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Stable Carbenes

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Contents

I. Introduction

Beginning as chemical curiosities with the pioneering work of Curtius,[1a] Staudinger,[1b] and even earlier efforts,[1c] carbenes have played an important role as transient intermediates over the last five decades.[2] Introduced by Doering into organic chemistry in the 1950s[3] and by Fischer into organometallic chemistry in 1964,[4] these fascinating species are involved in many reactions of high synthetic interest.

In the last 10 years,[5] our understanding of carbene chemistry has advanced dramatically with the preparation of persistent triplet diarylcarbenes **I**[6] and the *isolation* of heteroatom-substituted singlet carbenes (**II**−**XIV**)[7] (Figure 1). This review summarizes this fruitful part of carbene chemistry, which only started in the 1980s.[8]

The influence of the substituents on the ground-state spin multiplicity and stability of carbenes will be discussed first. Subsequently, the results concerning persistent triplet carbenes **I** will be presented. The next chapter will be devoted to the synthesis, structural, and spectroscopic features of singlet carbenes **II**−**XIV**. Last, their reactivity will be presented and compared with that observed for transient carbenes.

II. Influence of Substituents on the Electronic Structure and Stability of Carbenes

II.1. Ground-State Carbene Spin Multiplicity

Carbenes are neutral compounds featuring a divalent carbon atom with only six electrons in its valence shell. Considering a prototype carbene $-\ddot{C}-$, the carbon atom can be either linear or bent, each geometry describable by a certain degree of hybridization. The linear geometry implies an sp-hybridized

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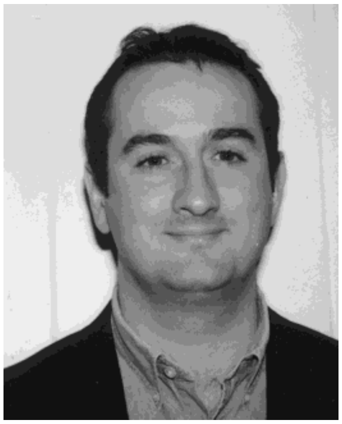
Olivier Guerret was born in 1971 in Montpellier. He entered the Ecole Polytechnique (Palaiseau) in 1991 and then joined Guy Bertrand's team in 1994 working on his Ph.D. degree, which he received in 1997. He is currently working for Elf Atochem in the Centre de Recherche Rhône Alpes and his research is mainly focused on the design of new organic catalysts for living radical polymerization.

carbene center with two nonbonding degenerate orbitals (p_x and p_y). Bending the molecule breaks this degeneracy and the carbon atom adopts an sp^2-type hybridization: the p_y orbital remains almost unchanged (it is usually called p_π), while the orbital that starts as pure p_x orbital is stabilized since it acquires some s character (it is therefore called σ) (Figure 2). The linear geometry is an extreme case; most carbenes are bent and their frontier orbitals will be systematically called σ and p_π.

As depicted in Figure 3, four electronic configurations can be envisaged. The two nonbonding electrons can be in two different orbitals with parallel spins (triplet state); hence, the molecule is correctly described by the $\sigma^1 p_\pi^1$ configuration ($^3B_1$ state). In contrast, for singlet carbenes, the two nonbonding electrons can be paired in the same σ or p_π orbital. Therefore, there are two different $^1A_1$ states, the σ^2 being generally more stable than the p_π^2. Last, an excited singlet state with $\sigma^1 p_\pi^1$ configuration can also be envisaged ($^1B_1$ state).



François Gabbaï was born in 1968 in Montpellier (France). Before joining the research group of A. H. Cowley at the University of Texas at Austin, he studied chemistry at the Université de Bordeaux (France). In 1992 and 1993, he fulfilled his French National Duties by taking part in a Franco-American cooperation under the supervision of G. Bertrand and A. H. Cowley. He completed his Ph.D. degree in 1994 and then was awarded an Alexander von Humboldt Fellowship to join the research group of H. Schmidbaur at the Technische Universität München (Germany). After two years of this collaboration, he was awarded a Marie Curie Fellowship of the European Commission and was generously offered to stay as a "Habilitand" in the Bavarian Institute. Since 1998 he has been an Assistant Professor at Texas A&M University where he is presently working on diverse aspects of p-block element chemistry.

Guy Bertrand was born in Limoges in 1952. He graduated (ingénieur ENSCM) from the Université de Montpellier and moved to the Université de Toulouse as an Attaché de Recherche CNRS in 1975. From 1988 to 1998 he was Directeur de Recherche at the Laboratoire de Chimie de Coordination du CNRS and is now the Director of the Laboratoire d'Hétérochimie Fondamentale et Appliquée at the Université Paul Sabatier. His research spans a wide range of topics at the border between organic and inorganic chemistry. He received the International Council on Main Group Chemistry Award in 1993, the Humboldt Award in 1994, and the médaille d'argent of the CNRS in 1998 and was elected Membre Correspondant of the French Academy of Sciences in 1996.

The ground-state spin multiplicity is a fundamental feature of carbenes that dictates their reactivity.[9] Indeed, singlet carbenes feature a filled and a vacant orbital, and therefore, they should possess an ambiphilic character. On the other hand, triplet carbenes have two singly occupied orbitals and are generally regarded as diradicals.

The carbene ground-state multiplicity is related to the relative energy of the σ and p_π orbitals. The singlet ground state is favored by a large $\sigma - p_\pi$ separation; Hoffmann determined that a value of at least 2 eV is necessary to impose a singlet ground state, whereas a value below 1.5 eV leads to a triplet

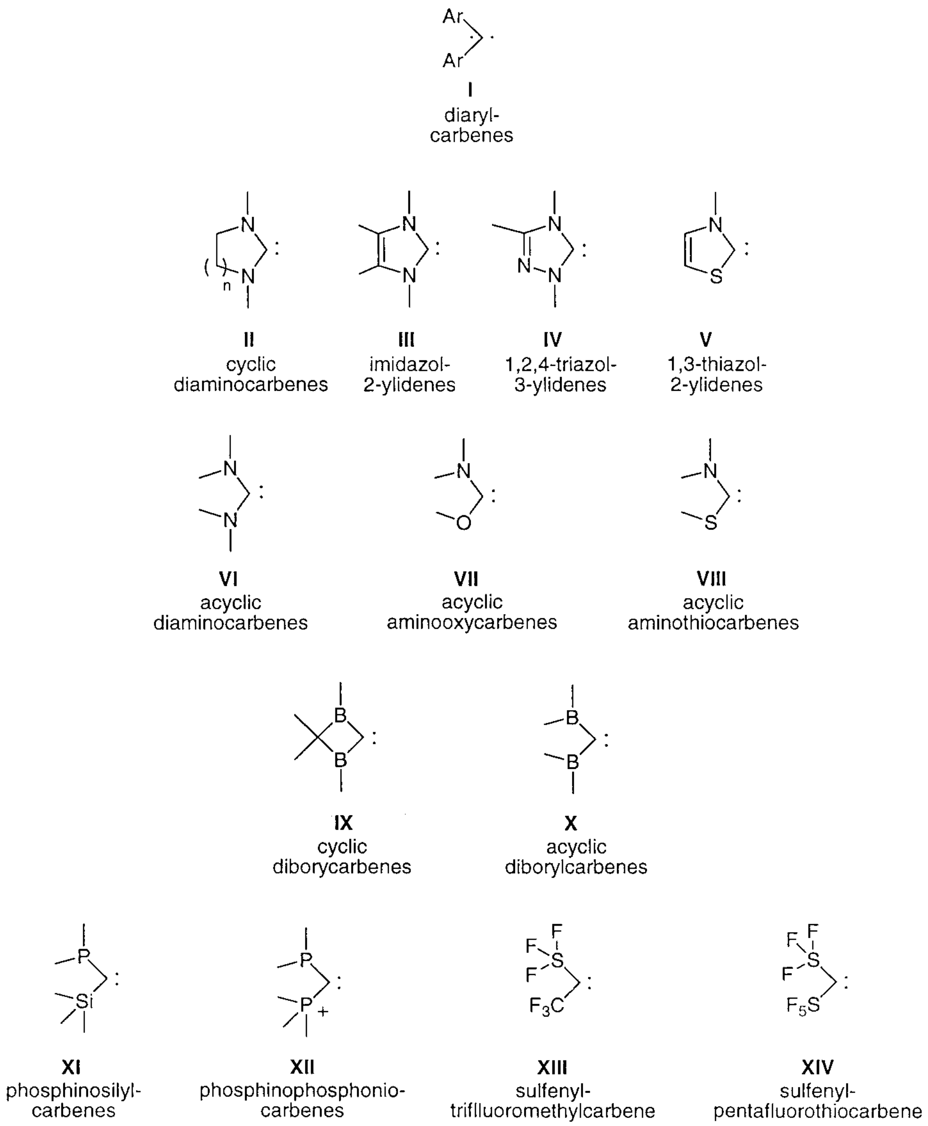


Figure 1. Triplet carbenes **I** and singlet carbenes **II**–**XIV**.

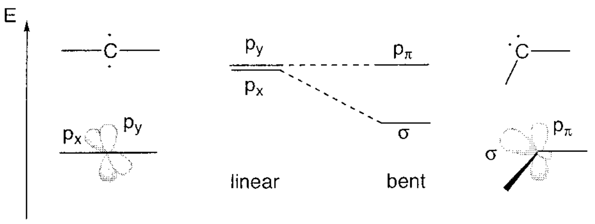


Figure 2. Relationship between the carbene bond angle and the nature of the frontier orbitals.

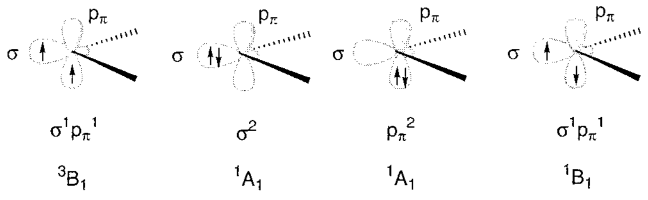


Figure 3. Electronic configurations of carbenes.

ground state.[10] There are some similarities with the crystal-field theory (strong-field low-spin and weak-field high-spin configurations).

Given these statements, the influence of the substituents on the carbene ground-state multiplicity can be easily analyzed in terms of electronic and steric effects.

II.1.1. Electronic Effects

II.1.1.1. Inductive Effects. The influence of the substituents' electronegativity on the carbene multiplicity was recognized relatively early on[11,12] and reexamined recently.[13] It is now well established that σ-electron-withdrawing substituents favor the singlet versus the triplet state. In particular, Harrison et al.[11a,c] showed that the ground state goes from triplet to singlet when the substituents are changed from electropositive lithium to hydrogen and to electronegative fluorine (although mesomeric effects surely also play a role for the latter element) (Figure 4). This effect is easily rationalized on the basis of pertubation orbital diagrams (C_{2v} symmetry). Indeed, σ-electron-withdrawing substituents inductively stabilize the σ nonbonding orbital by increasing its s character and leave the p_π orbital unchanged. The σ–p_π gap is thus increased and the singlet state is favored (Figure 5a). In contrast, σ-electron-donating substituents induce a small σ–p_π gap which favors the triplet state (Figure 5b).

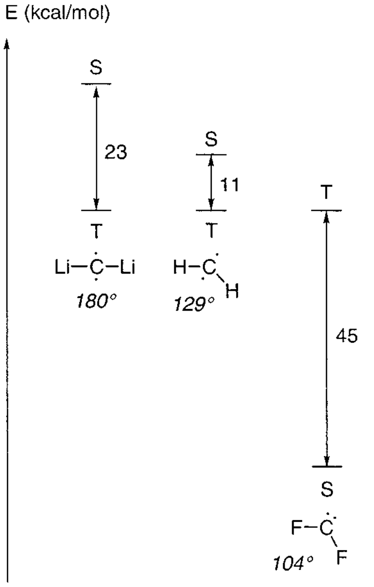
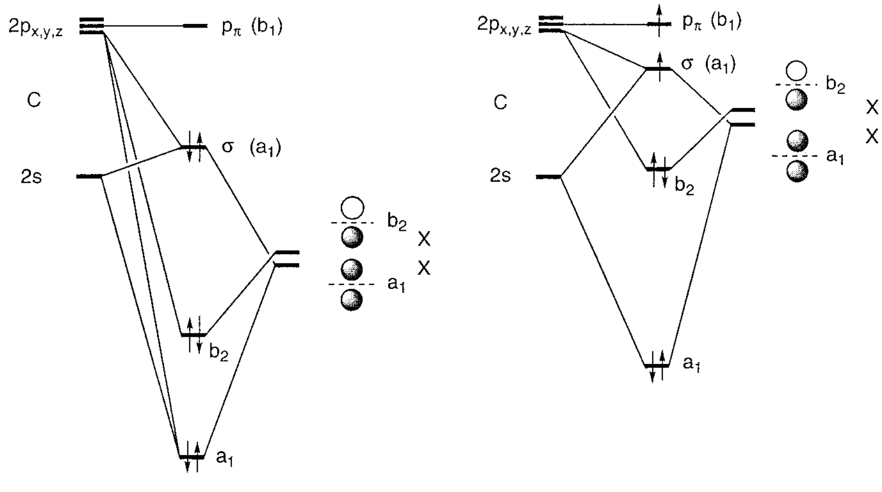


Figure 4. Influence of the substituents' electronegativity on the ground state carbene spin multiplicity.

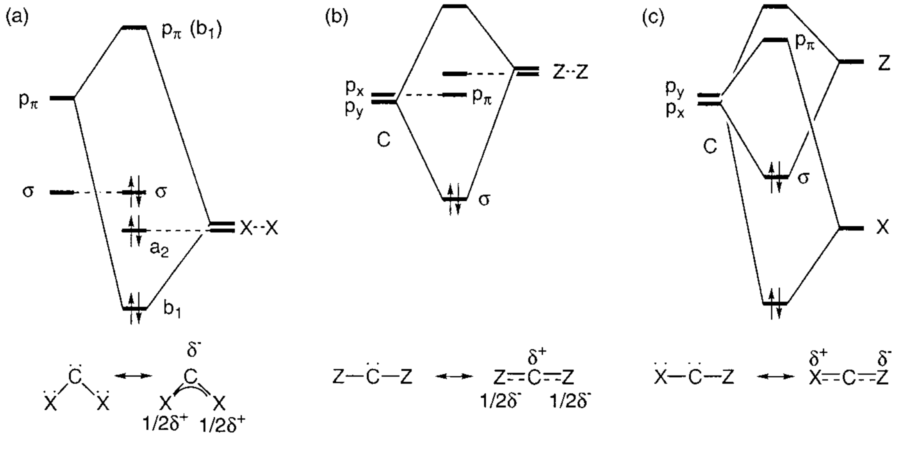
II.1.1.2. Mesomeric Effects. Although inductive effects dictate the ground-state multiplicity of a few carbenes such as the triplet Li−C−Li,[11c] mesomeric effects can play a more significant role.[14] Substituents interacting with the carbene center can be classified into two types, namely X (for π-electron-donating groups such as $-F$, $-Cl$, $-Br$, $-I$, $-NR_2$, $-PR_2$, $-OR$, $-SR$, $-SR_3$, ...) and Z (for π-electron-withdrawing groups such as $-COR$, $-CN$, CF_3, $-BR_2$, $-SiR_3$, $-PR_3^+$, ...). Therefore, the singlet carbenes considered in this review can be classified according to their substituents: the highly bent (X,X)-carbenes and the linear or quasi-linear (Z,Z)- and (X,Z)-carbenes. In all cases, the mesomeric effects consist of the interaction of the carbon orbitals (s, p_π or p_x, p_y) and appropriate p or π orbitals of the two carbene substituents. These interactions are clearly illustrated using perturbation orbital diagrams (Figure 6).

(X,X)-Carbenes are predicted to be bent singlet carbenes.[12,13] The energy of the vacant p_π orbital is increased by interaction with the symmetric combination of the substituent lone pairs (b_1). Since the σ orbital remains almost unchanged, the $\sigma-p_\pi$ gap is increased and the singlet state is favored (Figure 6a). Note that the σ orbital and the nonsymmetric combination of the substituent lone pairs (a_2) are close in energy, their relative position depending on the electronegativity of X compared to that of carbon. Donation of the X-substituent lone pairs results in a



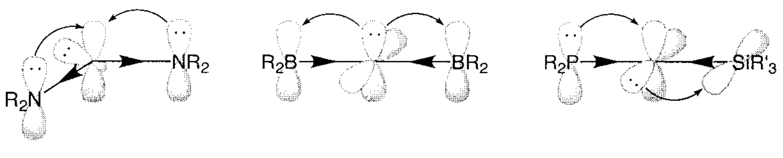
(a) σ-electron-withdrawing substituents (b) σ-electron-donating substituents

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



X: π-electron-donating substituents; Z: π-electron-withdrawing substituents

Figure 6. Pertubation orbital diagrams showing the influence of the mesomeric effects.



diaminocarbenes diborylcarbenes phosphinosilylcarbenes

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

polarized four-electron three-center π-system. The C−X bonds acquire some multiple bond character, which implies that (X,X)-carbenes are best described by the superposition of two zwitterionic structures with a negative charge at the carbene center. The most representative carbenes of this type are the transient dimethoxy-[15] and dihalocarbenes[16] and the stable diaminocarbenes that will be described in section IV.1.

Most of the (Z,Z)-carbenes are predicted to be linear singlet carbenes.[12,13] For this type of compound, the symmetric combination of the substituent vacant orbitals interacts with the p_y orbital, which is perpendicular to the valence plane (Figure 6b). This interaction does not affect the p_x orbital. Therefore, the (p_x,p_y) degeneracy is broken making these carbenes have a singlet ground state even though they are linear.[12] Note that this substitution pattern results in a polarized two-electron three-center π-system. Here also, the C−Z bonds have some multiple bond character; these (Z,Z)-carbenes are best described by the superposition of two zwitterionic structures featuring a positive charge at the carbon atom. Some of the most studied carbenes of this type are the transient dicarbomethoxycarbenes[17] and the “masked” diborylcarbenes (see section IV.2).

Last, the quasi-linear (X,Z) carbenes combine both types of electronic interaction (Figure 6c). The X substituent lone pair interacts with the p_y orbital, while the Z substituent vacant orbital interacts with the p_x orbital. These substituent effects are both stabilizing and both favor the singlet state (the vacant p_y orbital is destabilized, while the filled p_x orbital is stabilized). These two interactions result in a polarized allene-type system with XC and CZ multiple bonds. Good examples of this type of carbene are given by the transient halogenocarboethoxycarbenes[18] and by the stable phosphinosilyl- and phosphinophosphoniocarbenes (see section IV.3.1).

II.1.2. Steric Effects

Bulky substituents clearly kinetically stabilize all types of carbenes. Moreover, if electronic effects are negligible, the steric effects may also dictate the ground-state spin multiplicity.

Since the electronic stabilization of the triplet relative to the singlet state is at a maximum when the carbene frontier orbitals are degenerate (Figure 2), a linear geometry will favor the triplet state. This is illustrated by the influence of the carbene bond angle on the ground-state spin multiplicity of the parent carbene: below 90° the energy of the singlet methylene drops below that of the triplet state.[14] In the same way, increasing the steric bulk of carbene substituents broadens the carbene bond angle and therefore favors the triplet state.[19] Dimethylcarbene has a bent singlet ground state (111°),[20] while the di(*tert*-butyl)-[21a] and diadamantylcarbenes[21b] are triplets. In the latter compounds the two bulky substituents impose wide carbene bond angles (143° and 152°, respectively). Not surprisingly, cyclopentylidene[22a] has a singlet ground state due to angular constraint, as well as cyclopropenylidene,[22b,c] which combines both angular constraint and aromaticity.

II.2. Concluding Remarks

Undoubtedly, the best way to stabilize triplet carbenes kinetically consists of protecting the highly reactive carbene center by bulky substituents.

It is clear from the above discussion that it is much easier to design a substitution pattern for stabilizing singlet rather than triplet carbenes. In fact, as early as 1960, Pauling[12b] realized that the *ideal* substituents to stabilize singlet carbenes should preserve the electroneutrality of the carbene center. This can be achieved in three different ways (Figure 7), each of which has been studied experimentally.

(1) Two π-donor σ-attractor substituents, *i.e.*, a push,push mesomeric−pull,pull inductive substitution pattern. Good examples are diaminocarbenes in which the carbene electron deficiency is reduced by the donation of the two nitrogen lone pairs while the carbene lone pair is stabilized by the inductive effect of two electronegative nitrogen atoms.

(2) Two π-attractor σ-donor substituents, *i.e.*, a pull,pull mesomeric−push,push inductive substitution pattern. Diborylcarbenes are good representatives.

(3) A π-donor and a π-acceptor substituent, *i.e.*, a push,pull mesomeric substitution pattern; in this case, the inductive effects are not of primary importance. This category is illustrated by phosphinosilyl- and phosphinophosphoniocarbenes.

