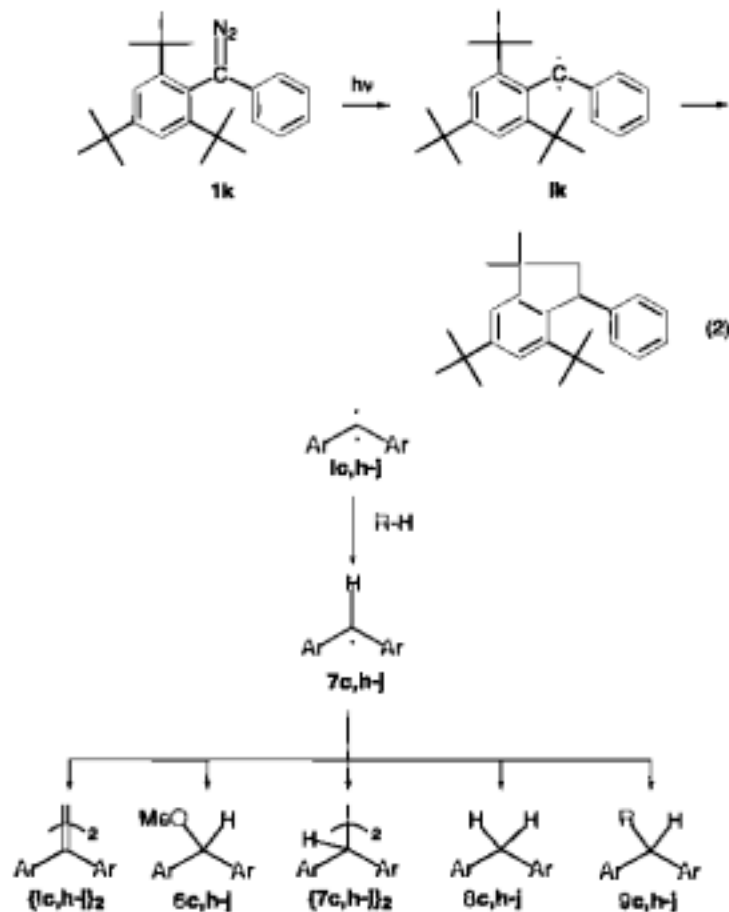
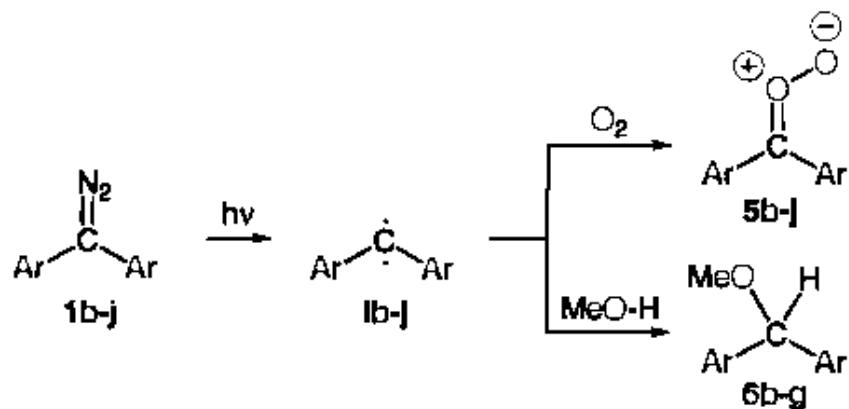
When they used bulky alkyl-substituted aryl groups such as Mesityl, Duryl or Me<sub>5</sub>C<sub>6</sub>, the half-lives increased, but the carbene reacted with the *ortho* substituents *via* a radical C-H activation process.

Thus they replaced the *o*-Me groups with a halogen of comparable size: Br. They also noticed that *meta* and *para* substituents stabilize the carbene even more. This is known as a “butressing” effect.

Table 1. Half-Life Times of Triplet Carbenes Ia–l at Room Temperature in Benzene Solution

	a	b	c	d	e	f	g	h	i	j	k	l
R <sub>1</sub>	H	F	Cl	Cl	Me	Me	Me	Br	Br	Br		
R <sub>2</sub>	H	F	H	Cl	H	Me	Me	H	H	H		
R <sub>3</sub>	H	F	Cl	Cl	Me	H	Me	Br	Me	<i>t</i> -Bu		
t <sub>1/2</sub> (ms)	0.002	0.0015	18	28	160	410	180	1000	220	16000	0.125	20
ref	26	27	28	29	30	30	30	31	31	31	30	32

In general the reactivity of triplet carbenes is as one would expect for a radical compound. The reactions include C-H and O-H cleavage or insertion as well as coupling reactions with other radicals (either with itself to give an alkene or with radicals such as  $O_2$ ).

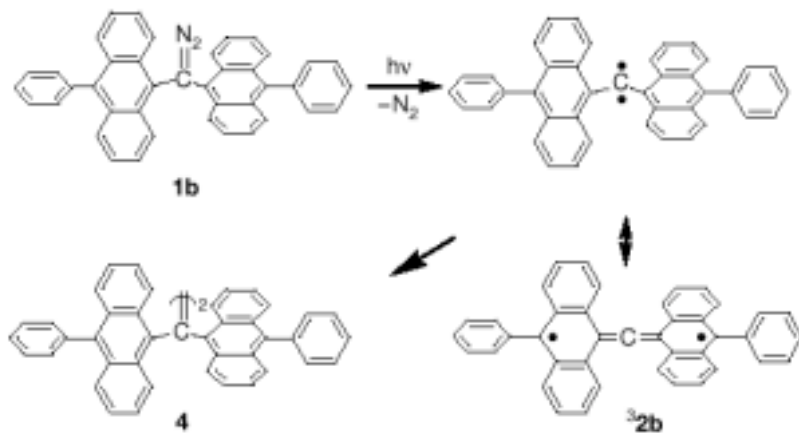


solvent	<b>(1c)2</b>	<b>6c</b>	<b>{7c}2</b>	<b>8c</b>	<b>9c</b>
PhH	> 99	-	trace	trace	-
<i>o</i> -C <sub>6</sub> H <sub>4</sub>	26	-	17	29	20
MeOH-PhH	14	61	1	24	-

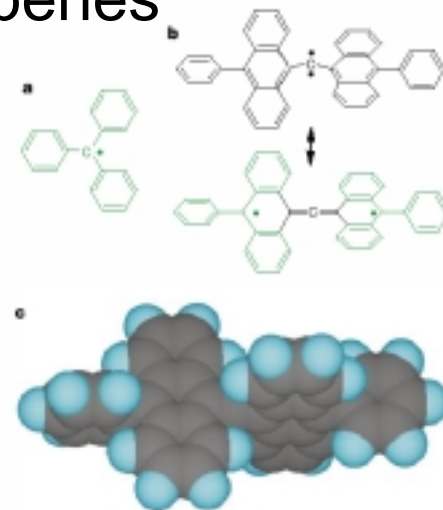
Product distribution in the photolysis of the diazo precursor **1c** at room temperature.

# Chem 59-651 The Most Stable Triplet Carbenes

The most stable triplet carbene (Tomioka, *Nature*, 2001, 412, 626) in solution actually exploits mesomeric effects in addition to steric protection. This carbene actually has a lifetime measured in minutes! Tomioka has also found that single crystal irradiation can produce triplet carbenes that are very long-lived in the solid state (Tomioka, *JACS*, 1995, 117, 6376).

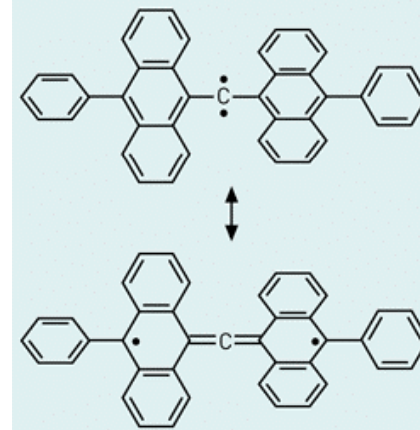


**Figure 2** Structure of triplet bis(9-anthryl)carbene (**3b**), generated by photolysis of the precursor diazomethane (**1b**), and the corresponding carbene dimer (**4**). The phenyl groups in **3b** are not expected to be in the same plane as the anthryl rings owing to the repulsion between *ortho*- and *peri*-hydrogens. This is in line with the similarity of the zero-field splitting parameters of **3b** to those of **3a**. It seems that the phenyl groups effectively prevent the unpaired electrons from 'leaking out' and thus prevent reaction at position 10.



**Figure 4** Structure of **3b** and Gomberg's radical. **a**, Structure of Gomberg's radical. **b**, Resonance structures of **3b**. The lower of these structures can be regarded as two Gomberg radicals connected by an alene bond. **c**, Space-filling model of **3b**, showing how well the carbene centre is shielded by two anthryl groups.

**LONG-LIVED**  
Delocalization stabilizes triplet carbene

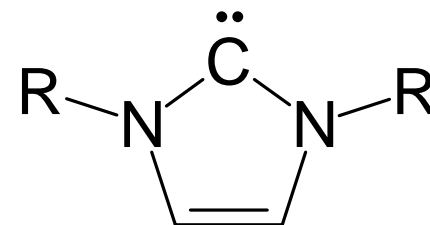
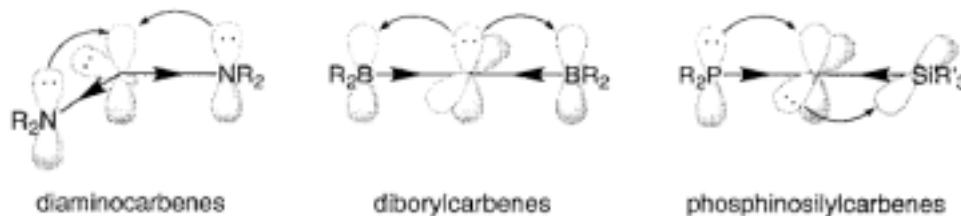


19 minute half-life!



Many simple singlet carbenes are just as short-lived as the triplet analogues. For example,  $\text{C}(\text{OMe})_2$  and  $\text{CCl}_2$  have lives in the ns to  $\mu\text{s}$  range. However they exhibit different types of reactivity than do the radical triplet carbenes. Because of their lone pair and vacant orbital, singlet carbenes can, in theory, act as either Lewis acids and Lewis bases.

The vast majority of very stable carbenes have some sort of “Push-Pull” substitution pattern that favours the singlet ground state. Furthermore, the majority of the known stable singlet carbenes are cyclic compounds in which the ring system requires the angle at the carbenic C to be less than  $180^\circ$  and also favours the singlet state.

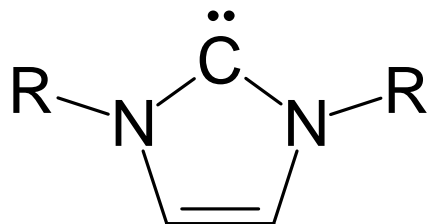


Arduengo Carbene

Figure 7. Electronic effects of the substituents for diamino-, phosphinosilyl-, and diboryl-carbenes.



The majority of stable carbenes that are commonly used today (and even commercially available) are *N*-heterocyclic carbenes of the type first isolated by A. J. Arduengo in 1991 (Arduengo, *JACS*, 1991, 113, 361; see also, Arduengo, *Acc. Chem. Res.*, 1999, 32, 913).



Arduengo Carbene  
*N*-heterocyclic carbene

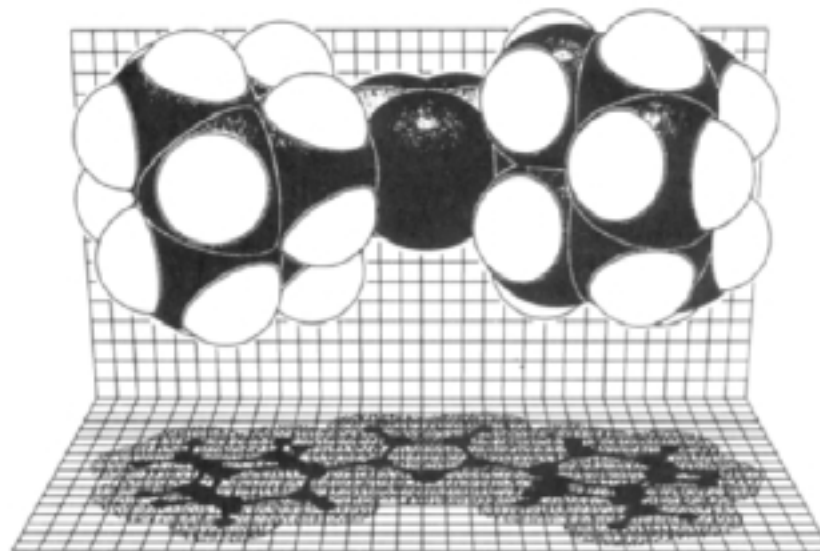
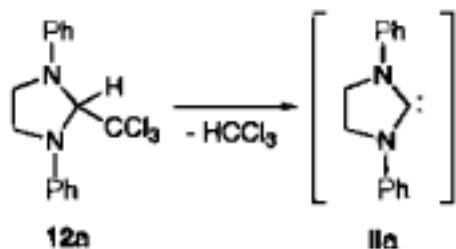


Figure 1. Space-filling KANVAS<sup>1</sup> drawing of the X-ray structure of 1.

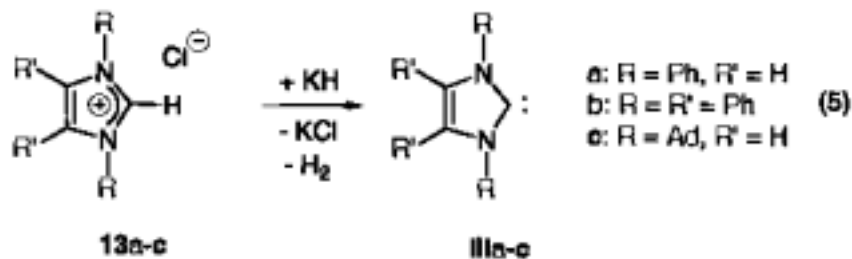
To obtain this first example of a crystalline carbene, Arduengo used a variety of methods to improve the stability of the compound. These include steric stabilization (the R groups are adamantyl ligands), the carbon has two adjacent amido substituents (*-I*, *+M* push-pull) in a cyclic system, and the  $\pi$ -system has 6 electrons and thus could be aromatic. It turns out that not all of these properties are necessary to obtain stable carbenes.

# Stable Singlet Carbenes: Synthesis

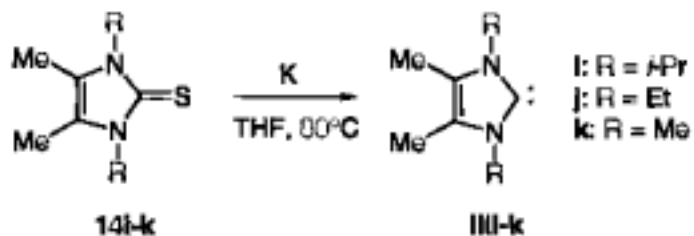
All of the *N*-heterocyclic carbenes are synthesized in a relatively straightforward manner under inert-atmosphere conditions by *in situ* reduction of a carbon (IV) center to a carbon (II) atom. (See: Bertrand, Chem. Rev., 2000, 100, 39, and references therein for the citations to the original work)