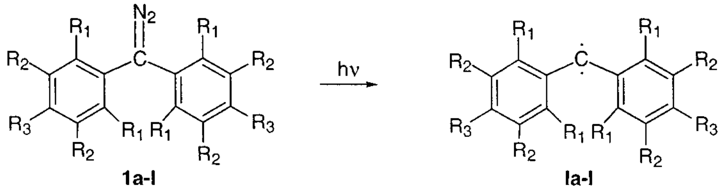
III. Persistent Triplet Carbenes

III.1. Synthesis and Stability

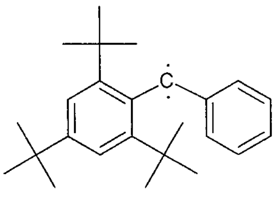
Apart from an early study by Zimmermann,[23] until the work of Tomioka et al.,[6] no attempts to generate triplet carbenes that would be stable under normal conditions had been reported. All the results obtained in this field have been recently reviewed;[6] here we will only recall the main achievements.

As discussed in the previous section, the use of bulky substituents is the only way to stabilize triplet carbenes; accordingly, sterically hindered diarylcarbenes, and especially polyhalogenated and polymethylated diphenylcarbenes, have been prepared. A recent result[24] suggests that the trifluoromethyl group on the phenyl ring could also be used efficiently to stabilize diarylcarbenes. Compounds **Ia**−**l** have

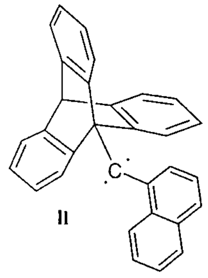
Table 1. Half-Life Times of Triplet Carbenes Ia–l at Room Temperature in Benzene Solution



I	a	b	c	d	e	f	g	h	i	j	k	l
R_1	H	F	Cl	Cl	Me	Me	Me	Br	Br	Br		
R_2	H	F	H	Cl	H	Me	Me	H	H	H		
R_3	H	F	Cl	Cl	Me	H	Me	Br	Me	t-Bu		
$t_{1/2}$ (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



Ik



Il

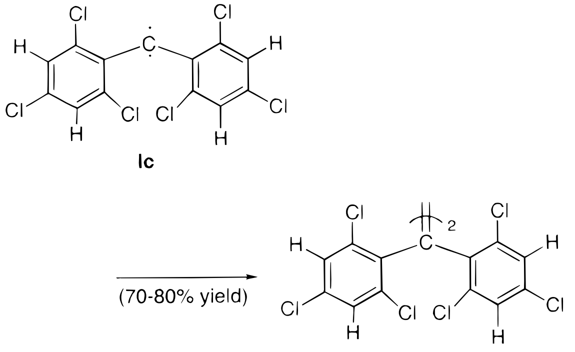
classically been prepared in low-temperature matrices by photolysis of their diazo precursors **1a–l** (Table 1) and characterized by UV and ESR spectroscopy.[25]

Their stability at room temperature is quantified by their half-life time in benzene measured by the laser flash photolysis (LFP) technique[33] (Table 1). The values obtained for the unsubstituted **Ia**,[26] the polyfluorinated **Ib**,[27] the polychlorinated **Ic**,**d**,[23,28,29] and the polybrominated **Ih–j**[31,34] diphenyl derivatives clearly demonstrate that the main factor is the steric bulk of the aryl substituents, especially at the *ortho* positions. Moreover, the results observed for polychlorinated **Ic**,**d**[23,28,29] and polymethylated **Ie–g**[23,30,35] diphenylcarbenes provide evidence for a buttressing effect[36] of the *meta* substituents. Up to now, the most stable triplet carbene is **Ij**. It is indefinitively stable at 130 K and has a half-life of 16 s at room temperature in fluid solution. It is of particular interest that it is also indefinitively stable in the crystal state at room temperature.[31,34b]

III.2. Reactivity

Zimmermann, Platz, and Tomioka have studied the reactivity of triplet carbenes **Ib–l**. The photolysis of the diazo precursors at room temperature generally leads to a highly complex mixture. However, clean reactions could be obtained by a strict control of the reaction conditions.

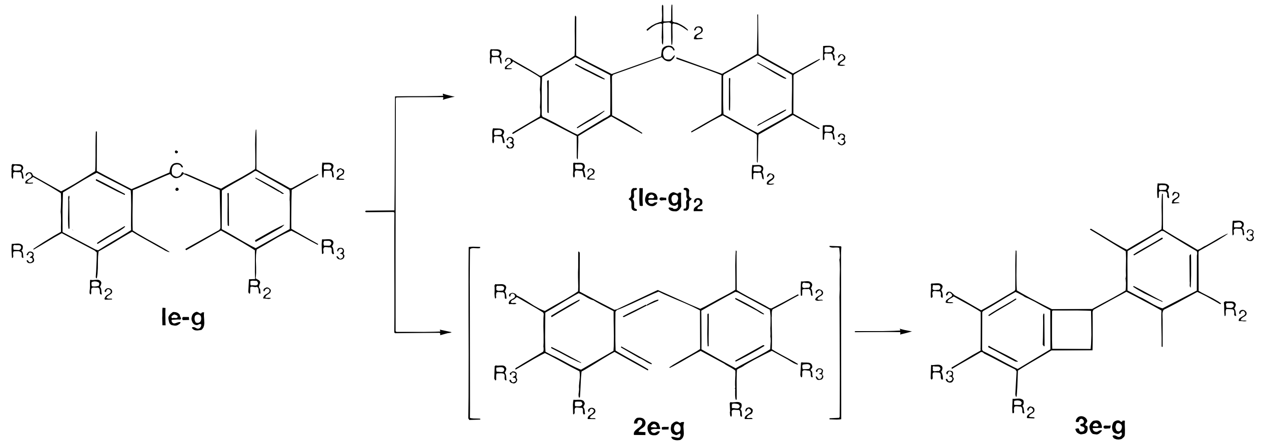
In degassed benzene, the polychlorinated diphenylcarbene **Ic** dimerizes[37] to give the corresponding tetrakis(aryl)ethylene {**Ic**}$_2$ in 70–80% yield (eq 1).[23,28,29] It is noteworthy that, so far, only small amounts of carbene dimers have been obtained with the polybrominated diphenylcarbenes **Ih–j**, probably because the carbene center is too hindered.[31] With the polymethylated diphenylcarbenes **Ie–g**, dimerization as well as intramolecular hydrogen abstraction followed by electrocyclization of the resulting transient *o*-xylylenes **2e–g** occurs (Scheme 1).[23,30,35a] The ratio {**Ie–g**}$_2$/benzocyclobutenes **3e–g** highlights the influence of the buttressing effect on the reactivity of the carbene center. Indeed, as the *ortho* methyl groups are buttressed more effectively, they are brought much closer to the carbene atom and, therefore, intramolecular H-abstraction is favored over dimerization (Scheme 1).[30,35a]



(1)

Irradiation of **1k** at room temperature gives the phenylindan **4**, presumably as the result of a stepwise

Scheme 1



Ie-g

{Ie-g}$_2$

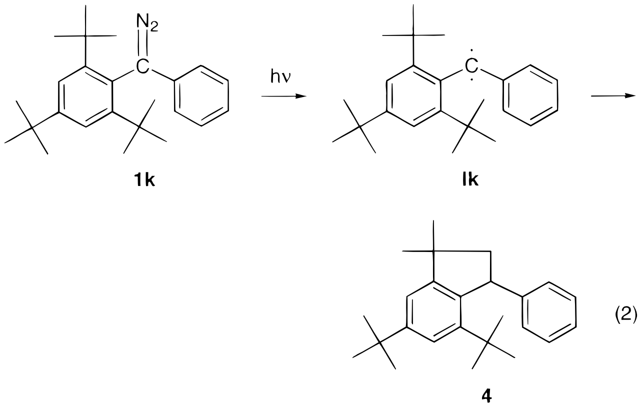
2e-g

3e-g

	R2	R3	{Ie-g}$_2$	3
e	H	Me	96	4
f	Me	H	54	46
g	Me	Me	4	96

Product distribution in the photolysis of the diazo precursors **1e-g** in benzene at 15°C.

insertion of the carbene center into a C−H bond of a *tert*-butyl group at an ortho position (eq 2).^{30,35b}



1k

Ik

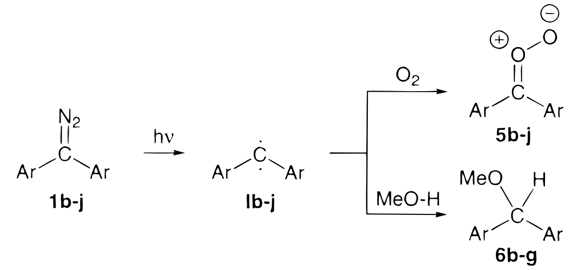
4

(2)

The reactivity of diarylcarbenes **Ib**−**j** toward various trapping agents has also been studied. Photolysis of the diazo precursors **1b**−**j** in the presence of oxygen gives the corresponding diaryl ketone oxides **5b**−**j**, which have been characterized by UV$^{27,29-32,35b}$ and even NMR^{30b} spectroscopy in the case of **5g**. Photolysis of **1b**−**g** in methanol results in the almost exclusive formation of the methyl ethers **6b**−**g**,$^{27-30,32}$ obviously produced by insertion of the carbene into the solvent O−H bond (Scheme 2).^{38}

Other hydrogen donors and especially 1,4-cyclohexadiene have been demonstrated to be effective quenchers for triplet carbenes, presumably by hydrogen-abstraction reactions. In the case of **1c** and **1h**−**j**,$^{23,27-29,31}$ the transient diaryl radicals **7c**,**h**−**j** have been spectroscopically characterized.^{28} The solvent has a dramatic effect on the product distribution as shown in the case of **Ic** (Scheme 3).^{29}

Scheme 2

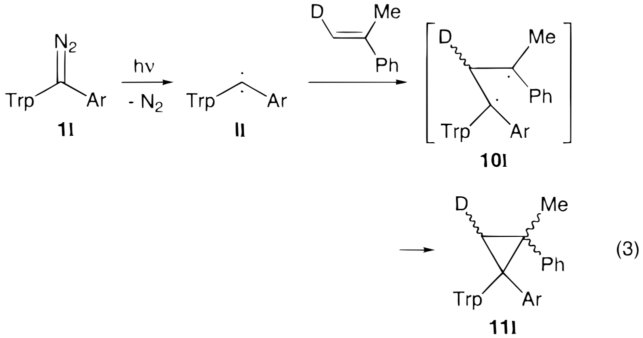


1b-j

Ib-j

5b-j

6b-g



1l

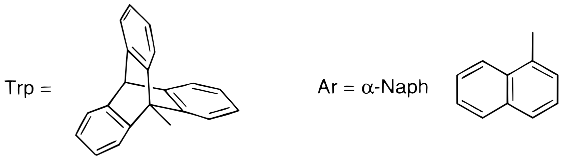
Il

10l

11l

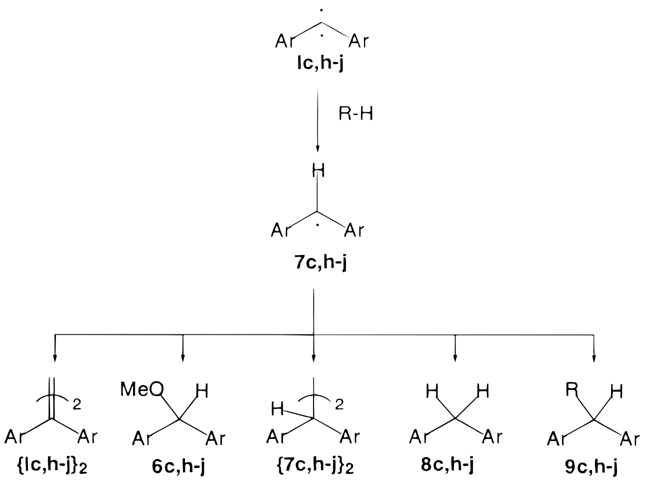
(60%)

(3)



On the other hand, the (9-triptycyl)(α-naphthyl)-carbene **Il** reacts with the (*E*)-*β*-deuterio-α-methylstyrene affording the corresponding cyclopropanes **11l** in ca. 60% yield (eq 3).^{32} During this reaction, the stereochemistry of the starting olefin was not retained in the product. Therefore, the formation of **11l** certainly results from a stepwise addition reaction via the transient biradical **10l**, the loss of

Scheme 3



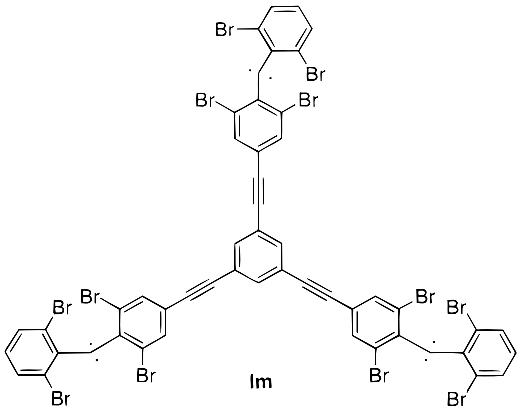
solvent	$\{Ic\}_2$	6c	$\{7c\}_2$	8c	9c
PhH	> 99	-	trace	trace	-
c-C_6H_8	26	-	17	29	28
MeOH-PhH	14	61	1	24	-

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

stereochemistry resulting from rotation about the σ C−C bonds of **10l**. So far, there is only one postulated example of three-membered ring closure by radical coupling occurring with retention of configuration.[39]

III.3. Concluding Remarks

The crystallographic characterization of a triplet carbene has yet to be achieved, and the synthesis of a triplet carbene that would be stable in room temperature solution remains an exciting challenge. These species would not only be of fundamental interest but could also find numerous applications. For example, Tomioka et al. recently characterized the triscarbene **Im** in a 2-methyltetrahydrofuran matrix.[40] The fine-structure ESR spectrum recorded at 5 K is due to a spin−septet species, and no noticeable peaks due to lower spin states were observed up to 90 K. This result demonstrates that diarylcarbenes can be efficiently connected by a topological linker, and polycarbene derivatives such as **Im** are undoubtedly of interest in the field of purely organic magnetic materials.[41]



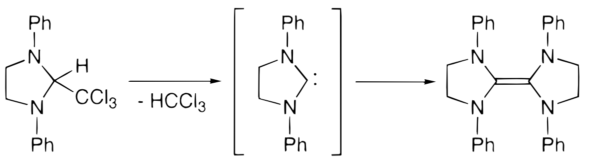
Im

IV. Stable Singlet Carbenes: Synthesis and Structural Data

As shown in section II, carbene centers are highly sensitive to electronic interactions with their substituents. Accordingly, the singlet carbenes considered in this review have been classified as (X,X)-, (Z,Z)-, and (X,Z)-carbenes. The nature of the stabilization is perceptible in the structure of the molecules, as well as in their reactivity. In the present section, the synthesis and the main structural features of each type of carbene will be successively presented. Special attention will be given to the nature of the bonding systems.

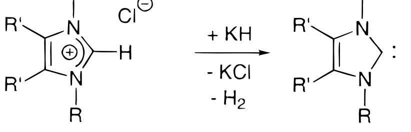
IV.1. (X,X)-Carbenes: Diaminocarbenes and Other Aminocarbenes

In the early 1960s, Wanzlick realized that the stability of carbenes could be dramatically enhanced by the presence of amino substituents and tried to prepare the 1,3-diphenylimidazolidin-2-ylidene **IIa** from **12a** by thermal elimination of chloroform (eq 4).[42] At that time, only the dimeric electron-rich olefin $\{$**IIa**$\}_2$ was isolated and cross-coupling experiments did not support an equilibrium between $\{$**IIa**$\}_2$ and the two carbene units **IIa**.[43a−c] However, recent results by Denk et al. were interpreted as providing some evidence for this equilibrium.[43d] In 1970, Wanzlick and co-workers demonstrated that imidazolium salts **13a**,**b** could be deprotonated by potassium *tert*-butoxide to afford the corresponding imidazol-2-ylidenes **IIIa**,**b**, which were trapped but not isolated.[44] Following this principle, almost two decades later Arduengo et al. prepared “*A Stable Crystalline Carbene*”.[45] Compound **IIIc** was obtained in near quantitative yield by deprotonation of the 1,3-di-1-adamantylimidazolium chloride **13c** with sodium or potassium hydride in the presence of catalytic amounts of either t-BuOK or the dimethyl sulfoxide anion (eq 5). The colorless crystals of **IIIc** are thermally stable and melt at 240−241 °C without decomposition. Interestingly, Herrmann and co-workers showed that the deprotonation occurs much faster with liquid ammonia as the solvent (homogeneous phase), and oxygen, nitrogen, and phosphorus N-functionalized **IIId**−**f** as well as chiral **IIIg** and bis-imidazol-2-



(4)

12a **IIa** $\{$**IIa**$\}_2$

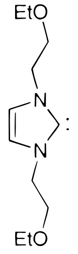


a: R = Ph, R' = H
b: R = R' = Ph
c: R = Ad, R' = H

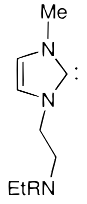
(5)

13a-c **IIIa-c**

ylidenes **IIIh** have been prepared following this procedure.[46] In 1993, Kuhn and co-workers developed a new and versatile approach to the alkyl-substituted N-heterocyclic carbenes **IIIi**−**k**.[47] This original synthetic strategy relied on the reduction of imidazol-2(3*H*)-thiones **14i**−**k** with potassium in boiling THF (eq 6). Last, Enders et al. reported in 1995 that the 1,2,4-triazol-5-ylidene **IVa** could be obtained in quantitative yield from the corresponding 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazole **15a** by thermal elimination (80 °C) of methanol in vacuo (0.1 mbar) (eq 7).[48] Compound **IVa** became the first carbene to be commercially available.

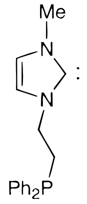


IIId

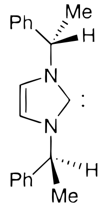


IIIe

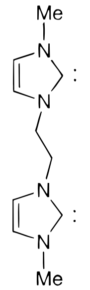
R = H, Et



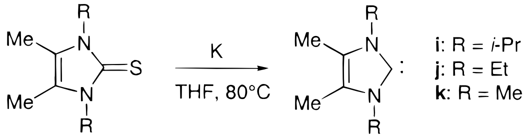
IIIf



IIIg

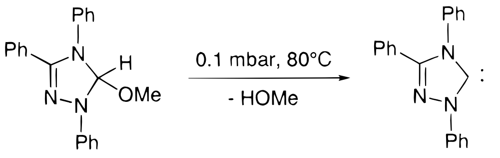


IIIh



(6)

14i-k **IIIi-k**



(7)

15a **IVa**

Following these synthetic routes, a number of stable aminocarbenes have been isolated: imidazolidin-2-ylidenes **II**,[49] tetrahydropyrimid-2-ylidene **II′**,[50] imidazol-2-ylidenes **III**,[45−47,51−54] 1,2,4-triazol-5-ylidenes **IV**,[48] 1,3-thiazol-2-ylidenes **V**,[55] as well as acyclic diamino- **VI**,[56,57] aminooxy- **VII**,[58] and aminothiocarbenes **VIII**[58] (Table 2). For all of these compounds, the carbene center bears two π-donor substituents, of which at least one is an amino group. The superior π-donor ability and therefore the superior stabilizing effect of amino versus alkoxy groups has been evidenced experimentally. Indeed, the bis(dimethylamino)carbene $Me_2N-\ddot{C}-NMe_2$ **VIc** can be observed by NMR spectroscopy at room temperature,[57] while the dimethoxycarbene $MeO-\ddot{C}-OMe$ has only been characterized in matrices at low temperature (lifetime in solution at room temperature: 2 ms).[15]

The carbene carbon of **II**−**VIII** resonates at rather low field in ^{13}C NMR spectroscopy ($\delta = 205-300$ ppm) (Table 2) compared to the corresponding carbon atom of the cationic precursors ($\delta = 135-180$ ppm). More precisely, the ^{13}C chemical shift of the carbene center is in the range 205−220 ppm for the unsaturated heterocyclic carbenes **III**−**IV** while it is approximately 15−25 ppm downfield for the corresponding saturated carbenes **II**, the benzimidazol-2-ylidene **IIIr** being at the border between both types (231 ppm). Last, the carbene center of all the acyclic aminocarbenes **VI**−**VIII** resonates at even lower fields (235−300 ppm).

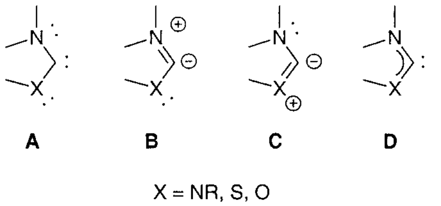


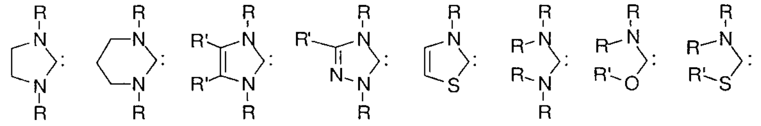
Figure 8. Resonance structures for aminocarbenes.