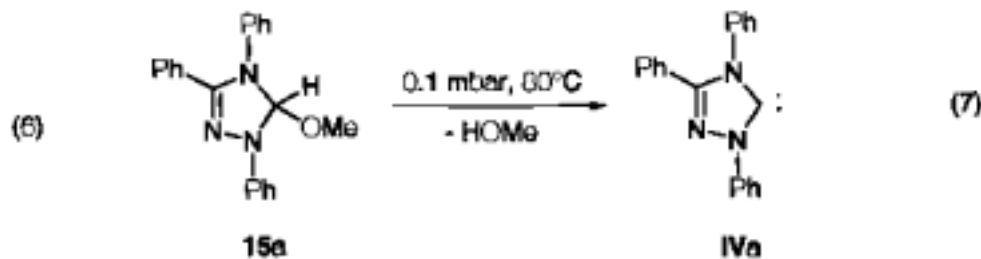
Wanzlick, 1960's



Wanzlick, 1970's; Arduengo, 1991



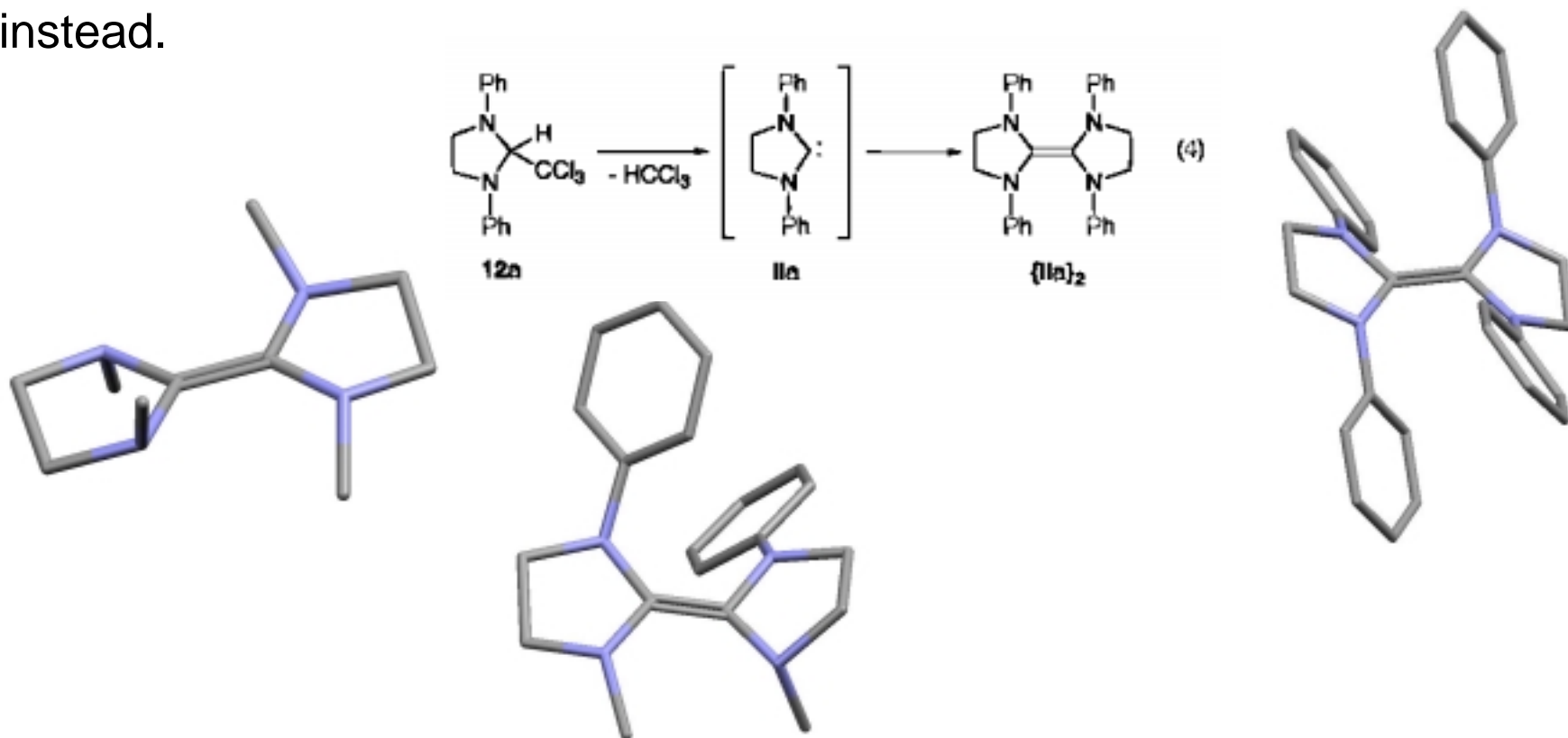
Kuhn, 1993



Enders, 1995

## Stable Singlet Carbenes

The stability of these carbenes is considered with respect to decomposition or dimerization to olefins. Unfortunately for Wanzlick, he was never able to isolate a monomeric carbene and he obtained electron-rich olefins (ERO) instead.



The difference between the results of Arduengo and Wanzlick was interpreted by some researchers to indicate that the steric bulk and “aromaticity” of Arduengo’s compound was necessary for the isolation of a stable carbene.



The need for bulky substituents was refuted by Arduengo with his synthesis of a carbene with only methyl substituents on the heterocycle (Arduengo, JACS, 1992, 114, 5530).

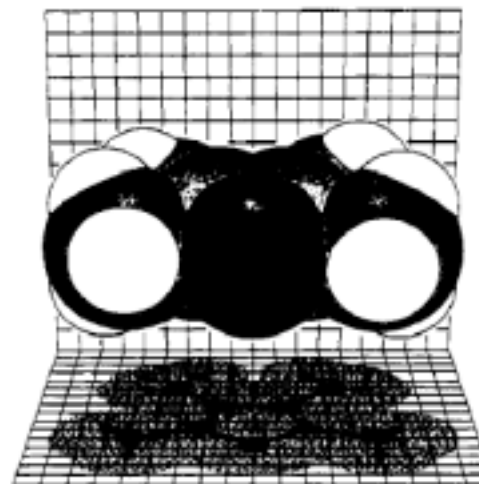
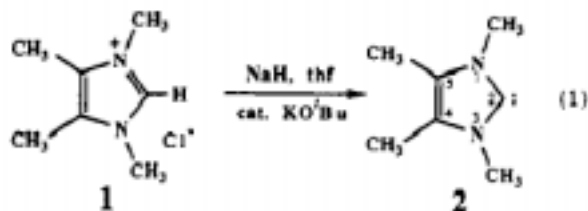


Figure 1. KANVAS<sup>5</sup> drawing of 2.

The need for “aromaticity” was refuted by Arduengo with his synthesis of a carbene with a saturated backbone (Arduengo, JACS, 1995, 117, 11027).

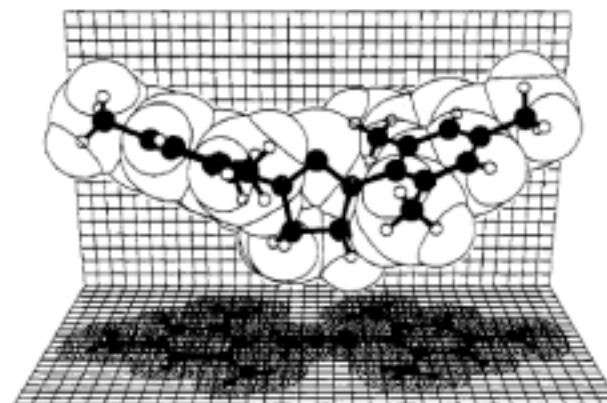
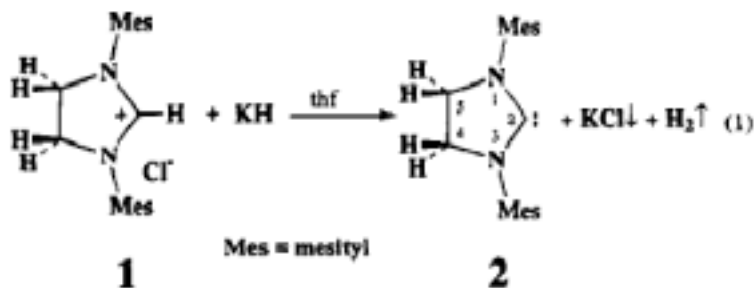
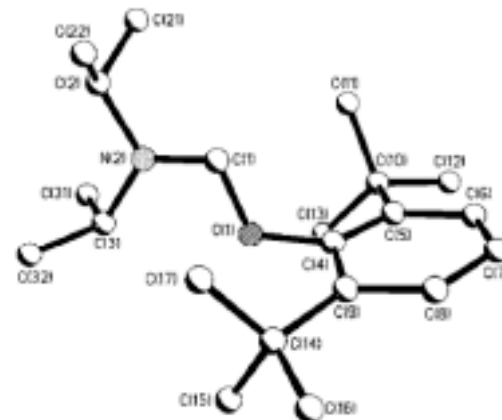
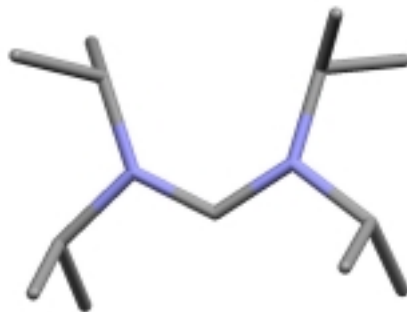
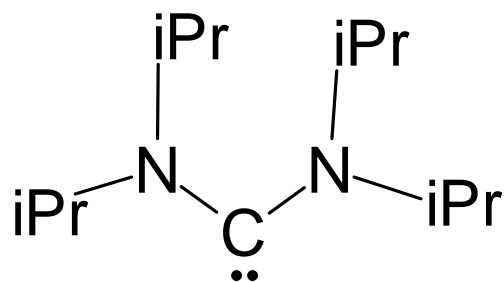


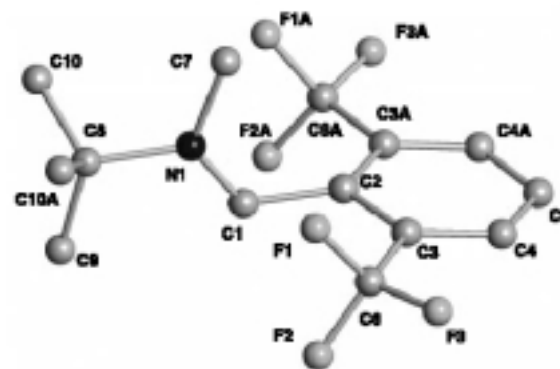
Figure 1. Space-filling KANVAS<sup>7</sup> drawing of the X-ray structure of 2.



The need for the carbenic center to be part of a heterocyclic system was disproven by Alder's synthesis of  $C(NiPr_2)_2$  (Alder, *Angew. Chem., Int. Ed.*, 1996, 35, 1121). This means that the electronic stabilization of such carbenes by the bis-amido substitution pattern makes for remarkably stable singlet carbenes. Note that the acyclic examples need at least some steric bulk or they will dimerize.

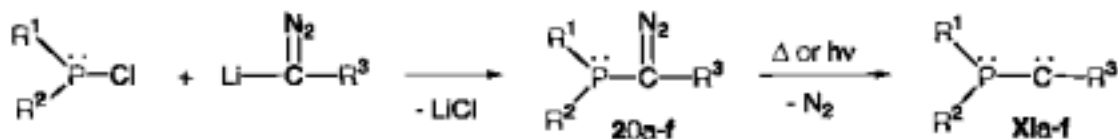


Overall, it is found that one amido substituent is capable of stabilizing the carbene if the other substituent is a heteroatom such as S, sometimes O (Alder, *JACS*, 1998, 120, 11526), and even appropriate aryl groups (Bertrand, *Science*, 2001, 292, 1901) in both cyclic and acyclic systems.



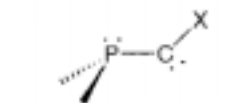
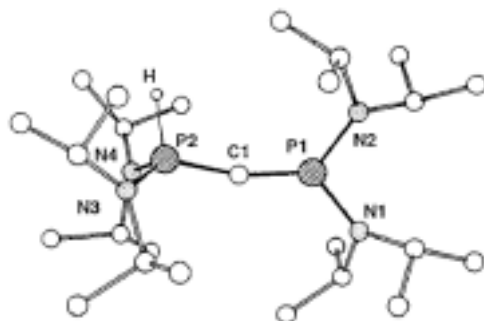


The other major class of stable singlet carbenes are the push-pull carbenes of Bertrand. These are made using the standard method used to make transient carbenes: the thermal or photochemical decomposition of a diazomethane derivative.

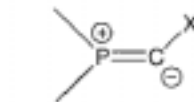


R = N*i*-Pr<sub>2</sub>; Tf = CF<sub>3</sub>SO<sub>2</sub>

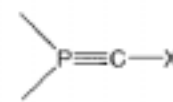
- a R<sup>1</sup> = R<sup>2</sup> = N*i*-Pr<sub>2</sub>, R<sup>3</sup> = SiMe<sub>3</sub>
  - b R<sup>1</sup> = Tmp, R<sup>2</sup> = N*i*-Pr<sub>2</sub>, R<sup>3</sup> = SiMe<sub>3</sub>
  - c R<sup>1</sup> = Tmp, R<sup>2</sup> = NMe<sub>2</sub>, R<sup>3</sup> = Si(*i*-Pr)<sub>3</sub>
  - d R<sup>1</sup> = Tmp, R<sup>2</sup> = NMe<sub>2</sub>, R<sup>3</sup> = SiMe<sub>3</sub>
  - e R<sup>1</sup> = Tmp, R<sup>2</sup> = Ph, R<sup>3</sup> = SiMe<sub>3</sub>
  - f R<sup>1</sup> = R<sup>2</sup> = N*o*-Hex<sub>2</sub>, R<sup>3</sup> = SiMe<sub>3</sub>
  - g R<sup>1</sup>, R<sup>2</sup> = N(*t*-Bu)SiMe<sub>2</sub>N(*t*-Bu), R<sup>3</sup> = SiMe<sub>3</sub>
- Tmp = 2,2,6,6-tetramethylpiperidino



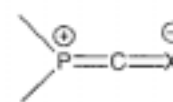
λ<sup>3</sup>-phosphinocarbene



λ<sup>4</sup>-phosphavinylidene



λ<sup>5</sup>-phosphaacetylene



λ<sup>4</sup>-phosphacumulene

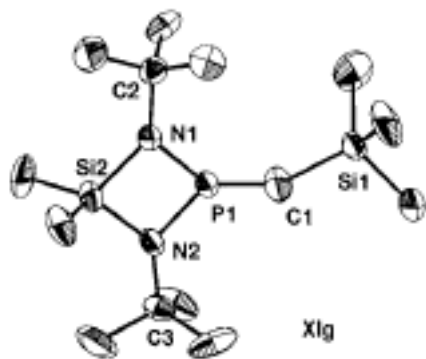
X = SiR<sub>3</sub> or PR<sub>3</sub><sup>⊖</sup>

# Stable Singlet Carbenes

Table 5. Stability of the Carbenes XI and XII and of Their Diazo Precursors 20 and 21

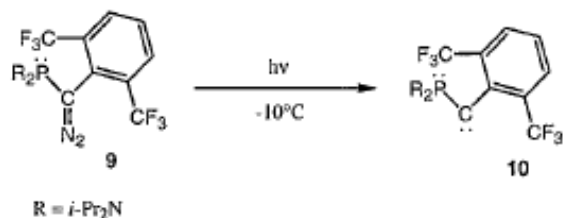


	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Diazo Stability	Carbene Stability
<b>20,XIa</b>	<i>i</i> -Pr <sub>2</sub> N	<i>i</i> -Pr <sub>2</sub> N	SiMe <sub>3</sub>	b.p. 85-90°C, 10 <sup>-2</sup> mmHg	b.p. 75-80°C, 10 <sup>-2</sup> mmHg Several weeks at 25°C
<b>20,XIb</b>	Tmp <sup>a</sup>	<i>i</i> -Pr <sub>2</sub> N	SiMe <sub>3</sub>	Few minutes at 25°C	Several weeks at 25°C
<b>20,XIc</b>	Tmp <sup>a</sup>	Me <sub>2</sub> N	Si( <i>i</i> -Pr) <sub>3</sub>	Several days at 25°C, 1 h at 35°C	Several weeks at 25°C
<b>20,XId</b>	Tmp <sup>a</sup>	Me <sub>2</sub> N	SiMe <sub>3</sub>	Several days at 25°C, 1 h at 35°C	Several weeks at 25°C
<b>20,XIe</b>	Tmp <sup>a</sup>	Ph	SiMe <sub>3</sub>	Few minutes at 25°C	Few hours at 25°C
<b>20,XIf</b>	<i>c</i> -Hex <sub>2</sub> N	<i>c</i> -Hex <sub>2</sub> N	SiMe <sub>3</sub>	Stable 24 h at 70°C	Several weeks at 25°C
<b>20,XIg</b>	<i>i</i> -BuNSiMe <sub>2</sub> N <i>t</i> -Bu	<i>i</i> -BuNSiMe <sub>2</sub> N <i>t</i> -Bu	SiMe <sub>3</sub>	Several days at 25°C	m.p. 122 °C Indefinitely at 25°C
<b>21,XIIa</b>	<i>i</i> -Pr <sub>2</sub> N	<i>i</i> -Pr <sub>2</sub> N	PR <sub>2</sub> H <sup>+b</sup>	Not observed at 25°C	m.p. 88 °C Indefinitely at 25°C
<b>21,XIIb</b>	<i>i</i> -Pr <sub>2</sub> N	<i>i</i> -Pr <sub>2</sub> N	PR <sub>2</sub> Cl <sup>+b</sup>	Not observed at 25°C	Few days at 25°C in solution



<sup>a</sup>Tmp = 2,2,6,6-tetramethylpiperidino; <sup>b</sup>R = Ni-Pr<sub>2</sub>.

The most impressive examples of the Bertrand type of push-pull carbenes are stable carbenes that exhibit the same type of reactivity as the transient carbene analogues. Generally, the groups used to stabilize carbenes result in reactivity that is different from those of the transient species.



Scheme 2.