The solid-state structure of derivatives **IIb**,**c**, **IIIb**,**c**,**k**−**n**,**p**,**q**, **IVa**, **Va**, **VIa**, and **VIIa** has been elucidated by single-crystal X-ray diffraction studies (Table 2). The bond angle observed at the carbene center (100−110°) is in good agreement with that expected for singlet carbenes of this type. The larger value observed in the acyclic diaminocarbene **VIa**[56] (121.0°) probably results from severe steric effects. The nitrogen atoms of the amino group are always in a planar environment, and the $N-\ddot{C}$ bond lengths are rather short (1.32−1.37 Å). It is noteworthy that similar structural data are observed for their iminium salt precursors, the N−C bond lengths being only a little shorter (1.28−1.33 Å). These data as a whole indicate that the CN bonds have some multiple bond character, which results from the donation of the nitrogen lone pairs to the carbene vacant orbital. This is confirmed by the large barriers to rotation about the $N-\ddot{C}$ bond determined for **VIa** and **VIIb** (13 and at least 21 kcal/mol, respectively) by variable-temperature solution NMR experiments.[56,58] Therefore, for many purposes, diaminocarbenes are best described by resonance forms **B** and **C**, which may be summarized by structure **D** (Figure 8). For aminothio **Va**,[55] **VIIIa**,[58] and aminooxycarbenes **VIIa**,[58] the $S-\ddot{C}$ and $O-\ddot{C}$ bonds have very little π-character,[59] and therefore, the best representation for these monoaminocarbenes is provided by resonance form **B**.

Several ab initio studies have been performed for the parent compounds **II***−**VI*** (Table 3).[60−66] The calculated structural data for the singlet ground state are in very good agreement with those determined experimentally. Indeed, the nitrogen atoms are predicted to deviate only slightly from planarity and the $N-\ddot{C}$ bond lengths are short (1.33−1.38 Å). In cyclic aminocarbenes **II***−**V***, the value of the carbene bond angle is predicted to be in the range 98−105°. A somewhat larger value is obtained for the parent acyclic diaminocarbene **VI*** (111−113°). These data not only highlight the influence of ring effects in derivatives **II**−**V**, but also corroborate the role of steric effects in **VIa**, for which a larger carbene bond angle has been experimentally observed (121.0°).

In the triplet state for **II***, **III***, and **VI***, the $N-\ddot{C}$ bonds are significantly elongated (by 6.2 pm on average), the geometry at the nitrogen atoms becomes pyramidal, and results classically[60] in an opening up of the carbene bond angle. These data as a whole indicate that the donation of the nitrogen lone pairs is now negligible. Interestingly, the cal-

Table 2. Pertinent Structural Data (Bond Lengths in Å and Bond Angles in Deg) and Chemical Shifts (in ppm) for the Aminocarbenes II–VIII



II II' III IV V VI VII VIII

	R	R'	X-ray data NC	CX	θ (NCX)	^{13}C RMN δ C:	ref
IIb	Mes		1.352	1.345	104.7	244.5	49a
IIc	*t*-Bu		1.348	1.347	106.4	238.3	49b
IId	Me					239.8	49b
IIe	Et					237.7	49b
IIf	*i*-Pr					236.8	49b
II'a	*i*-Pr					237.4	50
IIIb	Ph	Ph	1.369	1.369	102.1	219.6	51
IIIc	Ad	H	1.367	1.373	102.2	211.4	45
IIIi	*i*-Pr	Me				205.9	47
IIIj	Et	Me				211.1	47
IIIk	Me	Me	1.363	1.363	101.5	213.7	47,52
IIIl	Mes	H	1.365	1.371	101.4	219.7	53a
IIIm	Tol	H	1.371	1.375	101.2	215.8	53a
IIIn	*p*-ClPh	H	1.368	1.368	101.7	216.3	53a
IIIo	Me	H				215.2	53a
IIIp	*t*-Bu	H	1.362	1.362	102.0	213.2	52
IIIq	Mes	Cl	1.364	1.364	101.9	219.9	53b
IIIr	Dmpr[b]	$(CH)_4$	1.361	1.374	103.5	231.5	54
IVa	Ph	Ph	1.373	1.351	100.6	214.6	48
Va[a]	Dipp[c]	Me	1.344	1.711	104.2	254.3	55
			1.347	1.720			
VIa	*i*-Pr		1.363	1.381	121.0	255.5	56
VIb	Pip[d]					236.8	57
VIc	Me					244.4	57
VIIa	*i*-Pr	Dtbp[e]	1.319	1.379	109.3	267.3	58
VIIb	Me	Dtbp[e]				263.3	58
VIIc	*i*-Pr	Dmph[f]				262.8	58
VIId	Pip[d]	Me				277.8	58
VIIIa	Me	Dtbp[e]				296.6	58

[a] Two crystallographic unique molecules; [b] Dmpr = $-CH_2-C(CH_3)_3$; [c] Dipp = 2,6-(i-Pr)$_2C_6H_3$; [d] Pip = piperidino; [e] Dtbp = 2,6-(t-Bu)$_2C_6H_3$; [f] Dmph = 2,6-$Me_2C_6H_3$

culated bond angle for the triplet **VI***[60] (130.8°) is similar to that of the triplet methylene (130.2°).[13] This value can hardly be reached in the triplet state of the five-membered ring carbenes **II*** and **III***, which might, in part, explain why the calculated singlet–triplet gap is higher for **II*** and **III*** (69.4 and 84.5 kcal/mol, respectively) than for the acyclic diaminocarbene **VI*** (58.5 kcal/mol).[60] This large gap

Table 3. Calculated Geometrical Parameters (Bond Lengths in Å and Bond Angles in Deg) for the Parent Aminocarbenes II*–VI* (S for Singlet, *T* for triplet)

state	NC:	XC:	θ (NCN)	level of theory	ref
			II*		
S	1.337	1.337	105.0	HF/TZ2P	60
S	1.357	1.357	103.4	MP2/6-31G(d)	61a
T	*1.411*	*1.411*	*112.6*	*HF/TZ2P*	60
			III*		
S	1.352	1.352	101.9	TCSCF/DZ	62
S	1.345	1.345	101.6	HF/TZ2P	60
S	1.371	1.371	99.4	MP2(FC)/6-31G**	63
S	1.350	1.350	101.5	CASSCF/ANO	64
S	1.373	1.373	100.9	MP2/6-31G(d)	61
T	*1.419*	*1.419*	*112.2*	*HF/TZ2P*	60
T	*1.402*	*1.402*	*106.8*	*CASSCF/ANO*	64
			IV*		
S	1.377	1.353	98.5	MP2/6-31G**	66
			V*		
S	1.355	1.722	103.4	MP2(FC)/6-31G**	63
S	1.331	1.331	113.1	HF/TZ2P	60
S	1.346	1.346	111.5	MP2/6-31G(d)	61a
T	*1.391*	*1.391*	*130.8*	*HF/TZ2P*	60

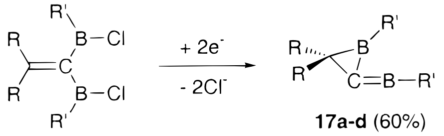
will have further consequences on the behavior of these diaminocarbenes toward dimerization (see section V.2.1).

The stability of singlet carbenes **II**–**VIII** mainly results from electronic effects [mesomeric (+M) as well as inductive (−I) effects], even though steric hindrance certainly plays an important contribution.[49b] In addition, the aromatic character of the 6-π-electron five-membered ring carbenes **III**–**V** has recently gained credence, despite being somewhat ill-defined and being a subject of controversy.[61,65] At the outset, Dixon and Arduengo[62] explained the extraordinary stability of these carbenes as essentially resulting from the inductive effect of the neighboring nitrogen atoms. The nitrogen lone pairs and the C=C double bond were supposed to ensure enough kinetic stability because of their high electron density, a notion that was supported by a variety of different experimental techniques.[52,67,68] A subsequent study by Cioslowski[69] even came to the conclusion that the π-donation by the nitrogen lone pairs plays only a minor role. The end of the controversy came in 1996 when Apeloig[61a] and Frenking[61b] independently investigated the importance of the aromaticity in carbenes **III**. According to structural, thermodynamic, and magnetic criteria as well as from the π populations and ionization potentials, it was concluded that cyclic electron delocalization does indeed occur in the imidazol-2-ylidenes **III**. This has been confirmed by inner-shell electron energy loss spectroscopy.[65] Although this aromatic character is less pronounced than in the imidazolium salt precursors **13**, it brings an additional stabilization of ca. 25 kcal/mol.[61a] However, aromaticity is not the major stabilizing effect for carbenes of type **III**. More important is the interaction of the carbene center with the π-donating σ-attracting amino substituents. This explains why aminocarbenes of types **II** and **VI**–**VIII** can also be isolated.

IV.2. (Z,Z)-Carbenes: Diborylcarbenes

No diborylcarbenes have yet been isolated. However, as shown below, the borylmethyleneboranes **17** and **19** can be considered as their masked analogues,[7b,c] and therefore, these (Z,Z)-type carbenes have been included in the present discussion.

In the early 1980s,[70] Berndt et al. prepared the boriranylideneboranes **17a**–**d** by reduction of the corresponding 1,1-bis(chloroboryl)ethylenes **16a**–**d** (eq 8).



16a-d

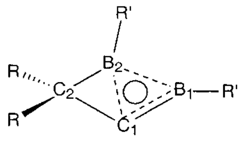
17a-d (60%)

(8)

a: R = SiMe$_3$, R' = *t*-Bu
b: R = SiMe$_3$, R' = Dur
c: R = SiMe$_3$, R' = Mes
d: R = GeMe$_3$, R' = Dur
Mes = 2,4,6-Me$_3$C$_6$H$_2$
Dur = 2,3,5,6-Me$_4$C$_6$H

The X-ray diffraction study performed on **17d**[71] and the ab initio calculations performed for the model methyleneborane **17***[72] were in excellent agreement and demonstrated that compounds **17** had a nonclassical structure. They feature both σ- and π-three-center–two-electron (3c,2e) bonds, as depicted in Table 4 (the circle designates the 3c,2e π-bond and the dotted triangle represents the 3c,2e σ-bond). The nonclassical bridging structure of **17** results not only from σ–π interaction[73] (hyperconjugation) between the strained endocyclic C–B single bond and the highly electrophilic dicoordinate boron atom, but also from a π–π interaction between the BC double bond and the electrophilic tricoordinate boron atom.

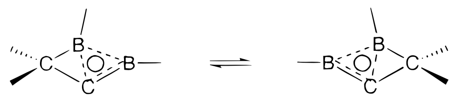
Table 4. Experimental and Calculated Structural Data for 17d and 17*, respectively (Distances in Å, Angles in Deg)



17d: R = GeMe$_3$, R' = Dur
17*: R = R' = H
Dur = 2,3,5,6-Me$_4$C$_6$H

	17d[71]	**17***	
		DZ + P[72a]	6-31G*[72b,c]
C$_2$-B$_2$	1.617(8)	1.590	1.581
C$_1$-B$_2$	1.545(9)	1.539	1.527
C$_1$-C$_2$	1.475(8)	1.456	1.454
C$_1$-B$_1$	1.351(9)	1.346	1.339
B$_1$-B$_2$	1.839(9)	1.824	1.825
B$_1$-C$_1$-B$_2$	78.5(4)	78.1	78.8

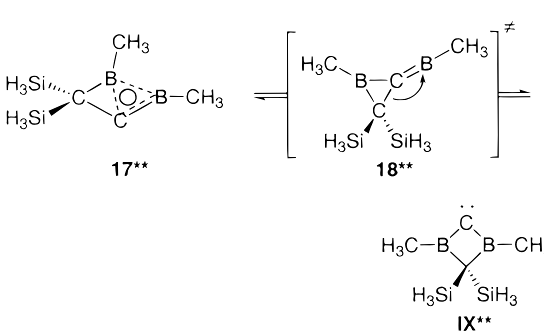
On the basis of variable-temperature multinuclear NMR spectroscopy, Berndt et al. noticed quickly that compounds **17** exhibit a topomeric equilibrium at room temperature in solution (eq 9).[70] From the



(9)

17 17'

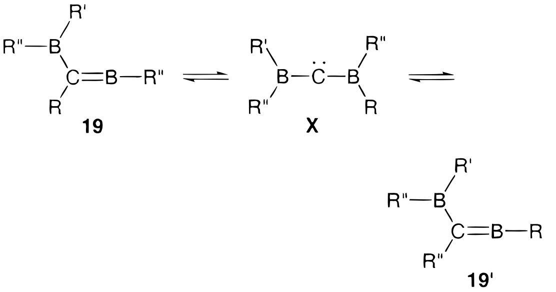
coalescence temperatures (−47, −30, and −11 °C for ^{1}H, ^{13}C, and ^{11}B NMR, respectively) and the accompanying chemical shift differences, the energy barrier of this reaction was estimated to be 11.4−12.5 kcal/mol. This value is in good agreement with that predicted by ab initio calculations (15.3 kcal/mol for the model compound **17**** at the HF/6-31G level).[72b,c] Moreover, Schleyer et al. showed that the topoisomerism proceeds via the transition state **18**** and through the intermediate cyclic di(boryl)carbene **IX****, which is predicted to be only 10.2 kcal/mol higher in energy than **17**** (eq 10).[72c] These results



(10)

as a whole suggested that the boriranylideneboranes **17** could act as masked cyclic diborylcarbenes **IX**.

More recently, Berndt et al. reported that facile topomerizations also occur for acyclic compounds **19** (eq 11).[74] The corresponding free activation enthal-



(11)

19a-Xa-19'a: R = Me, R' = All, R'' = Dur
19b-Xb-19'b: R = Et, R' = All, R'' = Dur
19c-Xc-19'c: R = Neopentyl, R' = All, R'' = Dur
19*-X*-19'*: R, R', R'' = Me
Dur: 2,3,5,6-Me_4C_6H
All: CR=C=C$(SiMe_3)_2$

pies were determined experimentally for **19b** (22.0 kcal/mol) and **19c** (23.0 kcal/mol). The intermediacy of acyclic diborylcarbenes **X** in these 1,2-migration reactions was supported by MP2/6-31G* calculations. Indeed, the model diborylcarbene **X*** (R = R′ = Me) was predicted to be 23.1 kcal/mol higher in energy than the related borylmethyleneborane **19***, and the corresponding energy barrier from **X*** to **19*** was assumed to be low (0.1−0.4 kcal/mol).[74,75]

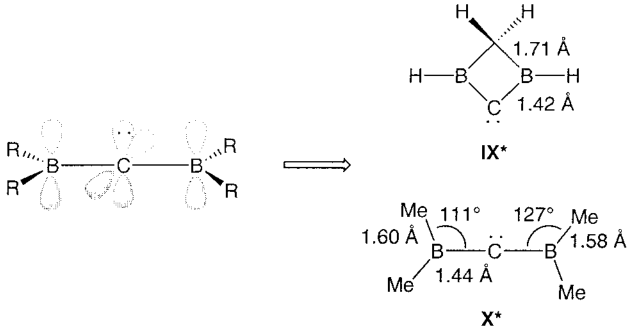


Figure 9. Influence of the electronic structure of diborylcarbenes on their geometry.

Opposite electronic effects are involved in diborylcarbenes and diaminocarbenes. In compounds of types **IX** and **X**, the carbene center strongly interacts with two σ-donor π-acceptor substituents [carbenes of the (Z,Z) series]. The carbene lone pair, which is in a p orbital, is stabilized by π delocalization with the parallel p orbital of the two boron atoms, and thus, the R_2BCBR_2 skeleton is perfectly planar, the BCB fragment being linear in unconstrained acyclic systems. Moreover, the vacant carbene p orbital, which lies in this plane, interacts with only one of the two B−R σ bonds of each of the boryl substituents (Figure 9). A preference for one of the two equivalent σ bonds is typically[73] observed for electron-deficient centers that strongly interact with neighboring σ bonds. These effects are reflected in the optimized structure of **X***:[74] the B−C̈ bonds (1.44 Å) are short and equal, the $CBCH_3$ angles are alternatively small and large (1110 and 127°), and the B−CH_3 bonds associated with the small angles are significantly elongated (1.60 compared to 1.58 Å). In cyclic diborylcarbenes such as **IX***,[72b,c] boron−carbon π bonding is also evident from the short B−C̈ bonds (1.42 compared to 1.71 Å for the B−CH_2 bonds) and π-orbital populations (C, 1.37; B, 0.29) (Figure 9).

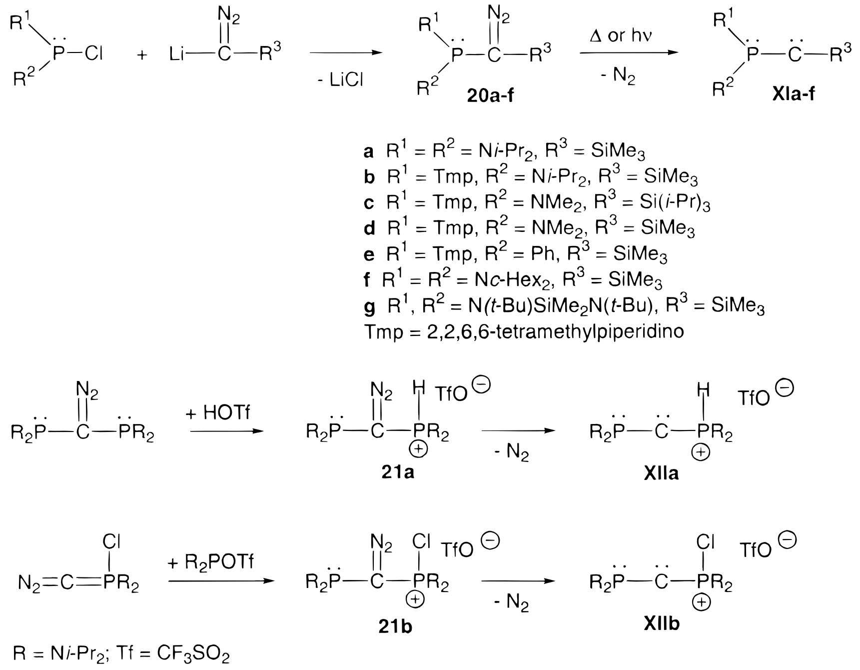
Although diborylcarbenes still have to be isolated in this form, borylmethyleneboranes **17** and **19** can be used as their synthetic equivalents as experimentally demonstrated by trapping reactions (see sections V.2.2 and V.6).

IV.3. (X,Z)-Carbenes

IV.3.1. Phosphinosilyl- and Phosphinophosphoniocarbenes

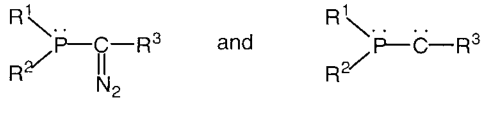
In contrast to the other stable carbenes, it is the most classical route to transient carbenes, namely, the decomposition of diazo compounds, which has been used to prepare stable phosphinocarbenes. λ^5-Phosphorus-substituted diazo derivatives have been known for a long time,[76] but the synthesis of the first α-diazophosphine was only reported in 1985.[77] The [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane **20a** was obtained by treatment of the lithium salt of trimethylsilyldiazomethane with 1 equiv of bis(diisopropylamino)chlorophosphine. Dinitrogen elimination occurs by photolysis (300 nm)[78] or thermolysis (250 °C under vacuum),[8c] and the corresponding phosphinosilylcarbene **XIa** was isolated as a red oily material in 80% yield (Scheme 4). It is stable for weeks at room temperature and can even be purified by flash distillation under vacuum (10^{-2} Torr) at 75−80 °C. A number of phosphinosi-

Scheme 4



lylcarbenes have been prepared using the same procedure,[7d−g] but only a few of them **XIa−g** are stable at room temperature. During the course of our study, we realized that, as expected, bulky substituents kinetically stabilize phosphinocarbenes, but interestingly, the stability of carbenes is often inversely proportional to that of the diazo precursors (Table 5).[79] The silyl group at the carbene center can

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

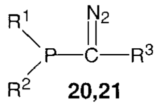


20,21 **XI,XII**

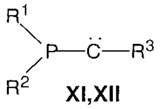
	R^1	R^2	R^3	Diazo Stability	Carbene Stability
20,XIa	$i\text{-}Pr_2N$	$i\text{-}Pr_2N$	$SiMe_3$	b.p. 85-90°C, 10^{-2} mmHg	b.p. 75-80°C, 10^{-2} mmHg Several weeks at 25°C
20,XIb	Tmp[a]	$i\text{-}Pr_2N$	$SiMe_3$	Few minutes at 25°C	Several weeks at 25°C
20,XIc	Tmp[a]	Me_2N	$Si(i\text{-}Pr)_3$	Several days at 25°C, 1 h at 35°C	Several weeks at 25°C
20,XId	Tmp[a]	Me_2N	$SiMe_3$	Several days at 25°C, 1 h at 35°C	Several weeks at 25°C
20,XIe	Tmp[a]	Ph	$SiMe_3$	Few minutes at 25°C	Few hours at 25°C
20,XIf	$c\text{-}Hex_2N$	$c\text{-}Hex_2N$	$SiMe_3$	Stable 24 h at 70°C	Several weeks at 25°C
20,XIg	$t\text{-}BuNSiMe_2Nt\text{-}Bu$		$SiMe_3$	Several days at 25°C	m.p. 122 °C Indefinitely at 25°C
21,XIIa	$i\text{-}Pr_2N$	$i\text{-}Pr_2N$	PR_2H^{+b}	Not observed at 25°C	m.p. 88 °C Indefinitely at 25°C
21,XIIb	$i\text{-}Pr_2N$	$i\text{-}Pr_2N$	PR_2Cl^{+b}	Not observed at 25°C	Few days at 25°C in solution

[a]Tmp = 2,2,6,6-tetramethylpiperidino; [b]R = $Ni\text{-}Pr_2$.