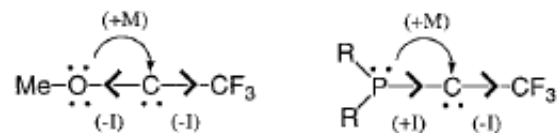
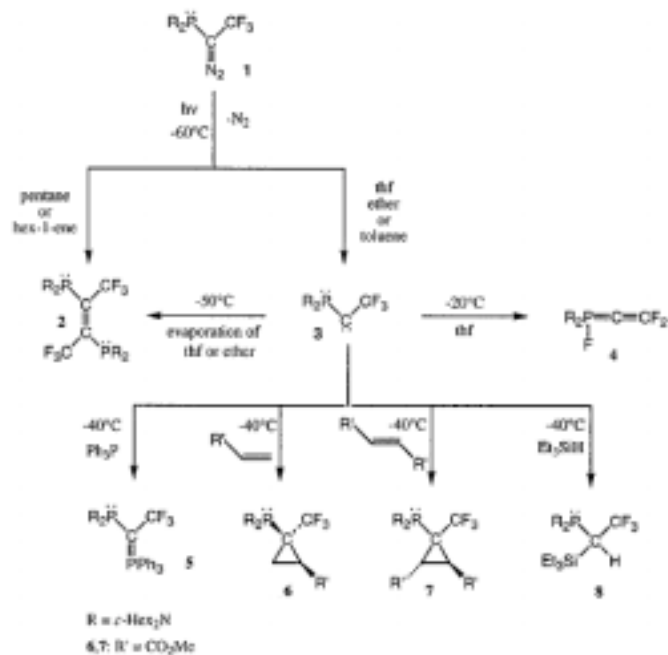
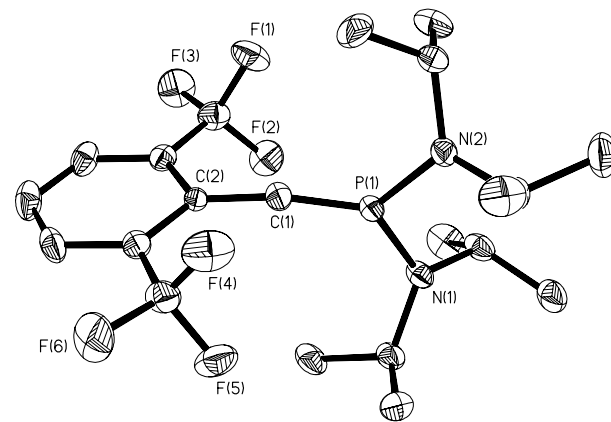


Fig. 1. Mesomeric and inductive effects of substituents on methoxytrifluoromethylcarbene and phosphanyltrifluoromethylcarbene. Me, methyl.



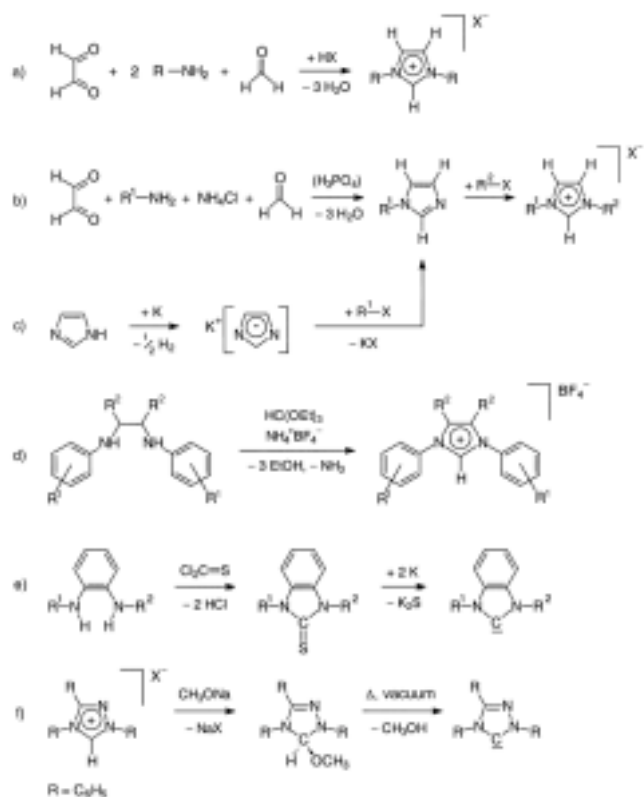
Scheme 1.  $h$ , Planck constant;  $\nu$ , photon frequency; Et, ethyl.



(Bertrand, Science, 2000, 288, 834)

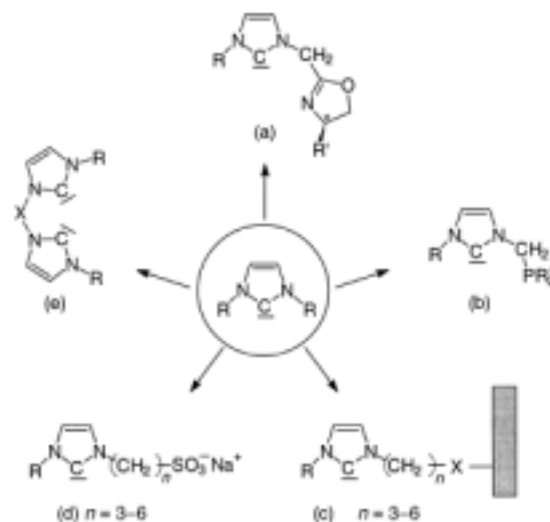
# Stable Singlet Carbenes: More Synthesis and Reactivity

Since the NHC type singlet carbenes are synthesized in a relatively simple way from suitable imidazolium precursors, the variety of substituents that can be attached to them is enormous. (See: Bertrand, *Chem. Rev.*, 2000, 100, 39, and Herrmann, *Angew. Chem., Int. Ed.*, 2002, 41, 1290 and the references therein for the citations to the original work)



Scheme 1. Convenient synthetic routes to imidazolium salts and imidazol(2)-ylidenes derived therefrom.

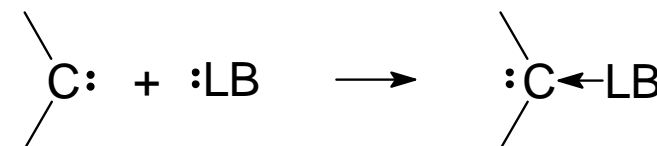
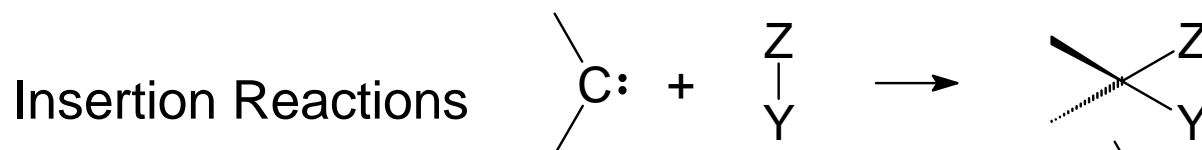
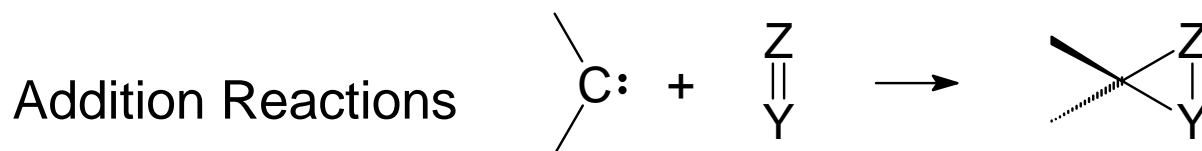
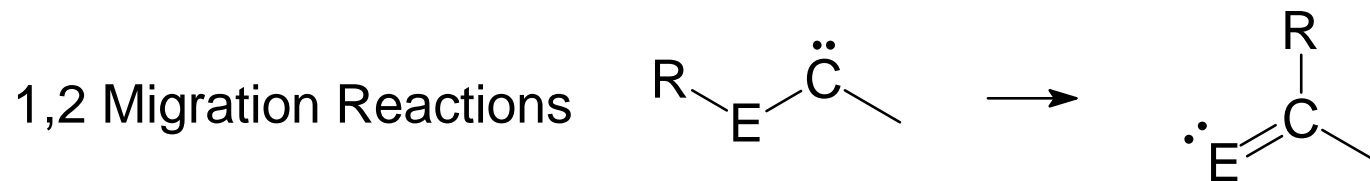
This has led to an incredible variety of carbenes that can be used for synthetic and catalytic purposes.



Scheme 6. The versatility of ylidenes derived from imidazolium compounds.

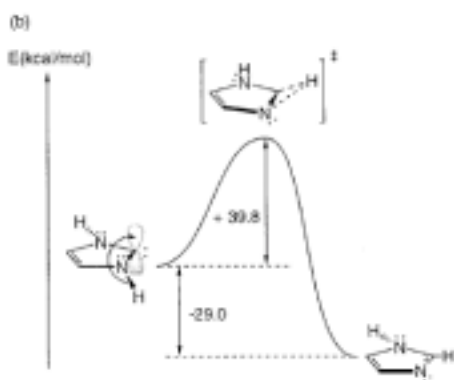
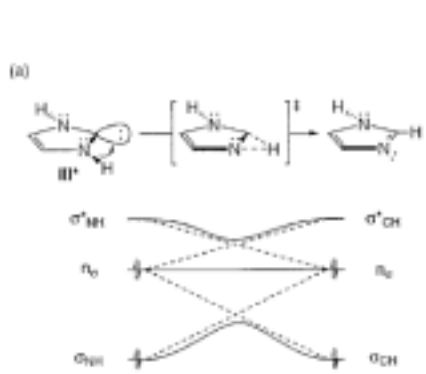
# Singlet Carbene Reactivity: Reactivity

In contrast to Bertrand's carbenes, *N*-heterocyclic carbenes (NHCs) exhibit some reactivity that is different from that of the transient singlet species. Common types of singlet carbene reactivity include:

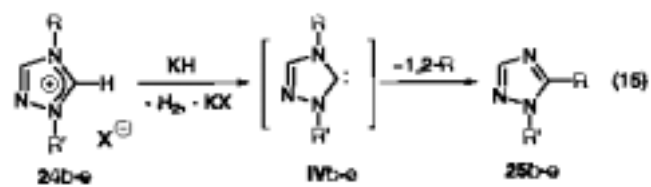


# Singlet Carbene Reactivity: Reactivity

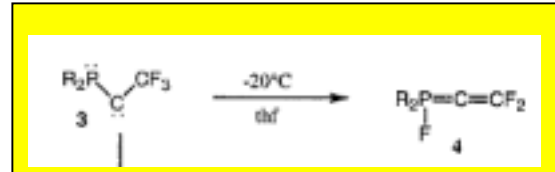
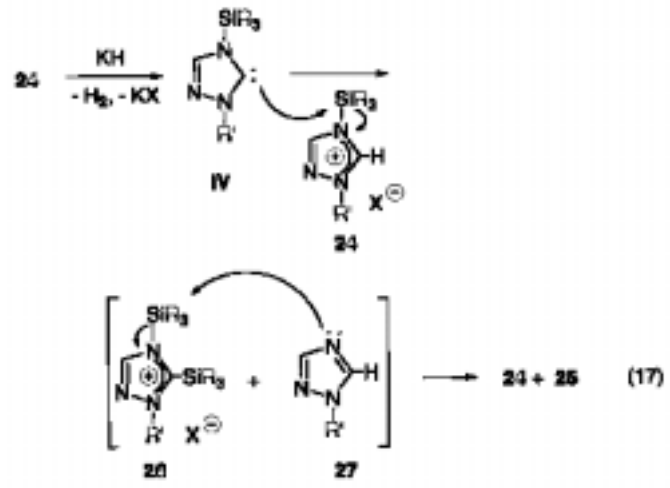
In contrast to transient singlet carbenes, *N*-heterocyclic carbenes (NHCs) do not generally undergo 1,2-migrations. When products are observed that appear to indicate a migration, they are almost always derived from an intermolecular process.



**Figure 16.** (a) Correlation diagram for the in-plane 1,2-H-migration in III\*. (b) Energy diagram for the calculated out-of-plane 1,2-H-migration in III\*.



- X: CF<sub>3</sub>SO<sub>3</sub>
- b: R = Si(i-Pr)<sub>3</sub>; R' = Me
- c: R = SiMe<sub>2</sub>NMe<sub>2</sub>; R' = Me
- d: R = Si(i-Pr)<sub>2</sub>; R' = Danz
- e: R = SiMe<sub>2</sub>NMe<sub>2</sub>; R' = Danz

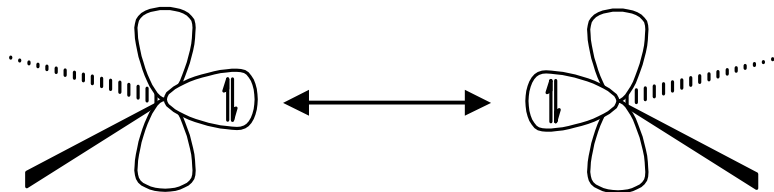


Notice that the Bertrand carbene does undergo a 1,2 migration of an F atom to the carbenic carbon, which is followed by a 1,2 migration of the F to the P atom.

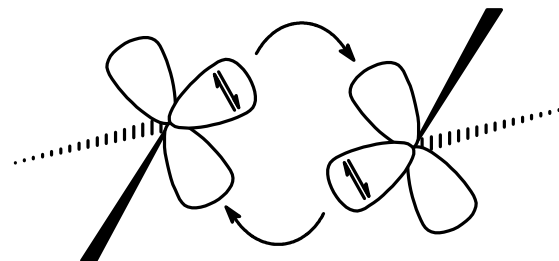
# Singlet Carbene Reactivity: Reactivity

Probably the most important aspect of singlet carbene reactivity for the purposes of this class is that of dimerization-type reactions. The types of reactions that fall into this category include the dimerization of two carbenes as well as the reaction of a carbene with another carbenoid. In contrast to the ready dimerization of transient carbenes, NHC's and related carbenes do not dimerize easily.

Reasons why NHCs do not dimerize readily can include partial population of the  $p_\pi$  orbital, steric interactions and loss of aromaticity. One feature of such reactions is that they do not occur by a least motion mechanistic pathway.



Least motion pathway

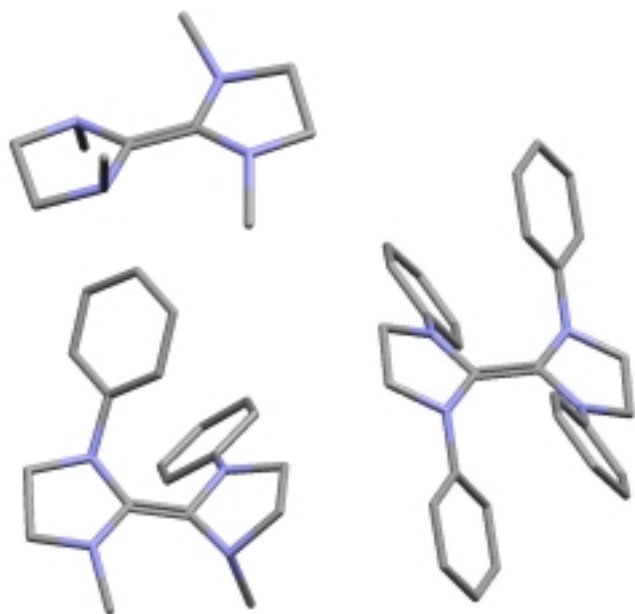


Non-least motion pathway

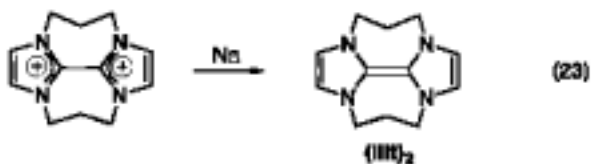
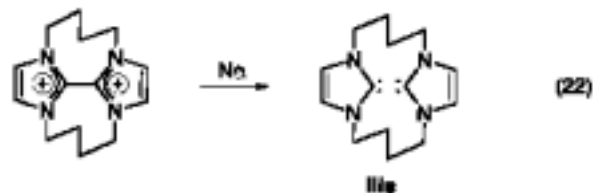
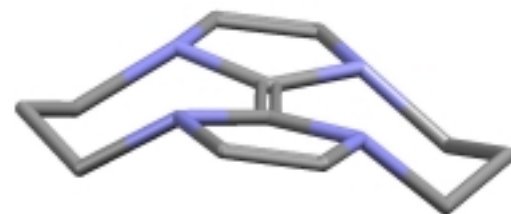
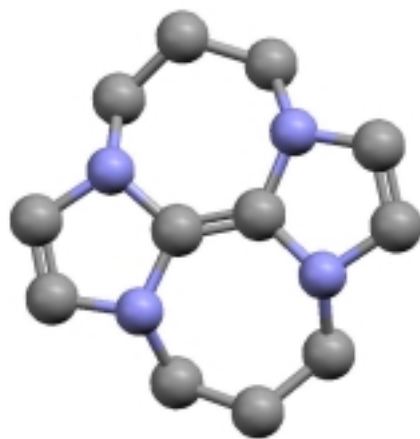