Table 6. Pertinent Chemical Shifts (in ppm) and Coupling Constants (in Hz) for the Phosphinocarbenes XI and XII and their Diazo Precursors 20 and 21



20,21



XI,XII

	R^1	R^2	R^3	Diazo	Carbene		
				$\delta^{31}P$	$\delta^{31}P$	$\delta^{13}C$ (J_{PC})	$\delta^{29}Si$ (J_{PSi})
20,XIa	*i*-Pr_2N	*i*-Pr_2N	$SiMe_3$	+ 56.1	- 40.0	142.7 (159)	-19.7 (59)
20,XIb	Tmp[a]	*i*-Pr_2N	$SiMe_3$	+ 88.0	- 49.7	145.5 (203)	- 21.3 (70)
20,XIc	Tmp[a]	Me_2N	Si(*i*-Pr)$_3$	+ 88.7	- 27.8	120.7 (181)	- 2.8 (47)
20,XId	Tmp[a]	Me_2N	$SiMe_3$	+ 83.8	- 24.1	133.5 (147)	- 13.2 (52)
20,XIe	Tmp[a]	Ph	$SiMe_3$	+ 25.0	- 38.1	136.9 (147)	- 17.0 (27)
20,XIf	*c*-Hex_2N	*c*-Hex_2N	$SiMe_3$	+ 58.0	- 31.4	139.3 (160)	- 19.7 (59)
20,XIg	*t*-BuNSiMe$_2$N*t*-Bu		$SiMe_3$	+ 137.9	- 26.7	77.6 (153)	- 17.8 (64)
21,XIIa	*i*-Pr_2N	*i*-Pr_2N	PR_2H^{+b}	not observed	+ 27.1	98.9 (157)	c
21,XIIb	*i*-Pr_2N	*i*-Pr_2N	PR_2Cl^{+b}	+ 73.9	+ 35.1	103.9 (154)	d

[a] Tmp = 2,2,6,6-tetramethylpiperidino; [b] R = N*i*-Pr_2; [c] J_{PP} = 121 Hz; [d] J_{PP} = 71 Hz

be replaced by an isoelectronic and isovalent phosphonio substituent without dramatic modification. Indeed, the stable phosphinophosphoniocarbenes **XIIa**[80] and **XIIb**[81] were synthesized from the corresponding diazo precursors **21a** and **21b** in 76% and 85% yields, respectively (Scheme 4).

In solution, multinuclear NMR spectroscopy is by far the most informative technique for analyzing the structure and bonding of phosphinocarbenes. In fact, prior to the synthesis and single-crystal X-ray analysis of the phosphinosilylcarbene **XIg**[82] and phosphinophosphoniocarbene **XIIa**,[80] the only spectroscopic evidence for the formation of carbenes came from NMR. Table 6 summarizes all pertinent chemical shifts and coupling constants for the known phosphinocarbenes **XIa**−**g** and **XIIa**,**b** and their respective diazo precursors **20a**−**g** and **21a**,**b**. The phosphinosilylcarbenes **XI** are all characterized by high-field chemical shifts for phosphorus (−24 to −50 ppm) and silicon (−3 to −21 ppm) and low-field chemical shifts for carbon (78−143 ppm) with large coupling constants to phosphorus (147−203 Hz). Classical shielding arguments indicate an electron-rich phosphorus atom or equally an increase in coordination number. The silicon atom seems also to be electron-rich, while the carbon has a chemical shift in the range expected for a multiply bonded species. The values of coupling constants are difficult to rationalize as it is not possible to predict the influence of orbital, spin−dipolar, Fermi contact, nor higher order quantum mechanical contributions to their magnitude. However, classical interpretation of the NMR data indicates that the P−C bond of phosphinosilylcarbenes has some multiple bond character. The silyl- and phosphoniophosphinocarbenes **XI** and **XII** are very similar, as deduced from the similarity of their NMR spectroscopic features (Table 6).

The exact nature of the bonding system in phosphinocarbenes was clarified to some extent by the X-ray analyses performed on the phosphinophosphoniocarbene **XIIa**[80] and more recently on the phosphinosilylcarbene **XIg**.[82] Ball and stick views of **XIIa** are shown in Figure 10, and the pertinent geometric parameters are in the legend. No interaction with the trifluoromethanesulfonate anion is observed, confirming the ionic character of **XIIa**. The shortness of the P1−C1 bond [1.548(4) Å] and the planar geometry around P1 indicate a strong interaction of the phosphorus lone pair with the carbene vacant orbital. In other words, the phosphorus−carbon bond has some multiple bond character. Moreover, since the P1−C1−P2 framework is bent [P1−C1−P2 angle = 165.1(4)−164.1(4)°], phosphinophosphoniocarbenes **XII** are best representated by the phosphavinylylide form **B** (Figure 11). Because of a disorder associated with the phosphonio part of the molecule [sof = 0.62(1)], the values of the P2−C1 and P2a−C1 bond lengths [1.605(5) and 1.615(5) Å] could not be very accurate. Anyway, the P2−C1 bond length is far too short for a phosphorus−carbon single bond and is more in the range observed for phosphorus ylides.[83] This datum indicates an interaction of the carbene lone pair with the π-acceptor phosphonio substituent (form **D**).

Similar conclusions can be drawn from the X-ray crystal structure analysis of the phosphinosilylcarbene **XIg** (Figure 12),[82] the silyl group playing the same role as the phosphonio group of **XIIa**. The Si2N2C3N1C2P1C1Si1 skeleton is planar (maximum

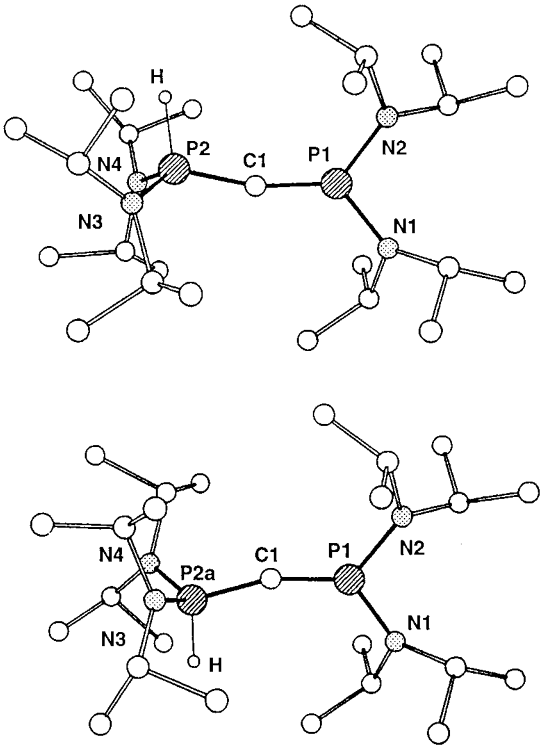


Figure 10. Ball and stick view of the two units of **XIIa**. Selected bond distances (Å) and bond angles (deg) are as follows: P2−N3 1.635(4), P2−N4 1.641(4), P2a−N3 1.622-(5), P2a−N4 1.638(5), P2−C̈1 1.605(5), P2a−C̈1 1.616(5), P1−C̈1 1.548(4), P1−N1 1.632(3), P1−N2 1.635(3); P2−C1−P1 165.1(4), P2a−C1−P1 164.1(4), C1−P1−N1 126.3-(2), C1−P1−N2 126.7(2), N1−P1−N2 107.0(2).

deviation from the best plane: 0.03 Å), the P1C1 bond length [1.532(3) Å] is short, and the P1C1Si1 framework is bent [152.6(3)°]. The presence of a strongly polarized P$^{\delta+}$C$^{\delta-}$ fragment (form **B**) is suggested by the short Si1C1 [1.795 compared with 1.86−1.88 Å for Si1−CH$_3$] and PN bond distances [1.664(2) Å].

Calculations perfomed on model compounds (Figure 13) not only corroborate the conclusions of the experimental analyses concerning the bonding system in phosphinocarbenes, but also give more insight into the role of the carbene and phosphorus substituents.

The first study by Hegarty and co-workers[84] concluded that the parent phosphinocarbene H$_2$PCH **XIg*** has a singlet ground state, with a singlet−triplet gap of 3 kcal/mol, while later on Hoffmann and Kuhler[85] predicted a somewhat larger gap (6.7 kcal/mol) using a more sophisticated level of theory. Together, the planar geometry of the singlet state and the shortness of the PC bond (1.616 Å) confirm the strong interaction of the phosphorus lone pair with the vacant orbital of the carbene center. The phosphavinylylide form **B** definitively describes this species (Figure 11). Interestingly, the structure **A** featuring a pyramidal phosphorus center is neither a minimum nor a saddle point on the potential energy surface. Moreover, the λ^5-phosphaacetylene structure **C** is the transition structure corresponding to the inversion at the carbene center with an energy barrier of only 10.3 kcal/mol. This small barrier probably explains why carbene **XIIa** has difficulty in maintaining one discrete form in the solid state. Indeed, the two units observed in the X-ray analysis[80] simply result from an inversion at the central carbon, followed by a 180° rotation around the P2−C1 bond. In contrast with the singlet state, the calculations associated with the triplet state predict a pyramidal geometry at phosphorus and a long P−C bond (1.782 Å). Moreover, the PCH bond angle is wider (133.9°) than that of the singlet state (123.5°), as classically predicted for most carbenes.[14]

Dixon et al. theoretically investigated the role of silicon substitution at carbon and of amino groups at phosphorus (Figure 13).[86] In the singlet state, the SiH$_3$ substituent induces a widening of the carbene angle (**XIh***, 131.2°). This effect, which has been previously reported for other silylcarbenes,[87] corroborates the prediction by Schoeller[12a] and Pauling[12b] that carbenes substituted by elements less electronegative than carbon preferentially adopt linear structures. Moreover, the shortness of the C−Si bond (1.843 Å), which is in the range typical for silicon−carbanion bond lengths,[88] indicates a significant back-donation of the carbene lone pair into the σ^* orbitals of the silyl group (Z-type substituent).[89] Replacement of the hydrogen atoms by amino groups at phosphorus (**XIi***) led to a shortening of the P−C and C−Si bonds, while the P−C−Si fragment becomes almost linear. These data might indicate that the carbene lone pair interacts with the σ^* orbitals of both the silyl and the phosphino groups (negative hyperconjugation).[90,91] However, the electron localization function (ELF) analysis[82] of both the bent and linear forms of **XIi*** leads to a rather different conclusion (Figure 14). For the ground-state bent form (Figure 14a), the lone pair on the carbon atom is directed away from both the phosphorus and silicon, indicating that neither the triple bond (**C**) nor the cumulene (**D**) structure is the best formulation for phosphinosilylcarbenes. Since the PC double bond is clearly evident, **XIi*** has to be regarded as the phosphavinylylide **B**. Interestingly, even the linear form of **XIi*** (Figure 14b) features the typical pattern for a PC double bond (purple) [for comparison, Figure 14c shows the ELF plot for $HC{\equiv}P$ which possesses a genuine triple bond (purple)]. The stretched shape of the light green isosurface is an indication of SiC

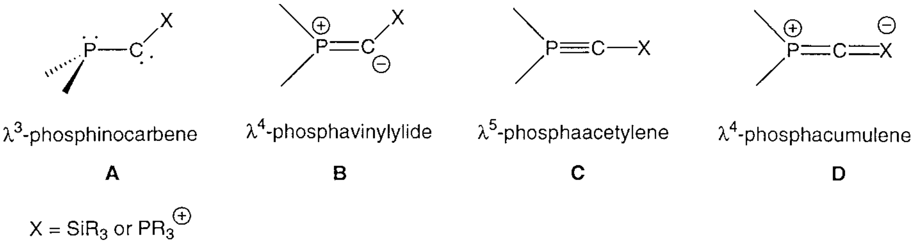


Figure 11. Possible representations for phosphinocarbenes.

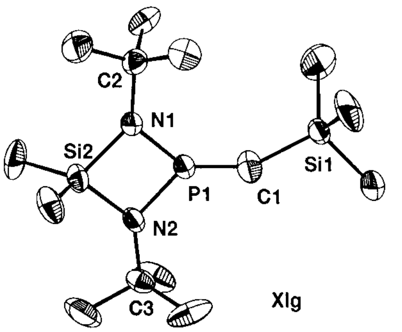


Figure 12. ORTEP view of **XIg**. Selected bond distances (Å) and bond angles (deg) are as follows: P1−N1 1.664(2), P1−N2 1.665(2), P1−Cl 1.532(3), C1−Si1 1.795(3); N1−P1−N2 87.01(11), N1−P1−C1 130.85(15), N2−P1−C1 142.12(14), P1−C1−Sil 152.6(3).

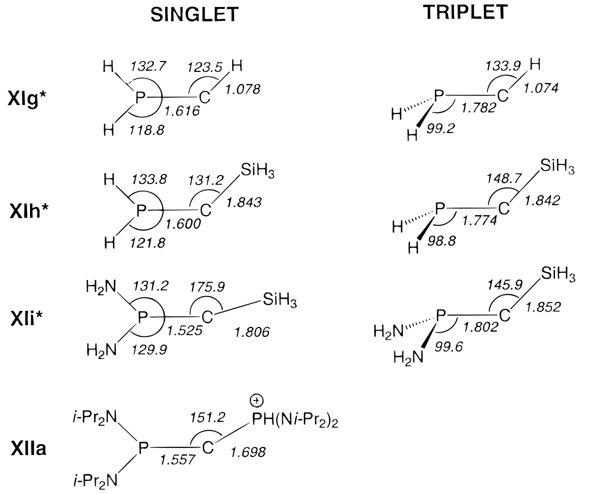


Figure 13. Calculated geometric parameters for singlet and triplet phosphinocarbenes **XI** and **XII** (bond lengths in Å; bond angles in deg).

double bond character, and since this isosurface is perpendicular to that attributed to the PC double bond, the linear form of **XIi*** is best described by the cumulenic structure **D**.

Note that the triplet state of both carbenes **XIh*** and **XIi*** is higher in energy, by 5.6 and 13.9 kcal/mol, respectively.[86] Their geometries are quite comparable to that of the parent triplet phosphinocarbene **XIg***, indicating a weaker influence of the carbene substituents.

Recently, Nyulaszi et al. studied the influence of a variety of substituents on the electronic structure of phosphinocarbenes.[92] Strongly bent geometries are predicted, except for the phosphinoborylcarbene H_2PCBH_2 which has a linear allene-type structure.

The study by Alhrichs and co-workers deals with the phosphinophosphoniocarbene **XIIa** itself (Figure 13).[93] The optimized geometry is very similar to that observed in the solid state. The σ^3P center is in a trigonal planar environment. The atomic charges (P^1, +1.1; C, −0.9; P^2, +1.1) indicate that the very short P^{1}C bond [experimental 1.548(4) Å; theoretical 1.557 Å] is a double bond reinforced by Coulombic attraction.[93] Interestingly, the σ^4P−C bond length is also short [experimental 1.605(5)−1.615(5) Å; theoretical 1.698 Å], in the range expected for phosphorus ylides,[83] which indicates a degree of back-donation of the carbene lone pair into the low-lying orbitals of the σ^4-phosphorus center.

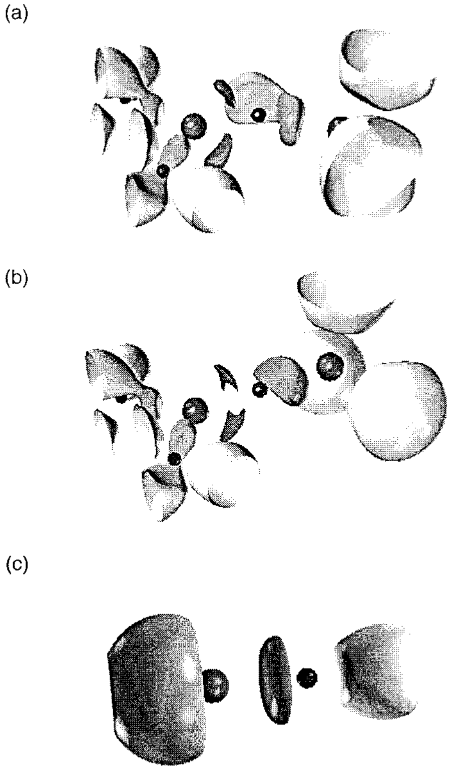


Figure 14. ELF plots, isosurfaces 0.85: (a) bent form of **XIi***; (b) linear form of **XIi***; (c) P≡CH.

In summary, the phosphino groups act as X substituents while the silyl and phosphonio groups are both able to act as Z substituents due to the aptitude of phosphorus and silicon for hypervalency.[95] In other words, the phosphorus lone pair of the phosphino substituent interacts with the carbene vacant orbital and there is an additional weak interaction between the carbene lone pair and low-lying σ^* orbitals at the silyl or phosphonio groups.

However, when compared to nitrogen, phosphorus is much more reluctant to achieve a planar configuration with sp^2 hybridization.[59,96−98] The ensuing smaller stabilizing effect of phosphorus compared to nitrogen is illustrated by the small singlet−triplet gap predicted for the phosphinocarbenes **XIg**−**i** (5.6−13.9 kcal/mol)[86] compared to that calculated for acyclic as well as cyclic diaminocarbenes (58.5−84.5 kcal/mol).[61,62] This means that the commitment of the lone pair to donation into the vacant orbital on the divalent carbon atom is less definitive for phosphorus than for nitrogen, and thus, the phosphinocarbenes retain more of a divalent-carbon behavior.

IV.3.2. Sulfinylcarbenes

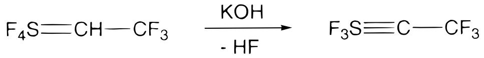
In the 1980s, Seppelt et al. prepared the (trifluoroethylidyne)sulfur trifluoride **XIII**[8a] and the [(pentafluorothio)methylidyne]sulfur trifluoride **XIV**[8b] by gas-phase dehydrofluorination of **22** and **23**,[99,100] respectively, with KOH at 70−80 °C (eqs 12 and 13).

Both compounds **XIII** and **XIV** are colorless gases of rather low thermal stability (**XIII** bp −15 to −10 °C, mp −122 °C, dec ≈ −50 °C; **XIV** mp −130 °C, dec −78 °C). Their IR spectra exhibit strong absorption bands in the expected range for CS triple bond stretching (**XIII**[01] 1740 cm^{-1}; **XIV**[8b] 1717 cm^{-1}); the CS bond lengths determined experimentally as well as theoretically (Table 7) are 9% and 20% shorter

Table 7. Experimental and Calculated Structural Data for XIII and XIV (Distances in Å, Angles in Deg)

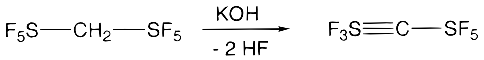
	XIII			XIV		
	d(CS)	<SCX	ref	*d*(CS)	<SCX	ref
X-Ray	1.424(3)[a]	171.4(3)[a]	8b	1.392(4)	180	8b
	1.431(2)[b]	162.9(2)[b]	103			
electron diffraction	1.43(1)	155(3)	101	1.40(1)	159(3)	104
calculations						
HF/3-3-21	1.404	180	105			
HF/DZ + D(C,S)	1.412	180	106			
MP2/3-21G*(*)//HF/3-21G*(*)	1.409	174	101			
MP4SD/3-21G*(*)//HF/6-31G*		160	101			
MP2/6-31G*//HF/6-31 G*	148	101			150	104

[a] Phase I (crystallization temperature: −125 °C. [b] Phase II (crystallization temperature: −142 °C).



22 **XIII** (80%) (12)

b.p. -15 to -10°C
m.p. -122°C
dec. -50°C

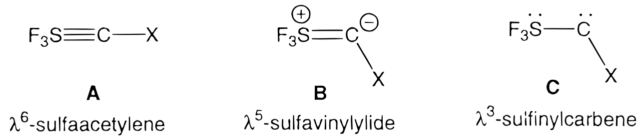


23 **XIV** (30%) (13)

b.p. not measurable
m.p. -130°C
dec. -78°C

than comparable double and single bonds, respectively. On the basis of these criteria, the authors claimed the isolation of the first compounds featuring a sulfur−carbon triple bond.[8a,b] However, the geometry of the bonding system (linear or bent X−C−S framework) has attracted much attention (Table 7). All the studies concluded that there was a nonclassical structure for the CS triple bond.[102,103] The X-ray data for **XIII**[8b,103] indicate a significant bending in the crystalline state (phase I, 171.4°; phase II, 162.9°), which is even accentuated in the gas phase, as deduced from a gas electron diffraction study (155°).[101] A similar trend is observed for **XIV**: the X-ray diffraction study yields a linear structure imposed by the cubic crystal symmetry,[8b] whereas the gas electron diffraction study revealed a bent structure (159°).[104] These conflicting results were paralleled by ab initio calculations for **XIII**: a linear geometry was first predicted at the HF/3-3-21[105] and HF/DZ+D(C,S)[106] levels, but using a larger basis set and including electron correlation,[101] bending angles from 174° to 148° were obtained. In any case, the bending potential is very flat, even at considerable bending angles (the barrier to linearity has been estimated to be only 0.35 kcal/mol at the MP2/6-31G*//HF/6-31G* level).[101] Therefore, weak lattice forces can certainly dictate the value of the CCS bond angle within certain limits.