# Singlet Carbene Reactivity: Reactivity

The mechanism of dimerization also explains the structural features of the dimers that we observe. Remember that the dimerization is more favourable if the  $p_\pi$  orbital is essentially empty. We will examine this in more detail with the heavier analogues, but notice the distortions of some of the double bonds and the pyramidal nitrogen atoms in structures of the olefin dimers of some NHCs:

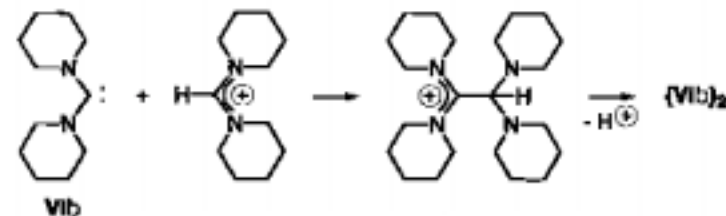
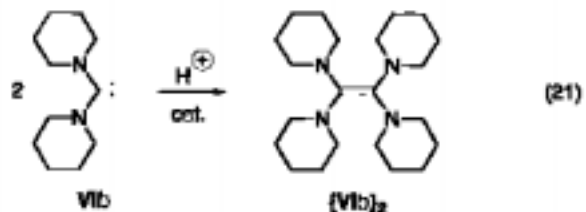
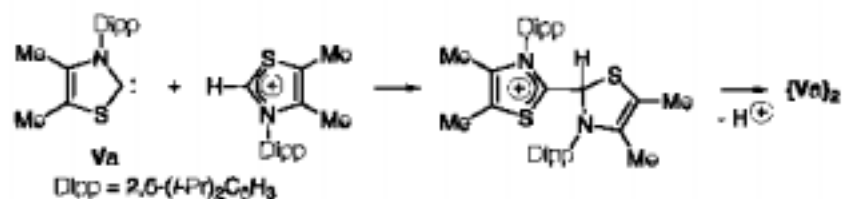
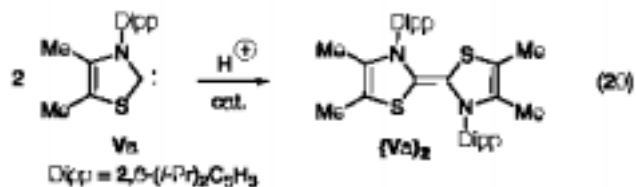


Wanzlick's ERO's

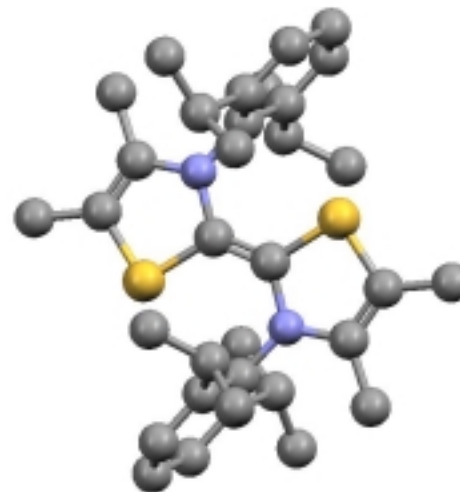
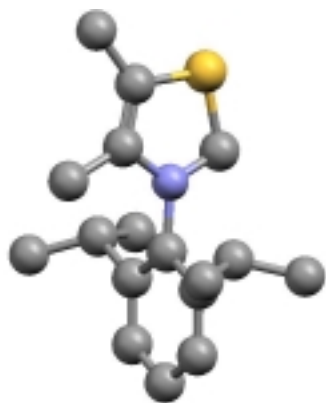


# Singlet Carbene Reactivity: Reactivity

In fact, many NHC's and related diamino carbenes will not dimerize unless there is either a Lewis acid or base present to catalyze the reaction.

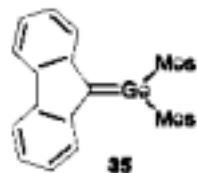
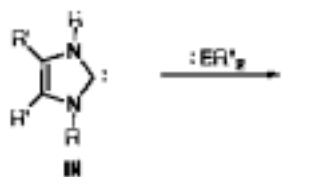


2



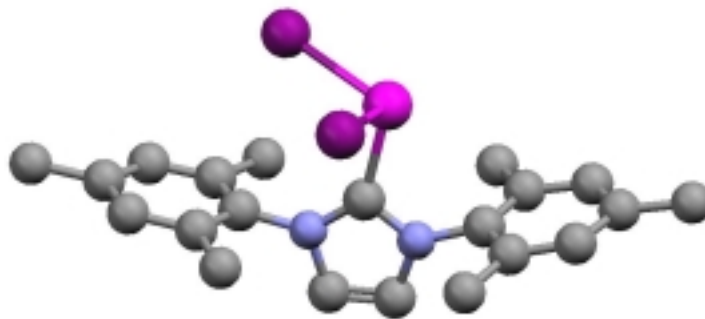
# Singlet Carbene Reactivity: Reactivity

The reaction of NHCs with other carbenoids follows a similar mechanism and generally produces highly-distorted C-element “double” bonds. Overall, the molecules often resemble the donor-acceptor complex intermediates that one would predict for the non-least motion pathway.

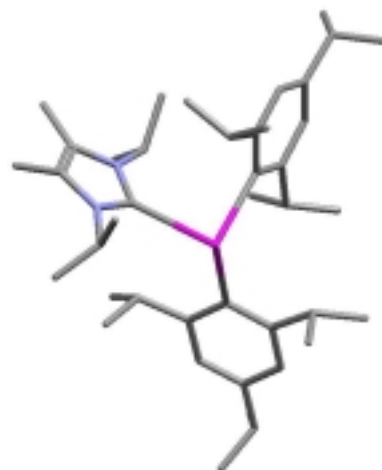


	R'	R	E	R'	yield
<b>31</b>	(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> (+Du)	Si	(NN)	83%
<b>32</b>	H	Mes	Ga	I	65%
<b>33a</b>	Me	<i>i</i> -Pr	Sn	Tipp	37%
<b>33b</b>	Me	<i>i</i> -Pr	Sn	Cl	30%
<b>34</b>	Me	<i>i</i> -Pr	Pb	Tipp	43%

(NN) = 1,2-[N(CH<sub>2</sub>+Du)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>  
Tipp = 2,4,6-(*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>



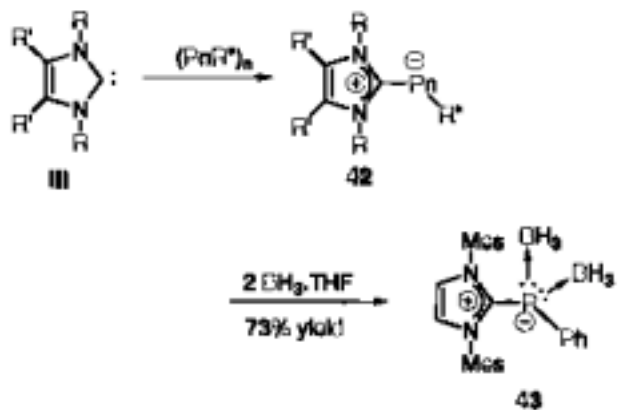
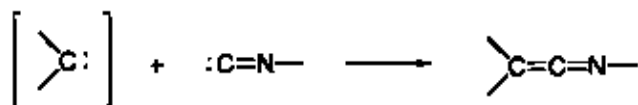
NHC-GaI<sub>2</sub> (**32**)



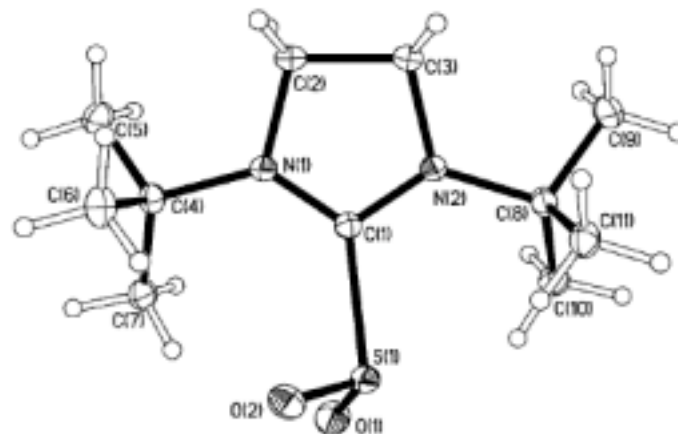
NHC-Pb(Tipp)<sub>2</sub> (**34**)

# Singlet Carbene Reactivity: Reactivity

The formation of donor-acceptor and distorted adducts is also found with other closed-shell fragments that are related to carbenoids, such as isonitriles or  $\text{SO}_2$ , while “normal” double bonded structures are sometimes obtained with triplet fragments such as nitrenes or phosphinidenes.