How can this weak bending potential be plausibly explained? The polarity of the CS bond clearly emerges from the calculated charge distribution for **XIII** ($C^{-0.7}S^{+1.6}$)[101] and from the surprisingly high ^{13}C NMR chemical shift for the central carbon atom (**XIII**, 30.4 ppm compared to 67.5 ppm for CF_3CH_2-SF_5).[102] Therefore, the λ^5-sulfavinylylide form **B** (Figure 15) is certainly of importance. This conclusion was corroborated by a crystal structure determination for **XIV**[8b] (although the electron density distribution has been only poorly evaluated in this case due to crystal disorder). A full theoretical understanding of the bending potential is hindered by the fact that the λ^3-sulfinylcarbene form **C** cannot be accurately investigated. However, the singlet state of the F_3S−$\ddot{C}$−CF_3 carbene was predicted to be separated from the corresponding acetylenic-type ground state (form **A**) by a barrier of only 12 kcal/mol. The authors concluded that the energetically close lying, certainly strongly bent, carbene state causes the weak bending potential.[7h]



A λ^6-sulfaacetylene

B λ^5-sulfavinylylide

C λ^3-sulfinylcarbene

X = CF_3 or SF_5

Figure 15. Possible representations for sulfinylcarbenes.

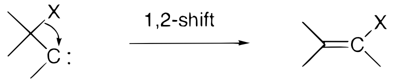
In summary, bending about the carbon is so easy that the carbon−sulfur triple-bonded compounds **XIII** and **XIV** may be considered as masked sulfinylcarbenes (form **C**); this is in line with their reactivity (see sections V.1, V.2.1, and V.4.3).

V. Reactivity of Stable Singlet Carbenes

Whereas triplet carbenes exhibit radical-like reactivity, singlet carbenes are expected to show nucleophilic as well as electrophilic behavior because of the lone pair and vacant orbital. Among the most typical reactions of transient singlet carbenes are the rearrangements resulting from 1,2-shifts, dimerizations, [1+2]-cycloadditions to carbon−carbon double bonds, and insertions into C−H bonds. Many other reactions involving transient carbenes have been observed, including the formation of ylides with Lewis bases. Here, we will compare, as often as possible, the reactivity of the different types of stable carbenes with that of their transient congeners.

V.1. 1,2-Migration Reactions

It is now well established that 1,2-migration (eq 14) is a fundamental reaction for singlet carbenes and occurs via a unimolecular concerted mechanism.[25,107]



(14)

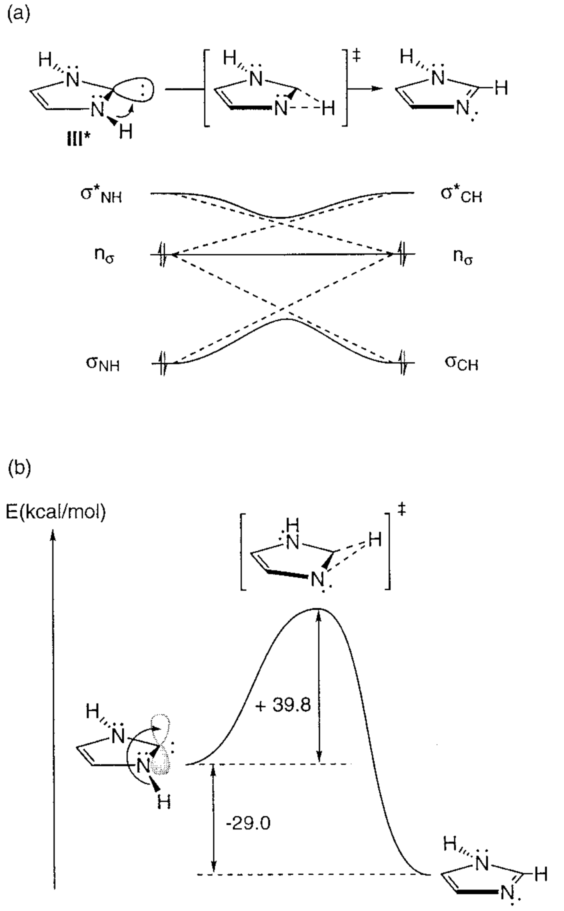
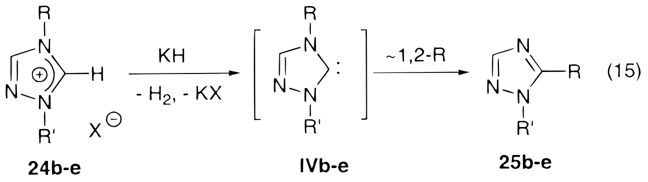


Figure 16. (a) Correlation diagram for the in-plane 1,2-H-migration in **III***. (b) Energy diagram for the calculated out-of-plane 1,2-H-migration in **III***.

Alternative intermolecular pathways, such as those involving carbene−olefin π-complexes,[108,109] have recently been ruled out.[107e]

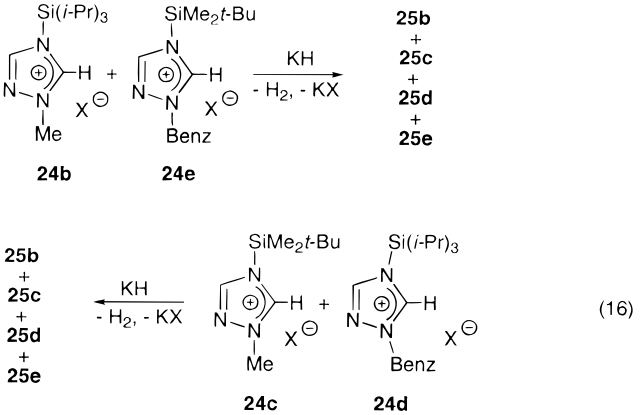
In aromatic carbenes **III**−**V**, 1,2-hydrogen migrations cannot proceed through an intramolecular process in the plane of the ring. This mechanism would impose the crossing of two orbitals with the same symmetry, as shown in the correlation diagram (Figure 16a). An alternative possibility, which has been theoretically studied,[60,110] involves the interaction of the N−H bond with the out of plane p_π orbital of the carbene. This process induces a deformation of the ring and thus the loss of the electronic delocalization of the nitrogen lone pairs (Figure 16b). Heinemann et al. predicted that even though the reaction would be exothermic (−26.1 kcal/mol at the RHF/MP2DSQ level[60] and −29 kcal/mol at the DFT/B3LYP level[110a]), the carbene **III*** should be kinetically stable toward 1,2-shifts, since the activation energy of this rearrangement is high (+46.8 kcal/mol,[60] +39.8 kcal/mol[110a]). Recently, Maier et al. obtained similar results for the 1,3-thiazol-2-ylidene system **V*** ($\Delta H = -34.0$ kcal/mol, $E^{\ddagger} = +42.3$ kcal/mol at the MP2(fc)/6-31G(d) level).[110b]

Our group has recently reported an example of a formal 1,2-silyl shift in the 1,2,4-triazol-5-ylidene series **IV** but has proved that this resulted from an intermolecular process.[111] Indeed, deprotonation of *N*-silyltriazolium salts **24b**−**e** with various bases readily occurred at 0 °C to lead, after workup, to triazoles **25b**−**e** (42−81% yields) (eq 15). Although



X: CF_3SO_3
b: R = Si(*i*-Pr)$_3$; R' = Me
c: R = SiMe$_2$*t*-Bu; R' = Me
d: R = Si(*i*-Pr)$_3$; R' = Benz
e: R = SiMe$_2$*t*-Bu; R' = Benz

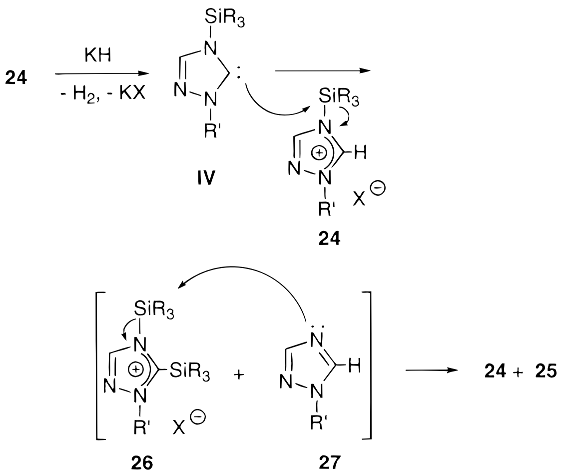
all attempts to spectroscopically characterize carbenes **IVb**−**e** failed, despite monitoring the deprotonation reaction at −78 °C, the transient formation of **IVb**−**e** was unambiguously established by trapping with a large excess of benzaldehyde.[112] The intermolecular nature of the 1,2-migration was proved by the deprotonation of a 1/1 mixture of triazolium salts **24b** and **24e**, bearing different substituents at both nitrogen atoms, which led to a mixture of the four rearrangement products **25b**−**e**. In the same way, starting from a 1/1 mixture of triazolium salts **24c** and **24d**, the same products **25b**−**e** were obtained (eq 16). Of course it was checked that in



solution no exchange reactions of the silyl groups occurred between the triazolium salts **24b** and **24e** and between **24c** and **24d** nor between the triazoles **25b**−**e**. We have shown that in fact a nucleophilic attack of a carbene of type **IV** on the silyl group of a starting cation **24** resulted in the formation of the C- and N-silyl-substituted triazolium salt **26**, along with triazole **27**. Then, a nucleophilic attack of the nitrogen of **27** at the *N*-silyl group of the cation **26** afforded the rearrangement product **25** and regenerated the starting salt **24** (eq 17).

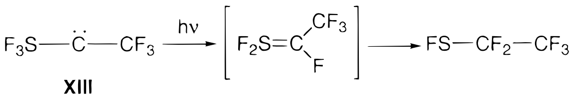
Therefore, 1,2-migrations can occur for aromatic carbenes such as **IVb**−**e**[113] but only via intermolecular processes. This rearrangement involves both the carbene and an electrophilic partner. This is reminiscent of the specific behavior of the stable aminocarbenes **II**−**VIII** toward dimerization, in which the protonated form is involved (see next section).

A 1,2-fluorine migration has been postulated to rationalize the formation of $FS{-}CF_2{-}CF_3$ in the matrix irradiation of the sulfenylcarbene **XIII**.[7h]



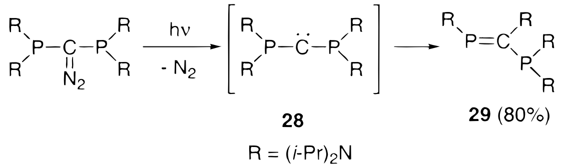
(17)

However, the presumably initially formed alkylidene sulfur difluoride has not been characterized (eq 18).



(18)

No 1,2-migration involving stable phosphinocarbenes has yet been observed. Note that, in contrast, the transient bis(phosphino)carbene **28** rearranges into the phosphaalkene **29**[114] (eq 19).



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V.2. Carbene Dimerization and Related Reactions

V.2.1. Carbene Dimerization

In the Carter and Goddard formulation,[115] the strength of the C=C double bond resulting from the dimerization of singlet carbenes should correspond to that of a canonical C=C double bond (usually that of ethene) minus twice the singlet−triplet energy gap for the carbene. For example, the singlet−triplet splitting in the parent imidazol-2-ylidene **III*** has been calculated to be ca. 85 kcal/mol;[60] accordingly, one expects the CC bond strength in the dimer to be approximately only [172 − (2 × 85)] 2 kcal/mol. In the same way, the calculated value for the energy of dimerization of Enders-type carbene **IV*** is only 9.5 kcal/mol.[66] These remarkably small values, at least partially due to the loss of aromaticity in the Arduengo and Enders carbene dimers, highlight the difficulty with which such carbenes dimerize. In contrast, in the case of the parent diaminocarbene **VI***, Heinemann and Thiel[60] found a dimerization energy of about 45 kcal/mol. This poses another question: What is the value of the energy barrier for the dimerization? Nowadays, the dimerization of singlet carbenes is believed to follow a nonleast motion pathway that involves the attack of the occupied in-plane σ lone pair of one singlet carbene center on the out-of-plane vacant p_π-orbital of a second carbene (Figure 17).[115,116] Calculations regarding the dimerization path indicate a significant barrier of about 19.4 kcal/mol for the carbene **IV***,[66] and Alder estimated the ΔG^* for the dimerization of the bis(*N*-piperidinyl)carbene **VIb** to be >25 kcal/mol.[57] These large values are not surprising since the dimerization reaction involves the carbene vacant orbital which is very high in energy due to electron donation by the nitrogen lone pairs.

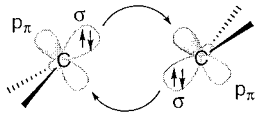
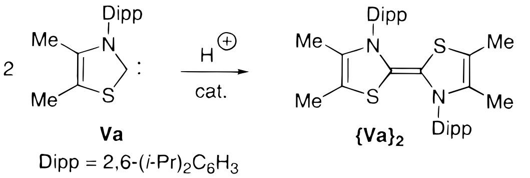


Figure 17. Schematic representation of the dimerization of singlet carbenes by a nonleast motion pathway.

However, besides the work by Wanzlick,[42] several examples of aminocarbene dimerizations have been reported.[49b,55,57,117] Noteworthy is the isolation by Arduengo[55] of both the thiazol-2-ylidene **Va** and of its dimer {**Va**}$_2$ (eq 20), the spectroscopic characterization by Alder and Blake of the bis(*N*-piperidinyl)carbene **VIb** and of the tetrakis(*N*-piperidinyl)ethene {**VIb**}$_2$[57] (eq 21), and the synthesis by Taton and Chen of bis(carbene) **IIIs** and tetraazafulvalene {**IIIt**}$_2$, depending on the length of the methylene bridges (eqs 22 and 23).[117a]



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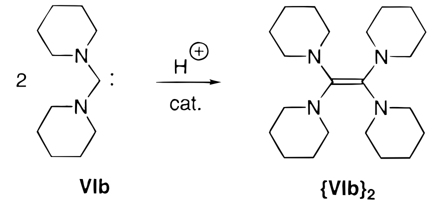

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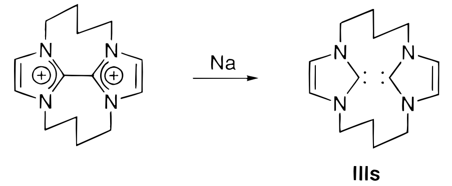

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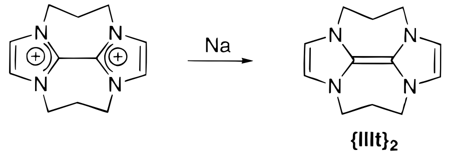
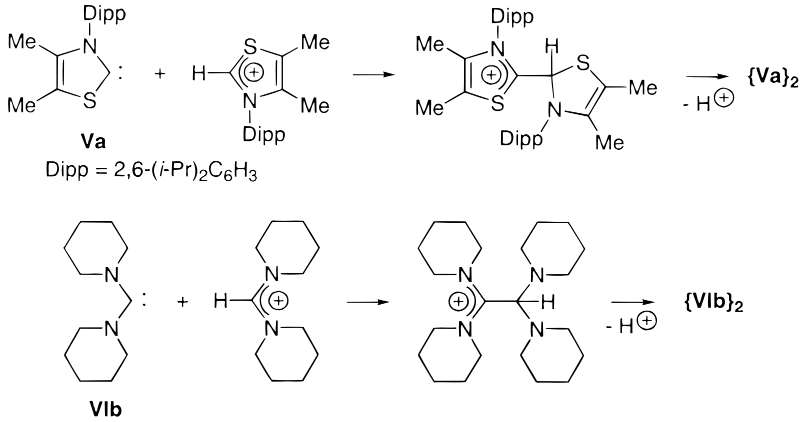


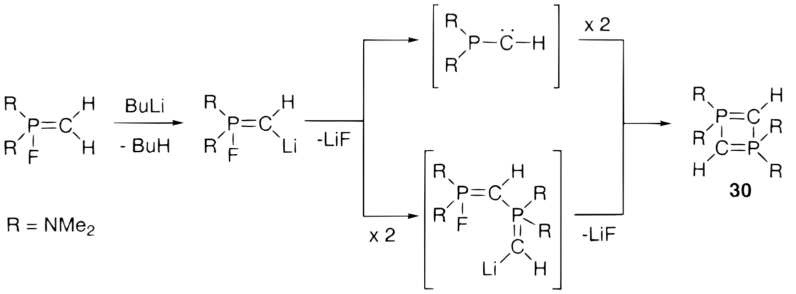
(23)

Interestingly, Arduengo observed that **Va** was stable with respect to dimerization in the absence of a Brönsted or Lewis acid catalyst.[55] Similarly, in the absence of an acid catalyst, dimerization of **VIb** is extremely slow and is first order in the carbene.[57] Therefore, the observed formal dimerization of **Va** and **VIb** does not involve the coupling of two carbenes but the nucleophilic attack of one carbene upon its conjugate acid, followed by proton elimination, as already suggested by Chen and Jordan[118] (Scheme 5).

Scheme 5

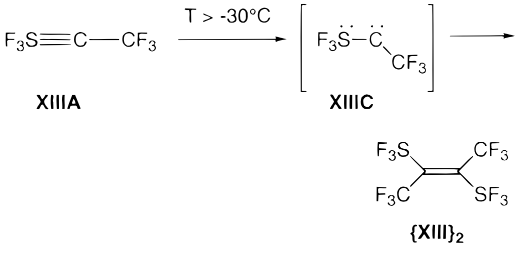


Scheme 6



Note that the formation of the tetraazafulvalene $\{\mathbf{IIIt}\}_2$ might involve a genuine intramolecular dimerization of singlet carbenes, which would be favored by the entropy factor[117a] (eq 23). However, a mechanism involving one carbene and an imidazolium salt can certainly not be excluded either.

In marked contrast with aminocarbenes, which are reluctant to dimerize, the formation of the *E* olefin $\{\mathbf{XIII}\}_2$ is the dominant reaction of the (trifluoroethylidyne)sulfur trifluoride **XIII**.[102,103] Surprisingly, a kinetic study of this reaction shows that the disappearance of **XIII** follows first-order kinetics over a range of 1 order of magnitude in concentration, at temperatures between −25 and +5 °C. Seppelt et al. concluded that the rate-determining step has to be the transformation of $F_3CC\equiv SF_3$ **XIII** (form **A**) into the carbene form **C** ($F_3C-\ddot{C}-SF_3$) ($\Delta H^* = 12$ kcal/mol) before the latter reacts further[103] (eq 24). This



(24)

conclusion clearly deserves further studies.

Last, no dimerizations leading to olefins have been observed for stable phosphinocarbenes **XI** and **XII**. However, it should be noted that transient (not spectroscopically observed) phosphinocarbenes have been reported to undergo head-to-tail dimerizations leading to $1\lambda^5,3\lambda^5$-diphosphetes[119,120] such as **30**[120] (Scheme 6). Here also, the mechanism is not clear.

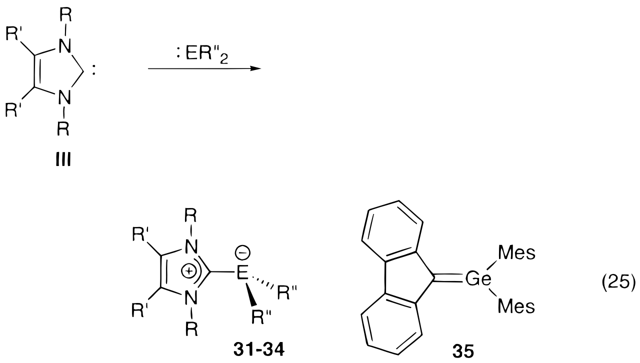
V.2.2. Carbene–Carbenoid Coupling Reactions

For carbenoids, we will not only consider the higher “analogues” of carbenes (silylenes, germylenes, stannylenes, plumbylenes, phosphinidenes), but also species which can behave as carbenoids, such as iminophosphines and isocyanides.

Coupling reactions of imidazol-2-ylidenes **III** with all the group 14 carbenoids have been reported, while diborylcarbenes **IX** and phosphinocarbenes **XI** have only been reacted with germylenes and stannylenes. The different electronic structure of the three types of carbene **III**, **IX**, and **XI** is well illustrated by the comparison of the geometry and stability of the germylene and stannylene adducts.

Reaction of the imidazol-2-ylidene **IIIl** with germanium diiodide affords the carbene−germylene adduct **32** in 65% yield (eq 25).[121] The stability of **32** is striking (mp 210−214 °C), since most of the germaethenes[122] are only short-lived intermediates.[122a,b] ^1H and ^{13}C NMR data support a structure for **32** in which the newly formed C−Ge bond is not a true double bond but rather highly polarized C^+-Ge^-. This is confirmed by the crystallographic data: the germanium center is distinctly in a pyramidal environment and the C−Ge bond is very long (2.102 Å). This geometry has to be compared with that of the germaethene **35**,[122c] where the germanium and carbon atoms exhibit trigonal-planar coordination and a short (1.803 Å) weakly twisted (5.9°) C−Ge bond. Therefore, it is clear that **32** is best described as a Lewis base−Lewis acid adduct.

Berndt’s carbene **IXa** reacts with germylenes[123] at room temperature to afford the corresponding germaethenes **36a,b** as the sole products (eq 26).[124] The

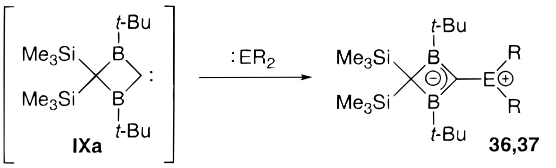


(25)

	R'	R	E	R"	yield
31	(CH)$_4$	CH$_2$(*t*-Bu)	Si	(NN)	83%
32	H	Mes	Ge	I	65%
33a	Me	*i*-Pr	Sn	Tipp	37%
33b	Me	*i*-Pr	Sn	Cl	38%
34	Me	*i*-Pr	Pb	Tipp	43%

(NN) = 1,2-[N(CH$_2$*t*-Bu)]$_2$C$_6$H$_4$
Tipp = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$

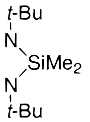
C−Ge bond distance (1.827 Å) is very similar to that found in **35**, but the average twist angle at the Ge=C bond is close to 36°. Moreover, although the Ge atom is in a practically planar environment, the carbon atom is slightly pyramidal. The X-ray structure analysis as well as the NMR data suggest some significance for the ylide resonance formula of type C$^-$−Ge$^+$, expected from the interaction between an electrophilic carbene and a nucleophilic germylene. Thus, the polarization of the GeC bond in **36** is stronger than that of **35** or standard germaethenes[122] and opposite to that of **32**.



(26)

	E	R	yield (spectro.)
36a	Ge	N(SiMe$_3$)$_2$	100%
36b	Ge	ring	100%
37	Sn	CH(SiMe$_3$)$_2$	100%

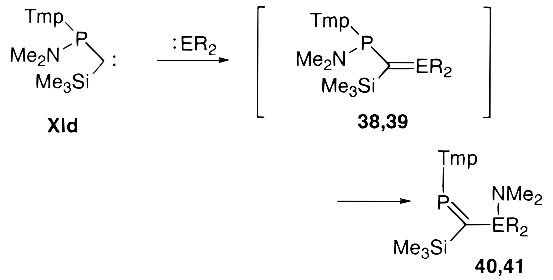
ring:



Phosphinosilylcarbene **XId** also reacts with germanium(II) compounds affording the *C*-germylphosphaalkenes **40a**,**b** in 78% and 46% yields, respectively (eq 27).[125] It is reasonable to postulate the primary formation of the germaethenes **38a**,**b**, which would undergo a subsequent 1,3-shift of the dimethylamino group from phosphorus to the germanium atom to produce derivatives **40a**,**b**. This reaction is highly chemiselective since we only observed the migration of the smallest phosphorus substituent. The instability of **38a**,**b** is not surprising whatever the polarity of the Ge=C bond, since the phosphorus center is not efficient enough to stabilize an adjacent positive charge and destabilizes a negative charge.

Interestingly, it is clear that because of their nucleophilicity, aminocarbenes react with germylenes through $\mathrm{HOMO_{carbene}}$−$\mathrm{LUMO_{germylene}}$ interactions. In contrast, since the diborylcarbenes are electrophilic, they react with germylenes via $\mathrm{HOMO_{germylene}}$−$\mathrm{LUMO_{carbene}}$ interactions. In the case of phosphinocarbenes, it is difficult to determine whether the HOMO or the LUMO of the carbene is involved (vide infra).

Similar reactions have been observed by reacting the imidazol-2-ylidene **IIIi**,[126] diborylcarbene **IXa**,[127] and phosphinocarbene **XId**[125] with stannylenes (eqs 25−27). The resulting adducts **33a**,**b** and **37** have geometries and therefore electronic structures comparable to those of their germanium analogues, while **39a**,**b** are unstable and rearrange as observed for **38**.



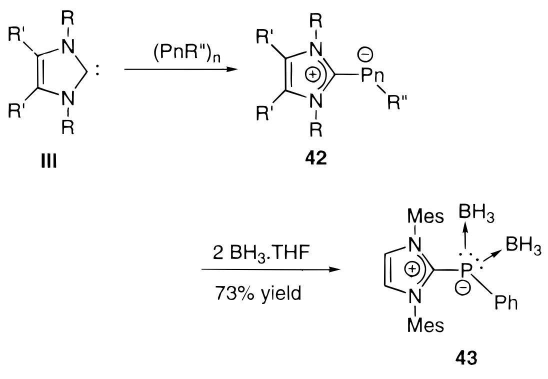
(27)

	E	R	yield
38a,40a	Ge	N(SiMe$_3$)$_2$	78%
38b,40b	Ge	NHMes*	46%
39a,41a	Sn	CH(SiMe$_3$)$_2$	48%
39b,41b	Sn	N(SiMe$_3$)$_2$	42%

Tmp = 2,2,6,6-Tetramethylpiperidino
Mes* = 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$

Interestingly, imidazol-2-ylidenes **III** also give stable adducts with silylenes[128a] and plumbylenes.[128b] As observed in the germanium and tin adducts, the C−Si and C−Pb bonds of **31** and **34**, respectively, are strongly polarized and can hardly be considered as double bonds.

Imidazol-2-ylidenes **III** also give adducts with pnictinidenes. In fact, carbenes **III** are sufficiently nucleophilic to depolymerize cyclopolyphosphines [(PPh)$_5$ and (PCF$_3$)$_4$] and cyclopolyarsines [(AsPh)$_6$ and (AsC$_6$F$_5$)$_4$] to produce adducts of the type carbene-PnR″ **42** (eq 28).[129] The strong electron-releasing characteristics of the imidazole ring render these “pnictaalkenes” strongly polarized, as shown by the

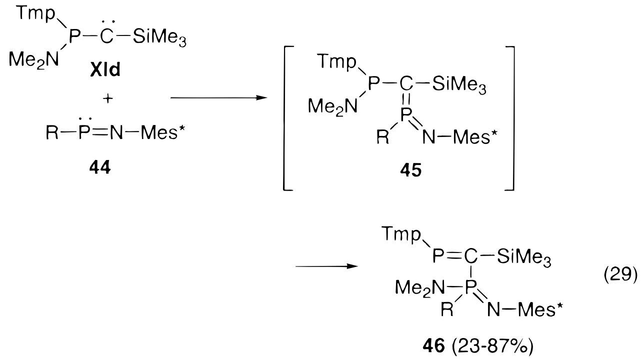


(28)

	R'	R	Pn	R"	yield
42a	Me	Me	P	Ph	79%
42b	H	Mes	P	Ph	67%
42c	H	Mes	P	CF$_3$	90%
42d	H	Mes	As	Ph	45%
42e	H	Mes	As	C$_6$F$_5$	61%

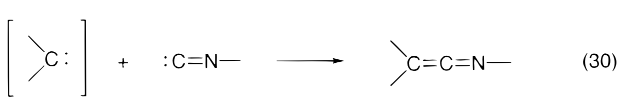
very high field ^{31}P NMR chemical shift (−23 ppm), the small C−Pn−C angles (97−102°), and the long carbene−Pn bonds (only 4% shorter than Pn−C single bonds), which allows a free rotation at room temperature. Further support for the carbene−phosphinidene bonding description stemmed from cyclic voltammetry experiments.[130] Indeed, an acetonitrile solution of **42b** exhibits an irreversible one-electron oxidation at −0.08 V (vs SCE). Such a low oxidation potential is consistent with an electron-rich phosphorus center since the one-electron oxidation potentials of typical phosphaalkenes fall in the range 1.07−2.94 V.[131] Therefore, the pnictinogen atom possesses two available lone pairs, as confirmed by the reaction of **42b** with BH_3·THF. Indeed, an exclusive formation of the diborane adduct **43** was observed (eq 28).[130]

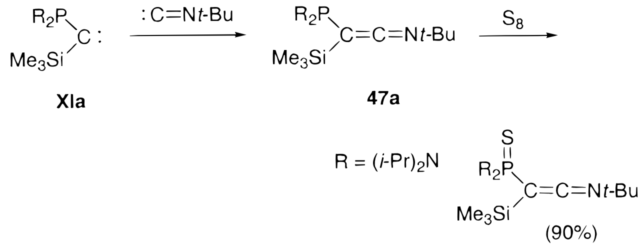
Due to the existence of two energetically close occupied MOs π and n, the orbital sequence HOMO/LUMO of iminophosphines **44** can be π/π^*, inducing an alkene-like reactivity, but also n/π^*, leading to a behavior analogous to that of carbenes.[132] Indeed, the phosphinocarbene **XId** reacts with iminophosphines **44** leading to the phosphaalkenes **46** (23−87% yield) (eq 29).[133] These results are strictly analogous to those observed in the reaction of **XId** with germylenes and stannylenes, and therefore, it is quite likely that a carbene−carbenoid coupling-type reaction occurs, leading to the transient (methylene)(imino)phosphoranes **45**, which would subsequently undergo a 1,3-migration of a dimethylamino substituent from the λ^3-phosphorus to the electrophilic λ^5-phosphorus atom. These reactions are also highly chemiselective since we only observed the migration of the smallest phosphorus substituent. Here again, it is difficult to know whether the phosphinocarbene **XId** reacts via its lone pair or its potentially available vacant orbital.



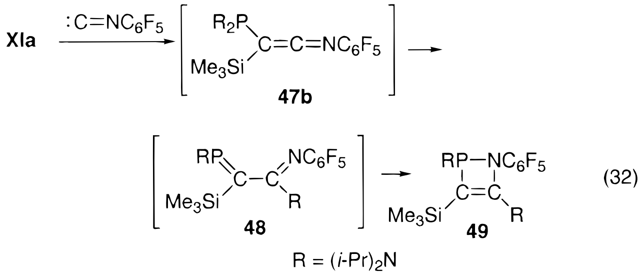
R = *t*-Bu, MeO, F
Tmp = 2,2,6,6-Tetramethylpiperidino
Mes* = 2,4,6-(t-Bu)$_3$C$_6$H$_2$

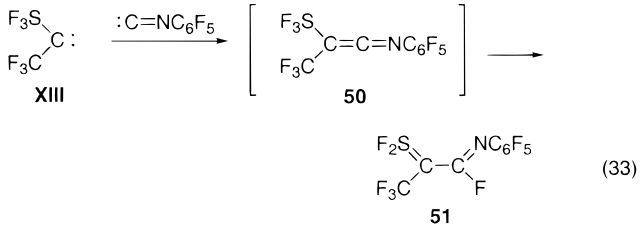
Transient carbenes are known to react with isonitriles to give the corresponding ketenimines (eq 30).[134] *tert*-Butyl isocyanide is one of the very rare reagents that reacts with almost all of the stable phosphinocarbenes **XI** and **XII**.[79,81,135,136] For example, it reacts with **XIa**, even at −78 °C, affording the ketenimine **47a**, which was isolated after treatment with elemental sulfur as its thioxophosphoranyl analogue in 90% yield (eq 31).[135]



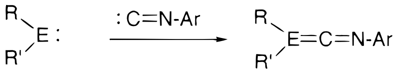


Pentafluorophenyl isocyanide also reacts with the phosphinocarbene **XIa** but gives the heterocycle **49** (eq 32).[137] Most probably, the initially formed ketenimine **47b** rearranges by a 1,3-shift of a diisopropylamino group from phosphorus to carbon leading to **48**, which subsequently undergoes an electrocyclization. Note that the 1,3-migration process is strictly analogous to that observed in the reaction of phosphinocarbenes with germylenes, stannylenes (eq 27), and iminophosphines (eq 29). Moreover, the sulfenylcarbene **XIII** gives a similar reaction which affords **51**, probably via the transient ketenimine **50** (eq 33).[103]





The great reactivity of isonitriles toward the carbenes **XI**, **XII**, and **XIII** can be easily explained in terms of steric factors: the reactive site of RN═C: is comparatively unhindered. However, the most important question is to know whether isonitriles act as Lewis acids toward carbenes or if they act as Lewis bases. Interestingly, according to Grützmacher[138] and Okazaki,[139] the stanna- and silaketenimines **52a** and **52b**, respectively, result from the reaction of the stannylene and silylene, acting as Lewis acids, with the isocyanide, acting as a Lewis base (eq 34). Similar conclusions have been drawn for matrix-isolated silaketenes R_2SiCO,[140,141] resulting from the interaction between carbon monoxide and silylenes. Note that the imidazol-2-ylidene **IIIc**−carbon monoxide



(34)

52a,b

a: E = Sn, R = R' = 2,4,6-$(CF_3)_3C_6H_2$, Ar = Mes
b: E = Si, R = 2,4,6-$[CH(SiMe_3)_2]_3C_6H_2$, R' = Mes,
Ar = 2,4,6-$(t\text{-}Bu)_3C_6H_2$, 2,4,6-$[CH(SiMe_3)_2]_3C_6H_2$,
2,4,6-$(CHMe_2)_3C_6H_2$

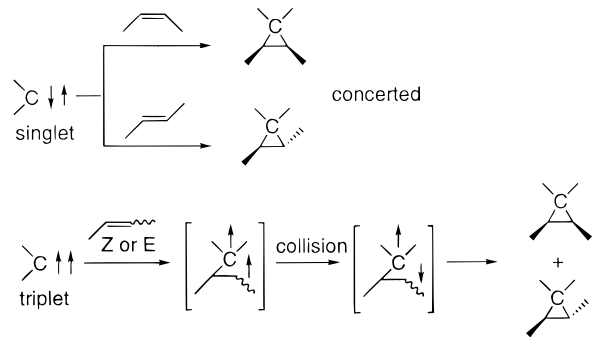
adduct has been reported,[142a] but more recently, this result has been refuted.[142b]

V.3. Addition to Multiple Bonds

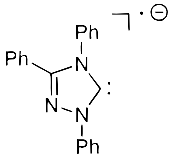
V.3.1. Addition to Carbon–Carbon Double Bonds

Both singlet and triplet transient carbenes react with olefins to give cyclopropanes, although by a totally different mechanism, as is apparent from the stereochemistry of the reaction (Scheme 7).[143,144]

Scheme 7



On the other hand, it has long been known that nucleophilic carbenes in which the singlet state is stabilized by interaction of the vacant p_π orbital with the lone pair of a heteroatom substituent do not react with electron-rich alkenes but with electrophilic ones.[145]



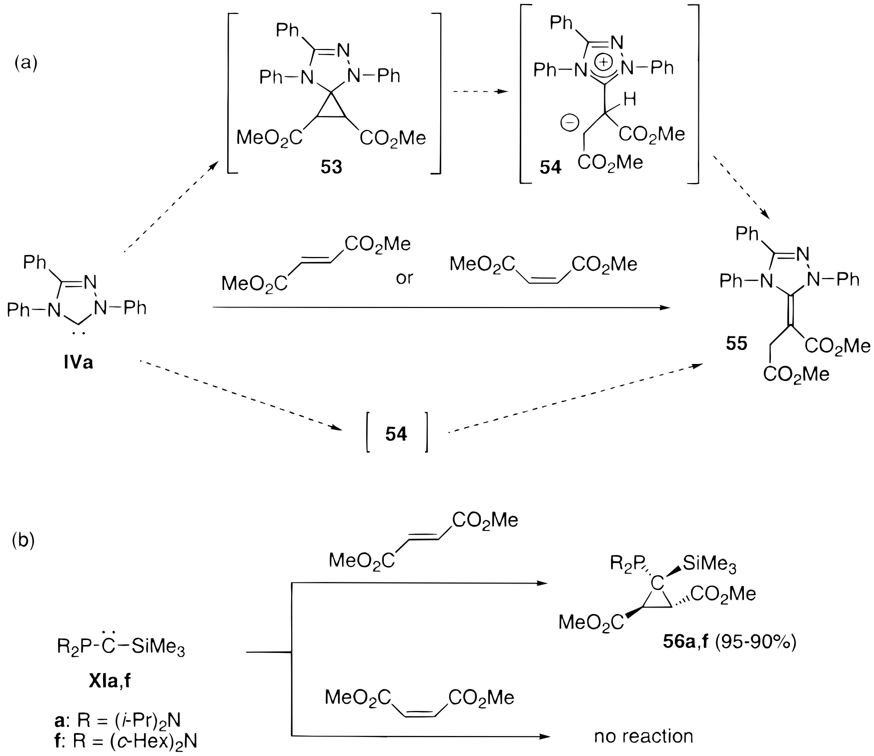
IVa·⊖

1,2,4-Triazol-5-ylidene **IVa** reacts with diethyl fumarate and also diethyl maleate, not giving the corresponding cyclopropane **53**, but the methylenetriazoline derivative **55** (Scheme 8a).[48] According to Enders et al.,[48] a [1+2]-cycloaddition first occurs, leading to the transient cyclopropane **53**. Then a ring opening would lead to the zwitterionic derivative **54**, which would undergo a 1,2-H shift[146] [AM1 calculations predict a strongly negative reaction enthalpy ($\Delta H = -18$ kcal/mol) for the rearrangement of **53** to **55**].[48] However, it is quite clear that a mechanism directly leading to the zwitterionic species **54** readily explains the experimental results (Scheme 8a).

The phosphinosilylcarbenes **XIa**,**f** also react with dimethyl fumarate, but not with dimethyl maleate, to give the corresponding cyclopropanes **56a**,**f** with retention of the stereochemistry about the double bond (Scheme 8b).[135] The difference in reactivity between cis and trans olefins toward carbenes has already been noted by Moss et al. with methoxy(phenyl)carbene.[147a]

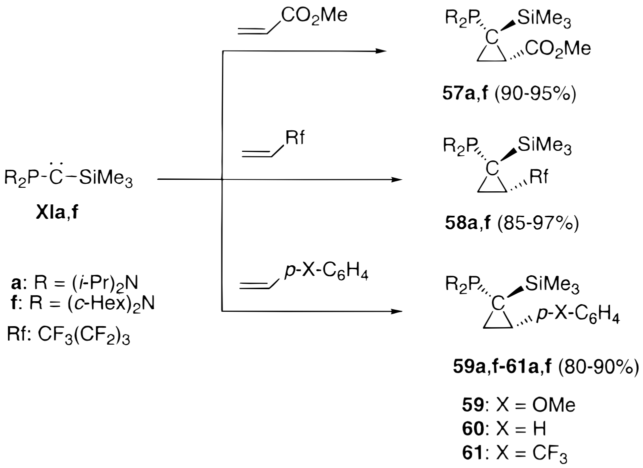
In fact, carbenes **XIa**,**f** undergo cyclopropanation reactions with a variety of monosubstituted electron-poor alkenes such as methyl acrylate,[135] perfluoro-

Scheme 8



alkyl-substituted olefins or styrene derivatives.[148] All these reactions occur at room temperature, and the corresponding cyclopropanes **57a**,**f**−**61a**,**f** are obtained in high yields (Scheme 9).

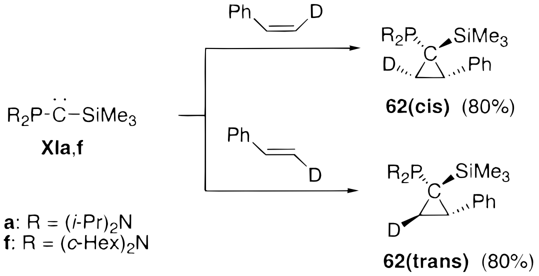
Scheme 9



Interestingly, in each case, only one diastereomer results. The NMR data for **57a**,**f**−**61a**,**f** are consistent with a "*syn*-attack"[149] of the phosphinocarbenes **XIa**,**f**, and this has been confirmed by a single-crystal X-ray diffraction study of **58f**.[148] So far, this stereoselectivity is not well understood, especially since steric effects should favor a "trans attack" [the bis(amino)-phosphino group being more sterically demanding than the trimethylsilyl group].

The singlet nature of **XIa**,**f** was without debate from the calculations and the spectroscopic data, but it was of importance to bring evidence that a concerted mechanism[150] was involved in the cyclopropanation reactions, hence establishing the genuine carbene nature of **XIa**,**f**. Recently, using pure cis and trans monodeuterated styrene isomers,[147b] we have observed the stereospecific formation of the corresponding cyclopropanes **62(cis)** and **62(trans)**, respectively (Scheme 10).[148] The concerted nature of the cyclopropanation reactions has been corroborated by the results observed by reacting **XIa**,**f** with a variety of carbon−heteroatom double and triple bonds (see sections V.3.2 and V.3.3).

Scheme 10

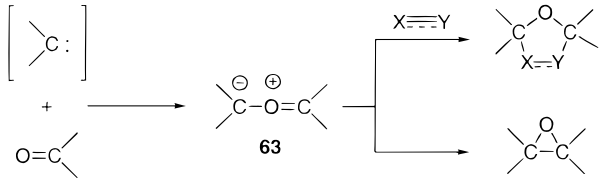


No cyclopropanation reactions have been reported with Berndt and Seppelt carbenes **IX**,**X** and **XIII**,**XIV**, respectively.

V.3.2 Addition to Carbonyl Derivatives

Electrophilic transient carbenes are known to react with carbonyl derivatives through the oxygen lone pair to give carbonyl ylides **63** (Scheme 11).[151a,152]

Scheme 11



These 1,3-dipolar species are usually trapped by [3+2]-cycloaddition reactions or can even be isolated; a small amount of the corresponding oxiranes is sometimes obtained.[151]

The phosphinosilylcarbene **XIa** does not react with aliphatic ketones. However, it readily and cleanly adds to the more electrophilic benzaldehyde and cinnamaldehyde, affording the oxiranes **64a** and **64b**, respectively, as only one diastereomer.[135] These results strongly suggest a concerted mechanism, since the formation of a zwitterionic intermediate, such as **65**, would result in the formation of a phosphoryl alkene via oxygen atom attack at the phosphorus center (Scheme 12).