	R'	R	Pn	R*	yield
42a	Me	Me	P	Ph	70%
42b	H	Mes	P	Ph	87%
42c	H	Mes	P	CF <sub>3</sub>	90%
42d	H	Mes	As	Ph	46%
42e	H	Mes	As	C <sub>7</sub> F <sub>8</sub>	81%



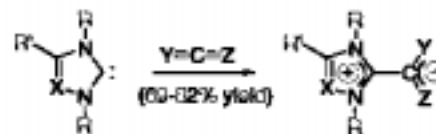
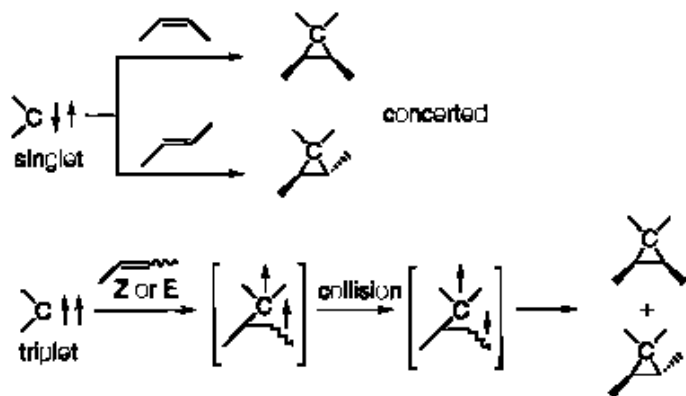
NHC-SO<sub>2</sub>

(Denk, Eur. J. Inorg. Chem., 2003, 224)

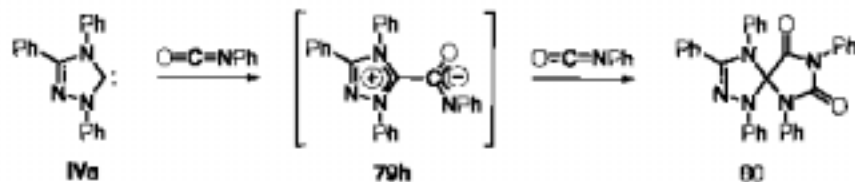


Similarly, whereas transient singlet carbenes add rapidly (and concertedly) to multiple bonds, NHCs generally do not. The NHCs will usually act as strong Lewis bases or nucleophiles instead.

Scheme 7



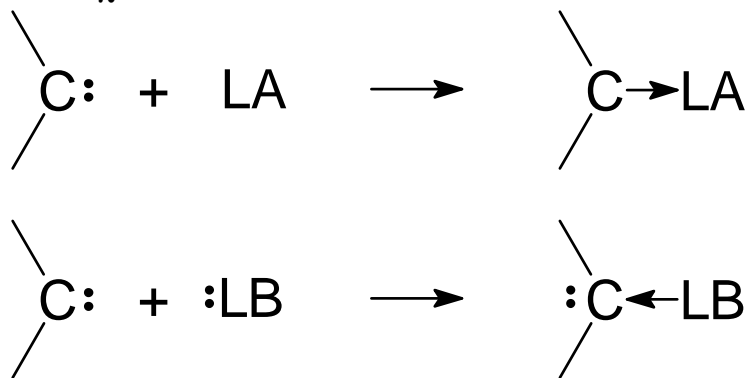
	R	R'	X	Y	Z	
III	iPr	Me	CMo	O	O	70a
III	iPr	Me	CMo	S	S	70b
III	Et	Me	CMo	S	S	70c
III	Me	Me	CMo	S	S	70d
IVa	Ph	Ph	N	S	S	70e
IVa	Ph	Ph	N	S	NPh	70f
III	iPr	Me	CMo	NPh	NPh	70g



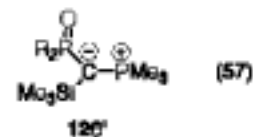
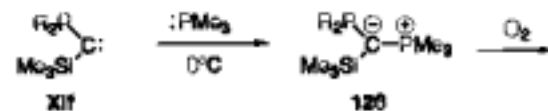
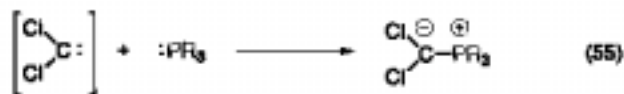
All of these observations, in conjunction with theoretical treatments of the energetics of the bonding process, were used to formulate a general theory to explain multiple bonding for the main group elements.

# Singlet Carbene Reactivity: Reactivity

Despite their potential amphiphilic/amphoteric electronic structure, NHCs most commonly react as electron donors. This is a consequence of the partial occupation of the  $p_{\pi}$  orbital that renders the NHCs stable.



Numerous examples of the Lewis base reactivity are listed in the review articles that I have given you. These include Lewis acids from  $\text{H}^+$  to many of the main group elements from the s- and p-blocks. NHCs acting as Lewis acids are essentially unknown, while transient carbenes and some of Bertrand's carbenes do exhibit such reactivity.

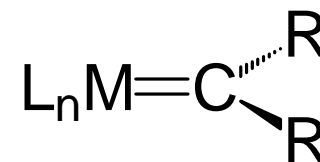


R = (o-Hex)<sub>2</sub>N

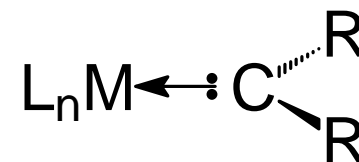
# Singlet Carbene Reactivity: Transition Metal Ligands

N-heterocyclic carbenes (NHC) have become one of the most useful and investigated classes of ligands since their discovery. NHCs are very basic and they are very strong nucleophiles. This makes them excellent donors that form stronger bonds to transition metals than ligands such as phosphines. The adducts that they make are generally best considered as Fischer carbene complexes (“electrophilic carbene” complexes in the organometallic nomenclature) and the NHC ligands are primarily strong sigma-donors and weaker pi-acceptors.

The transition metal chemistry of NHCs has been reviewed numerous times (See, for example: Herrmann, *Angew. Chem., Int. Ed.*, 2002, 41, 1290 and *Angew. Chem., Int. Ed.*, 1997, 36, 2162 or the entire issue of *J.O.M.C.*, 2001, 217-218) and the utility of NHCs as ligands has certainly been demonstrated both in the academic and patent literature.



Schrock Carbene  
(nucleophilic)



Fischer Carbene  
(electrophilic)

# Singlet Carbenes in Transition Metal Catalysts

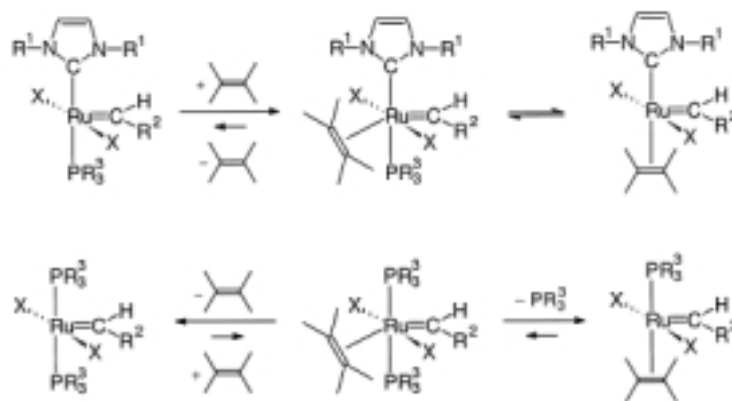
NHC ligands are advantageous for a large number of transition metal catalysts. Specific processes include: Heck and Suzuki coupling, aryl amination, Amide  $\alpha$ -arylation, hydrosilation, olefin metathesis, metathesis cross coupling, Sonogashira coupling, ethylene-CO copolymerization, Kumada coupling, Stille coupling, C-H activation, hydrogenation, hydroformylation and many more.

The NHC ligands are extremely versatile and can be designed as chelates, they can bear chiral substituents and they can even be attached to surfaces.

## Olefin Metathesis

Such ligands are now tried almost anywhere that a phosphine ligand was used in older catalysts.

Sometimes, the strength of the carbene-metal bond is not good for the catalytic cycle so one must be wise in choosing the ligands for any particular catalyst.



Scheme 2. Equilibria govern the activities of the ruthenium catalysts in olefin metathesis: olefin association versus phosphine dissociation; R<sup>1</sup> = alkyl, aryl; R<sup>2</sup> = C<sub>6</sub>H<sub>5</sub>; R<sup>3</sup> = alkyl, cycloalkyl.