In marked contrast, the 1,2,4-triazol-5-ylidene **IVa** reacts with paraformaldehyde to afford the corresponding acyl anion equivalent **66**, which has been isolated as its protonated form **67** in up to 65% yield[153a] (Scheme 13). It is noteworthy that when only a catalytic amount of **IVa** is used, a formoin condensation reaction occurs and hydroxyacetaldehyde is obtained in 59% yield (Scheme 13). In this reaction, the heterocyclic carbene acts as a nucleophilic catalyst, which is reminiscent of the thiazolium salt-catalyzed benzoin condensation reactions described by Ukai[154] and Breslow.[155]

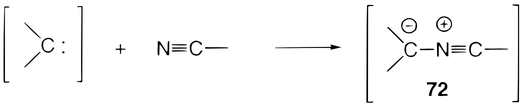
Thiazolium **68**, imidazolium **69**, and triazolium salts **70** are well-known catalysts for various C−C coupling reactions in basic media. Major examples are the benzoin condensation of aldehydes to α-hydroxyketones, the Michael−Stetter reaction yielding 1,4-dicarbonyl derivatives, and the formoin condensation reactions affording C2 to C6 carbohydrates (Scheme 14).[153]

Even asymmetric benzoin condensation and Michael−Stetter reactions have been reported using the optically active triazolium salt **71** (Scheme 15).[156]

It is interesting to note that, as early as 1958, Breslow[155] recognized the role of heterocyclic carbenes as key catalysts in enzymatic reactions for which thiamine pyrophosphate is a cofactor. Castells[157] and Myles[158] recently demonstrated that the carbene dimers can also be the catalytic species in the benzoin condensation catalyzed by thiazolium salts plus base.

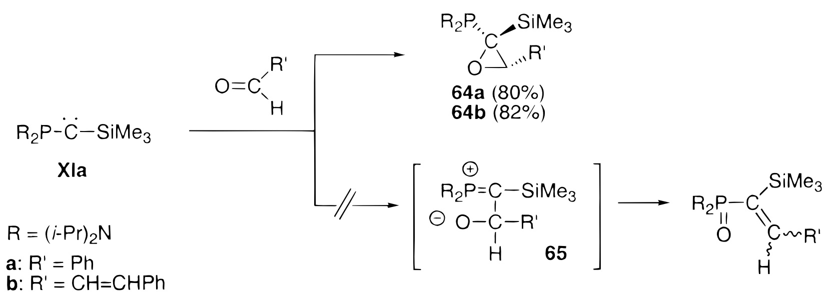
V.3.3. Addition to Carbon-Heteroatom Triple Bonds

Transient electrophilic carbenes are known to react with nitriles to give transient[152] or even stable nitrile ylides **72** (eq 35).[159] No reaction of transient nucleophilic carbenes with nitriles has been reported.

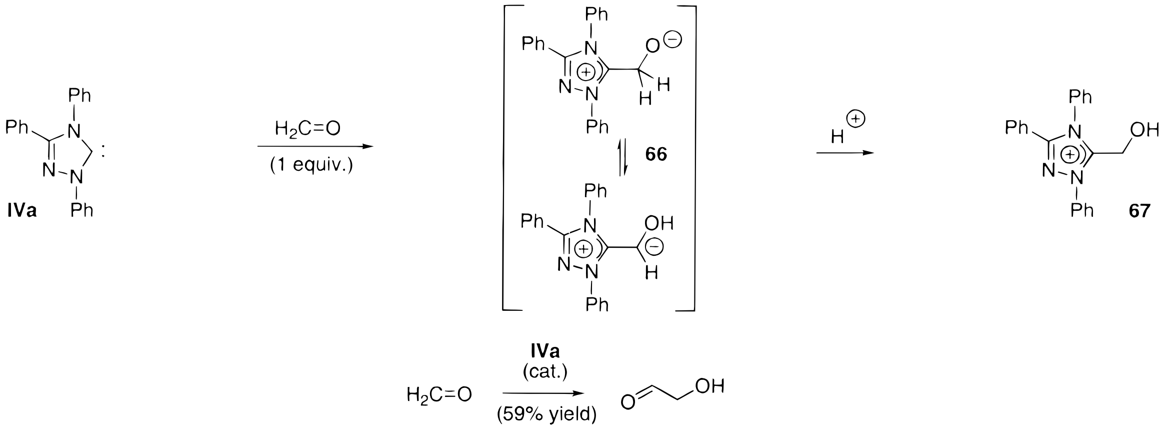


$$\left[>C: \right] + N{\equiv}C- \longrightarrow \left[>\overset{\ominus}{C}-\overset{\oplus}{N}{\equiv}C- \right] \quad (35)$$

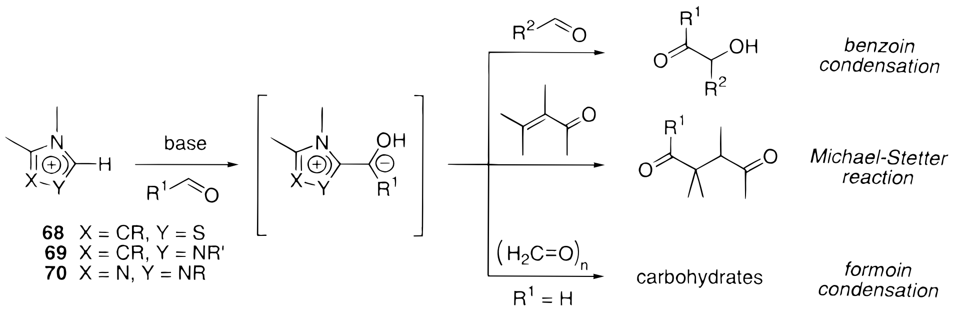
Scheme 12



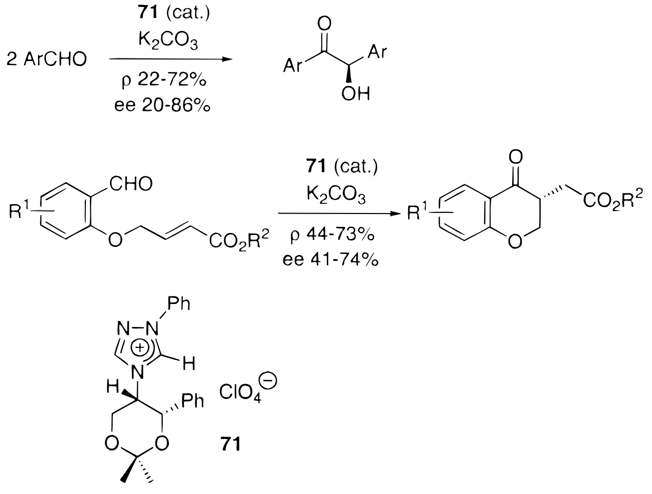
Scheme 13



Scheme 14

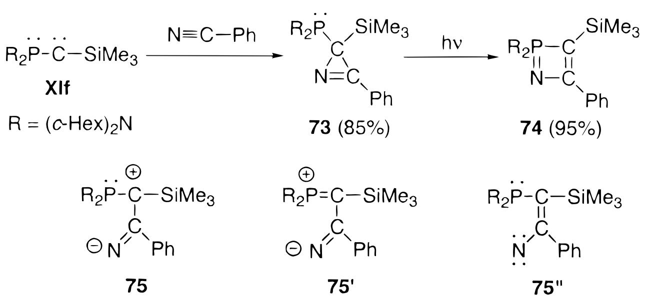


Scheme 15

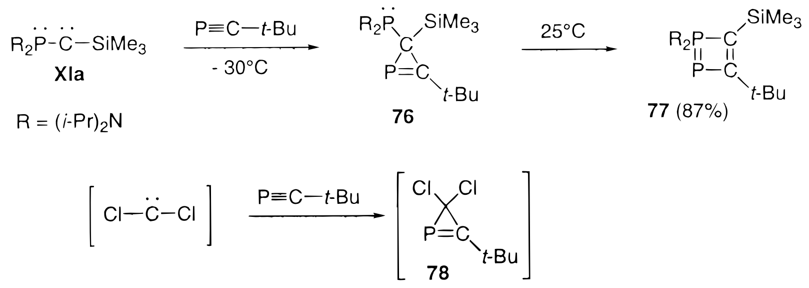


The first example of azirine formation from a carbene and a nitrile has been observed by addition of the phosphinocarbene **XIf** to benzonitrile.[160] It is quite likely that the formation of the azirine **73** results from a concerted [1+2]-cycloaddition. A stepwise mechanism, involving the initial nucleophilic attack of the carbene at the carbon atom of the nitrile, would have led to the 1,3-dipole **75**, which can also be regarded as the azabetaine **75′** or the vinyl nitrene **75″** (Scheme 16). The ring closure of vinyl nitrenes to produce azirines is known,[161] but it has been shown that these unsaturated species are efficiently trapped by phosphines to give phosphazene adducts;[162,163] therefore, in the case of the vinyl nitrene **75″**, an

Scheme 16



Scheme 17



intramolecular reaction of this type should have led to the azaphosphete **74**.[164,165] Interestingly, irradiation of the phosphinoazirine **73** at 254 nm led to the azaphosphete **74** in 95% yield (Scheme 16).[160]

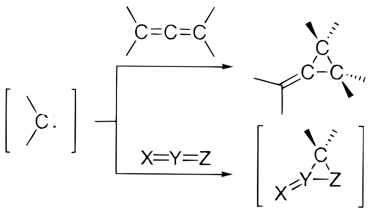
Similarly, the phosphinosilylcarbene **XIa** reacts at −30 °C with a slight excess of *tert*-butylphosphaalkyne cleanly affording the 2-phosphino-2*H*-phosphirene **76**.[166] The reaction leading to **76** is related to that observed on reacting transient dichlorocarbene with the *tert*-butylphosphaalkyne, in which the transient 2*H*-phosphirene **78** was postulated.[167] At room temperature, the three-membered heterocycle **76** appeared to be rather unstable and rearranged quantitatively to afford the 1λ^5,2λ^3-diphosphete **77** after 3 h (Scheme 17).[166,168]

So far, no reactions involving the other stable carbenes with triply bonded compounds have been reported.

V.3.4. Addition to Cumulenes

The addition of variously substituted transient carbenes or carbenoid systems to allenes has been extensively applied to the synthesis of alkylidenecyclopropanes.[169] There are also a few reactions of transient carbenes with heterocumulenes, but usually the expected three-membered heterocycles are not stable and undergo subsequent rearrangements or fragmentations (Scheme 18).

Scheme 18



No reaction involving phosphino- or sulfenylcarbenes with cumulenes have yet been reported.

The imidazol-2-ylidenes **IIIi**−**k** and the 1,2,4-triazol-5-ylidene **IVa** cleanly react with heterocumulenes such as carbon dioxide, carbon disulfide, phenyl isothiocyanate, and diisopropylcarbodiimide, giving the corresponding betaines **79a**−**g** (69−82% yield).[170] Upon treatment of **IVa** with phenyl isocyanate, the intermediate dipole **79h** rapidly reacts with excess PhNCO in a [3+2]-cycloaddition cleanly affording the spiro derivative **80** (Scheme 19).

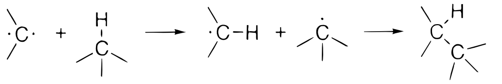
V.3.5. Addition to 1,3-Dipoles

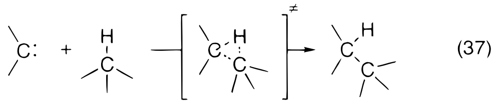
Due to the possible hypervalency of phosphorus[95] and to the phosphorus−carbon multiple bond character of phosphinocarbenes, trimethylsilyl azide and nitrogen oxide react with **XIa** affording the diazo derivatives **82** and **84** in 92% and 86% yield, respectively. These results have been explained by [2+3]-cycloaddition reactions followed by ring opening of the resulting five-membered rings **81** and **83**. Indeed, the initial 1,2,3,4λ^5-triazaphosphole **81** was characterized in solution at 4 °C.[8c]

V.4. Insertion Reactions

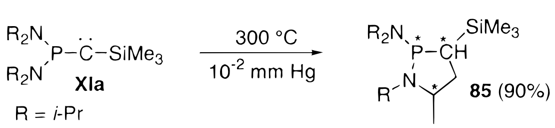
V.4.1. Insertion into Unpolarized C−H Bonds

Insertion into C−H bonds is a characteristic and well-documented feature for singlet and triplet carbenes. However, here also, the mechanism of the reaction is totally different depending on the spin multiplicity. Triplet carbenes first abstract hydrogen to give radicals (eq 36), while consideration of the spin conservation rule leads to the formulation of the insertion of a singlet carbene as a one-step process involving a three-center cyclic transition state (eq 37).[171]


(36)


(37)

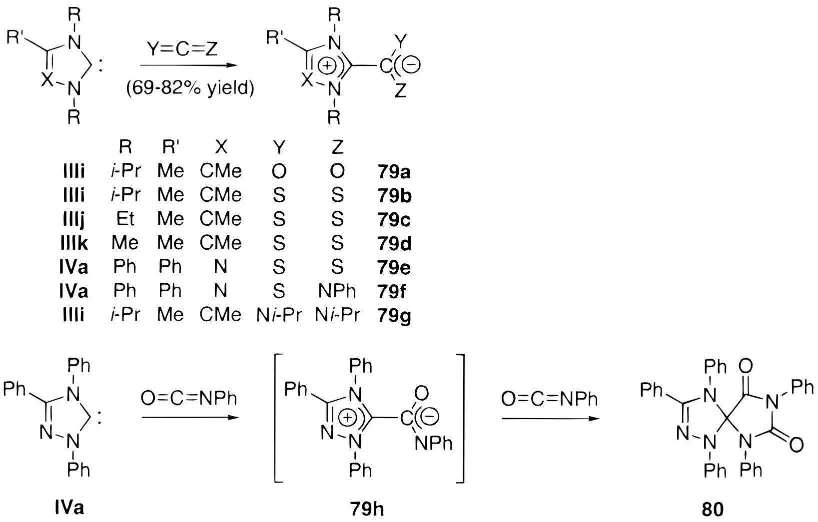
So far, among the stable carbenes, C−H insertion has only been observed with the phosphinosilylcarbene **XIa**. Under rather drastic conditions (300 °C, 10^{-2} mmHg), **XIa** has been converted into the azaphospholidine **85**, in high yield, as a mixture of four diastereomers, due to the presence of three stereogenic centers (eq 38).[8c,135] The high regioselectivity



(38)

of the carbene insertion (no formation of four-membered rings was detected) is intriguing, especially since the same regioselectivity is observed upon thermolysis of the bis(diisopropylamino)phosphino-

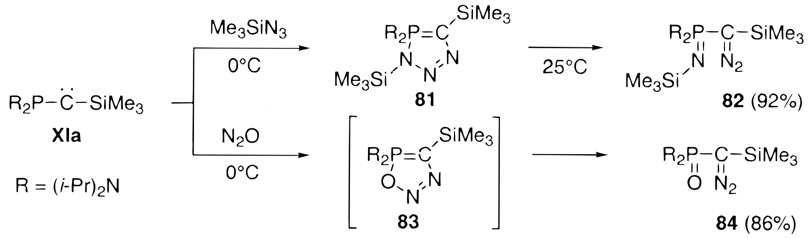
Scheme 19



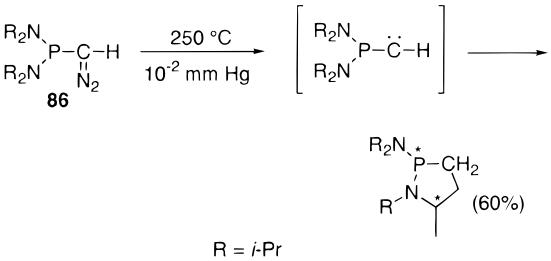
	R	R'	X	Y	Z	
IIIi	*i*-Pr	Me	CMe	O	O	**79a**
IIIi	*i*-Pr	Me	CMe	S	S	**79b**
IIIj	Et	Me	CMe	S	S	**79c**
IIIk	Me	Me	CMe	S	S	**79d**
IVa	Ph	Ph	N	S	S	**79e**
IVa	Ph	Ph	N	S	NPh	**79f**
IIIi	*i*-Pr	Me	CMe	N*i*-Pr	N*i*-Pr	**79g**

IVa **79h** **80**

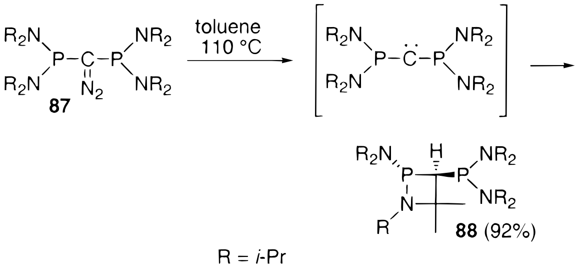
Scheme 20



diazomethane **86** (eq 39).[8c] Yet, in contrast, heating the bis[bis(diisopropylamino)phosphino]diazomethane **87** in refluxing toluene affords the four-membered heterocycle **88** as a single diastereomer in 92% yield (eq 40).[172] The difference in the regioselectivity and stereoselectivity observed has not yet been explained.



(39)

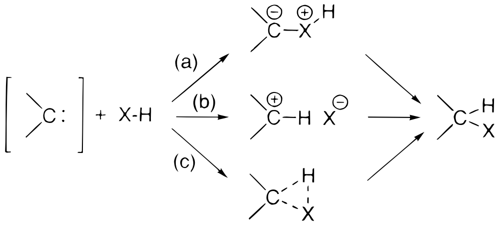


(40)

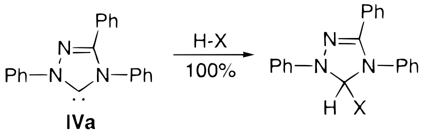
V.4.2. Insertion into Polarized X–H Bonds

Insertion of transient carbenes into strongly polarized X−H bonds has been discussed primarily in terms of stepwise mechanisms: (a) electrophilic attack of the carbene on the heteroatom X, followed by proton transfer (ylid mechanism), and (b) protonation of the carbene to give a carbocation (ion pair), followed by nucleophilic addition (carbocation mechanism) (Scheme 21). A concerted process (c) cannot be excluded but has not received definitive experimental support.[38]

Scheme 21



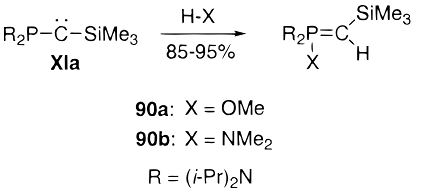
Enders et al. observed the quantitative formation of the 1,1-addition products, namely the 5-alkoxy- and 5-amino-triazolines **89** by treatment of the 1,2,4-triazol-5-ylidene **IVa** with alcohols and amines (eq 41).[48] In contrast, the 1,2-addition products **90** and **91** were obtained by reacting the phosphinosilylcarbene **XIa** with methanol and dimethylamine (eq 42)[8c]



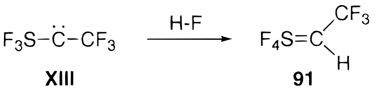
(41)

89a: X = OMe
89b: X = OEt
89c: X = N

and the trifluoroethylidynesulfur trifluoride **XIII** with H$-$F[102] (eq 43).



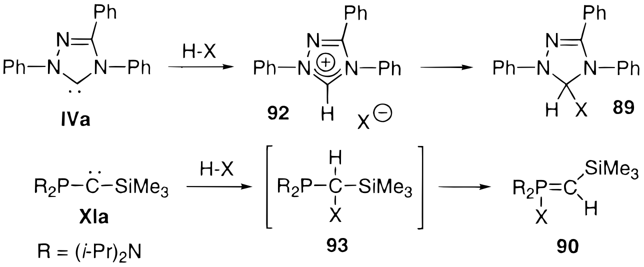
(42)



(43)

At a first glance, derivatives **89** result from a concerted insertion of the carbene **IVa** into the O$-$H and N$-$H bonds while compounds **90** and **91** result from stepwise 1,2-addition reactions. However, each of these results can be rationalized by alternative mechanisms (1) Alder has demonstrated that imidazol-2-ylidenes **III** are stronger bases than DBN, DBU, and proton sponges,[173a] and the proton affinity of the model imidazol-2-ylidene **III*** has been calculated to be ca. 260 kcal/mol.[62,63] For example, the 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene **IIIi** has an apparent pK_a value of 24.0 (DMSO)[173] and a 20/80 ratio of elimination to substitution occurred in the reaction of **IIIi** with 2-bromopropane. Therefore, a stepwise mechanism first involving the protonation of the carbene **IVa**, followed by the nucleophilic addition of the anion, easily explains the formation of **89** (Scheme 22). This hypothesis is reinforced by the fact that **92**(ClO_4^-) reacts with sodium methoxide to give **89a**.[48]

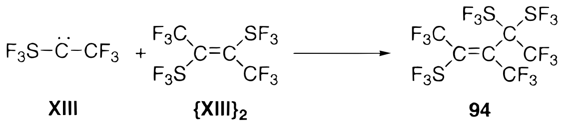
Scheme 22



(2) For the phosphinosilylcarbene **XIa**, a concerted insertion into the O$-$H and N$-$H bonds would lead to **93**. However, it is well-known[174] that phosphines such as **93** are not stable and rearrange by 1,2-shift into the corresponding phosphorus ylides **90** (Scheme 22).

V.4.3. Insertion into Other Bonds

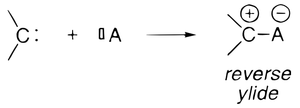
To be comprehensive, it should be noted that Seppelt assigned the trimeric structure **94** to the byproduct obtained during the dimerization of **XIII**. Derivative **94** would result from the insertion of the sulfenyl carbene **XIII** into a C$-$S bond of its dimer {**XIII**}$_2$ (eq 44).[103]



(44)

V.5. Carbene–Lewis Acid Adducts

Little is known about the reactivity of transient carbenes with Lewis acids, but because of the nucleophilicity of the stable amino- and phosphinocarbenes, numerous examples of carbene$-$Lewis acid adducts (*reverse ylides*) have been reported (eq 45), the symbol [] indicates an empty low-energy orbital.

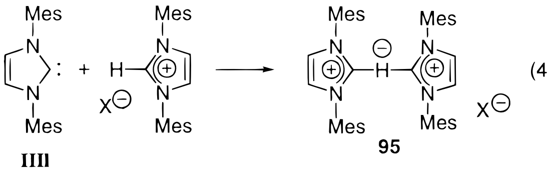


(45)

Because of the superior π-donating ability of amino compared to phosphino groups, the electronic structure of the adducts is somewhat different as illustrated in detail with carbene$-$group 13 elements.

V.5.1. Protonation of Carbenes

As we have seen in section V.4.2, aminocarbenes and, in particular, imidazol-2-ylidenes **III** are strong bases. Although the rate of proton exchange between the free carbene and its conjugate acid is close to the exchange limit at room temperature, Arduengo et al. were able to isolate the bis(carbene)$-$proton complexes **95**[175] (eq 46). These compounds are the first structurally characterized species featuring a C$-$H$-$C 3-center 4-electron interaction. Compounds **95** are high-melting solids, in which the central C$-$H$-$C unit is approximately linear (172.5°), with very different C$-$H bond lengths to the bridging proton (202.6 and 115.9 pm). The observation of averaged resonances in solution indicates that the system undergoes rapid exchange on the NMR time scale. The authors pointed out the analogy between the C$-$H$-$C fragment of **95** and the N$-$H$-$N hydrogen bonds in pyridine systems.



(46)

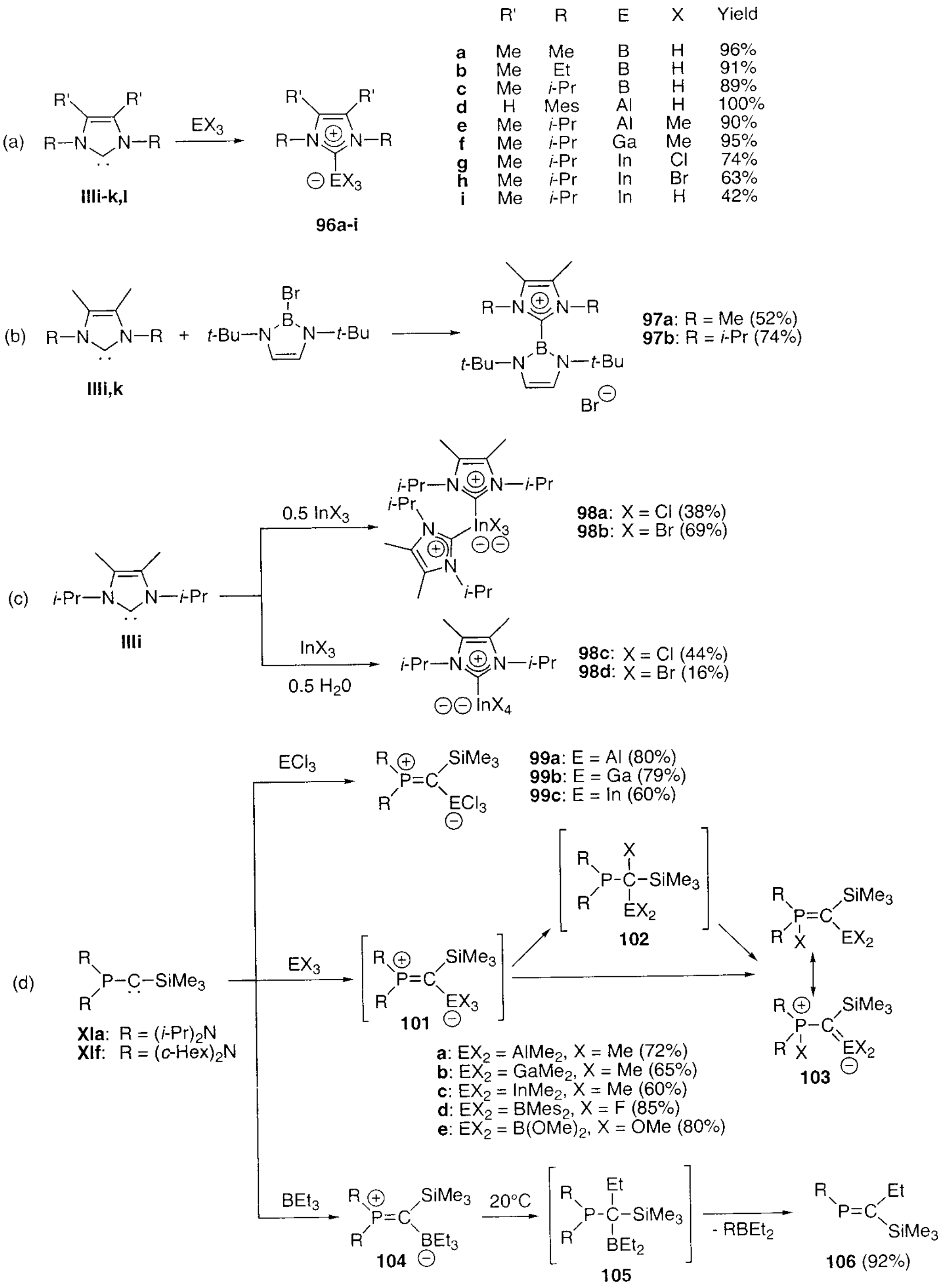
X = PF_6 (60% yield)
X = CF_3SO_3 (100% yield)

So far, the basicity of the other stable carbenes has not been experimentally studied. The proton affinity for the model phosphinosilylcarbene **XIi*** has been estimated by ab initio calculations (257 kcal/mol).[86]

V.5.2. Carbene–Group 13 Element Adducts

The imidazol-2-ylidene$-$alane complex **96d** was the first group 13 element$-$carbene complex to be reported (Scheme 23a).[176] The ^1H NMR spectrum of **96d** showed a resonance for the imidazole ring protons at 7.42 ppm, which is downfield from the corresponding resonance for the free carbene (7.02 ppm). The ^{13}C NMR signal for the carbon bonded to the alumi-

Scheme 23



	R'	R	E	X	Yield
a	Me	Me	B	H	96%
b	Me	Et	B	H	91%
c	Me	i-Pr	B	H	89%
d	H	Mes	Al	H	100%
e	Me	i-Pr	Al	Me	90%
f	Me	i-Pr	Ga	Me	95%
g	Me	i-Pr	In	Cl	74%
h	Me	i-Pr	In	Br	63%
i	Me	i-Pr	In	H	42%

num atom appeared at 175 ppm, substantially upfield from that of the free carbene (220 ppm) and downfield from that of the imidazolium salt (~136 ppm). Last, the ^{27}Al NMR resonance (107 ppm) for **96d** is typical of four-coordinate aluminum species. On the basis of these results, Arduengo suggested that the imidazole fragment has an electronic structure which is intermediate between those of the free carbene and imidazolium ion. More recently, Robinson et al. reported the imidazol-2-ylidene–trimethyl alane and gallane complexes **96e** and **96f** and drew similar conclusions (Scheme 23a).[177]

Several imidazol-2-ylidene BH$_3$ complexes **96a–c**[178] have been prepared (Scheme 23a). In the case of **96a**, the ^{11}B NMR chemical shift (−35 ppm) is typical for ylide–borane adducts and the $^1J_{HB}$ coupling constant (86 Hz) is very similar to that of the anionic analogue PhBH$_3^-$ (76 Hz).[179]

A different type of adduct has been obtained using a bromodiazaborole.[180] Indeed, Weber et al. observed halide displacements and isolated 1,3,2-diazaborolyl-functionalized imidazolium salts **97a**,**b**, which feature two linked 6-π-electron heterocycles (Scheme 23b).

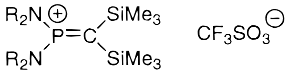
In the indium series, Jones et al. obtained complexes **96g**,**h** and **98a**,**b** in moderate yields by treatment of a THF solution of InX$_3$ (X = Cl, Br) with 1 and 2 equiv of imidazol-2-ylidene **IIIi**, respectively (Scheme 23a, c).[181a] The formation of 2:1 complexes **98a**,**b** highlights the propensity of indium to achieve higher coordination numbers than those of aluminum and gallium for which only 1:1 adducts are known.

Two additional results in the indium series are noteworthy. The use of imidazol-2-ylidene **IIIi** has allowed for the isolation of the first structurally authenticated indium trihydride complex **96i** (Scheme 23a).[181b] This compound has been obtained in moderate yields by treatment of an ether solution of $InH_3(NMe_3)$, generated in situ, or $LiInH_4$ with 2 equiv of carbene at −40 °C. On the other hand, thanks to the high nucleophilicity of imidazol-2-ylidenes, the indium salts **98c**,**d** have been prepared (Scheme 23c).[181a]

All the imidazol-2-ylidene−group 13 complexes are thermally very stable, except the indium trihydride adduct **96i**, but in this special case one has to remember that, so far, only the bulky tricyclohexylphosphine has been able to stabilize the InH_3 fragment.[181c] The stability of the alane and borane complexes **96a**−**d** is especially remarkable considering the fact that they contain a potential hydride donor adjacent to a potentially electrophilic center. This clearly demonstrates that the vacant orbital at the carbon is very high in energy and therefore not available. This is in line with the fact that no cyclopropanation has as yet been reported with diaminocarbenes and especially imidazol-2-ylidenes **III**.

In marked contrast, the stability or even the existence of phosphinosilylcarbene−group 13 complexes is strongly related to the element and also the substituents of the Lewis acid. So far, only the aluminum, gallium, and indium trichloride adducts **99a**−**c** have been isolated (Scheme 23d).[182]

The deshielded ^{31}P and ^{13}C NMR chemical shifts observed for **99a**−**c** ($\delta^{31}P \approx +130$ ppm, $\delta^{13}C \approx +76$ ppm, $J_{PC} \approx 85$ Hz) are consistent with the presence of a P═C double bond and positive charge development at phosphorus. These spectroscopic data are very similar to those observed for the methylenephosphonium salt **100** (see section V.5.3).[94a] This similarity is reinforced by the X-ray analysis of the gallium adduct **99b**: (i) the phosphorus and carbon atoms adopt a trigonal planar geometry, (ii) there is a twist angle between the two planes of 34.1°, (iii) the phosphorus−carbon bond distance is rather short (1.61 Å).



R = *i*-Pr **100**

When trimethylaluminum, -gallium, and -indium were used, instead of the corresponding trichloride derivatives, phosphorus ylides **103a**−**c** were obtained in good yields; no intermediates were spectroscopically detected.[182] In the same way, addition of dimesitylfluoroborane and trimethoxyborane[183] led to the phosphorus ylides **103d** and **103e**, respectively. Once again, it is reasonable to postulate the initial formation of the carbene−Lewis acid adducts **101**. Then the formation of **103** could result either from a direct 1,3-migration or alternatively from a 1,2-migration leading to phosphines **102** followed by the well-known methylenephosphine−phosphorus ylide conversion[174] (Scheme 23d).

Although numerous so-called stabilized phosphorus ylides, in which the negative charge is delocalized into an organic or organometallic framework, have been studied, compounds **103b**[182] and **103d**[183] were the first examples of phosphorus ylides C-substituted by a group 13 element to be studied by X-ray diffraction. These species are of interest since they can also be considered as boron− and gallium−carbon doubly bonded compounds, C-substituted by a phosphonio group. Indeed, the boron−carbon bond length in **103d** (1.52 Å) is shorter than a usual boron−carbon single bond (1.58−1.62 Å), although a little longer than a boron−carbon double bond (1.44 Å in $Mes_2B{=}CH_2^-$);[184] this boron−carbon π-type interaction was confirmed by NMR in solution. In the same way, the gallium−carbon bond length in **103b** (1.93 Å) is remarkably short.

The hypothesis of a 1,2-migration process to explain the formation of the phosphorus ylides **103** is reinforced by the results obtained by reaction of the carbene **XIf** with triethylborane (Scheme 23d). The initial borane−carbene adduct **104** is stable in solution for several weeks at −20 °C. However, after a day at room temperature,[185] elimination of diethyl(dicyclohexylamino)borane occurs leading to the phosphaalkene **106**, which was isolated in a nearly quantitative yield. This fragmentation is best rationalized by a classical migration of an ethyl group from the four-coordinate boron atom to the electron-deficient α-carbon[186] to form **105**, followed by a 1,2-elimination of diethyl(dicyclohexylamino)borane.

The lower stability of phosphinosilylcarbene−group 13 element Lewis acid adducts compared to that of the corresponding imidazol-2-ylidene adducts is easily rationalized by considering the inferior ability of phosphorus to stabilize a positive charge in the α-position. In other words, once complexed the carbene center of phosphinocarbenes still has an easily accessible vacant orbital, which is not the case for the aminocarbenes and their adducts.

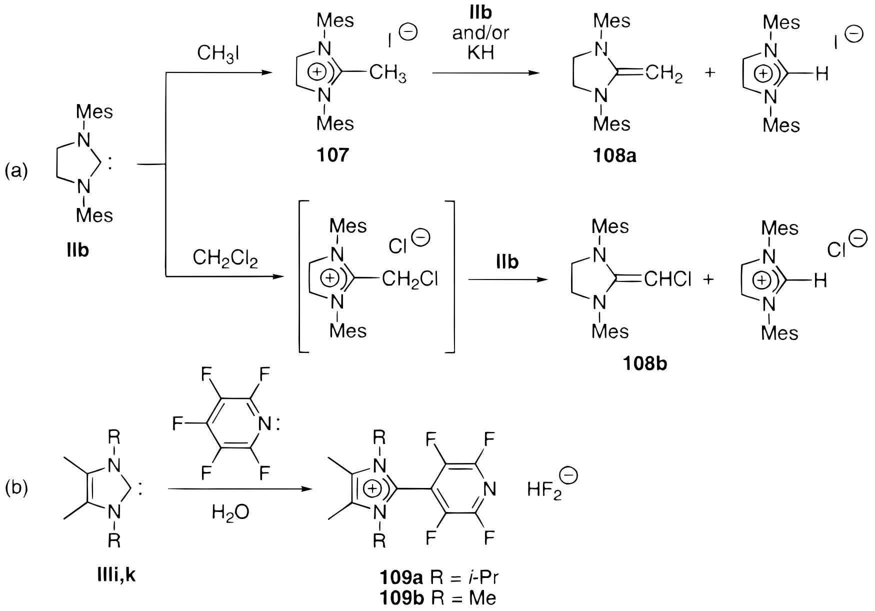
V.5.3. Carbene–Group 14 Element Adducts

The carbene adducts with heavier carbene analogues have already been discussed (see section V.2.2), and thus, we will now focus on the adducts with tri- and tetravalent derivatives of group 14 elements. Here also, the behavior of amino- and phosphinocarbenes is often very different.

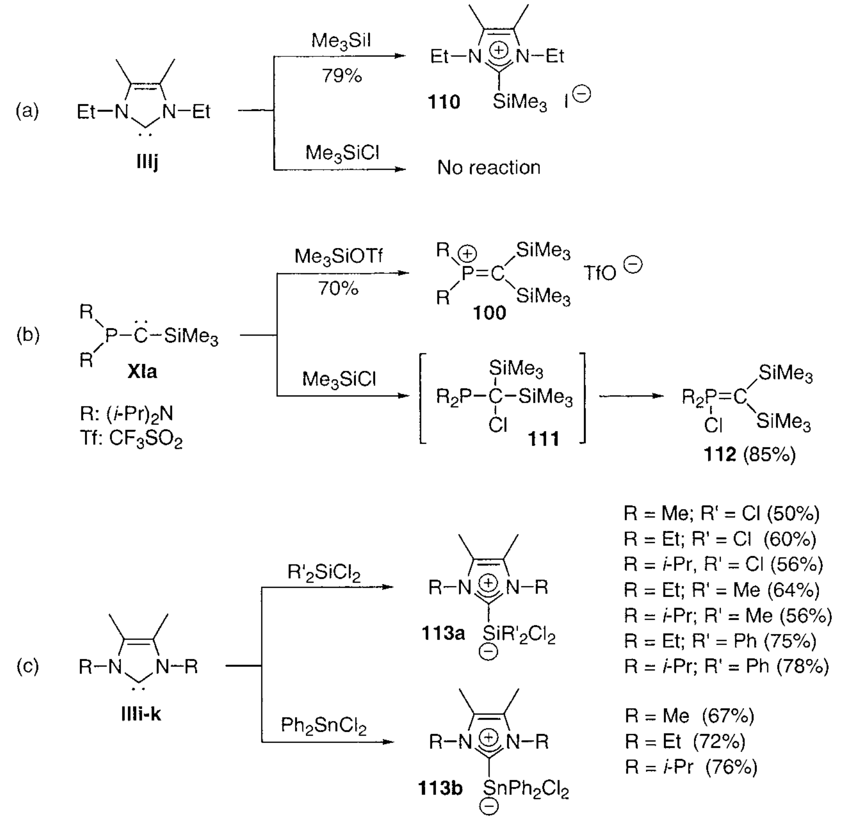
Imidazolidin-2-ylidene **IIb** reacts with methyl iodide and methylene chloride to afford olefins **108a** and **108b**, respectively, along with the corresponding imidazolidinium salt (Scheme 24a).[53b] In the case of methyl iodide, the initially formed 2-methylimidazolidinium salt **107** has been characterized, which demonstrates that the olefins **108a**,**b** do not result from a carbene−carbene coupling reaction. NMR as well as X-ray diffraction data reveal highly polarized olefinic structures.

A nucleophilic aromatic substitution has also been reported with the imidazol-2-ylidenes **IIIi,k** and

Scheme 24



Scheme 25



pentafluoropyridine, derivatives **109a**,**b** being isolated in 78–80% yield (Scheme 24b).[187]

Trimethylsilyl iodide reacts with the imidazol-2-ylidene **IIIj** affording the corresponding ionic 2-(trimethylsilyl)imidazolium salt **110** in 79% yield (Scheme 25a).[126a] In the same way, trimethylsilyl trifluoromethanesulfonate adds to the phosphinosilylcarbene **XIa** giving rise to the corresponding salt **100** which has been isolated in 70% yield (Scheme 25b).[94a] Compound **100** was the first representative of a new type of phosphorus cation, namely, the methylene phosphonium salts.[188a,b] This extremely air-sensitive compound, which is valence isoelectronic with an olefin, has been structurally characterized by an X-ray diffraction study. It has a short carbon–phosphorus double bond (1.62 Å); the phosphorus and carbon atoms are in trigonal planar environments with a dihedral angle of 60°. This value is significantly larger than that reported for the most crowded olefin.[189] Formally, this compound can be viewed as the product of a carbene–carbenoid coupling between the bis(trimethylsilyl)carbene and bis(diisopropylamino)phosphenium triflate. Note that another route to methylene phosphonium salts has been reported by Grützmacher et al.[188c]

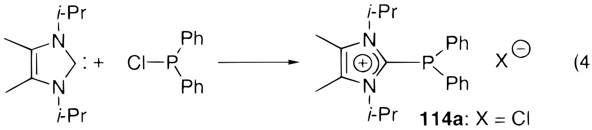
Imidazol-2-ylidene **IIIj** does not react with trimethylsilyl chloride. In contrast, a clean reaction occurs when trimethylsilyl chloride is added to the phosphinocarbene **XIa**, affording the *P*-chlorophosphorus ylide **112** (Scheme 25b).[8c] At first glance, these results are surprising since it is clear that the imidazol-2-ylidene **IIIj** is more nucleophilic than **XIa**. However, it is quite possible that **XIa** first inserts into the Si−Cl bond giving rise to phosphine **111**, which subsequently undergoes a classical 1,2-shift of the chlorine atom from the carbon to the phosphorus atom.[174]

When tetrachlorosilane or even dimethyl- or diphenyldichlorosilane was added to the imidazol-2-ylidenes **IIIi**−**k**, the corresponding pentavalent silicon derivatives **113a** were obtained in 50−75% yields (Scheme 25c).[126] These results demonstrate again the very strong Lewis base character of aminocarbenes.

Since the tendency to form adducts is more pronounced for tetravalent tin than for silicon, it is not surprising that the pentavalent tin adducts **113b** were obtained by reacting the imidazol-2-ylidenes **IIIi**−**k** with diphenyldichlorostannane (Scheme 25c).[126]

V.5.4. Carbene–Group 15 Element Adducts

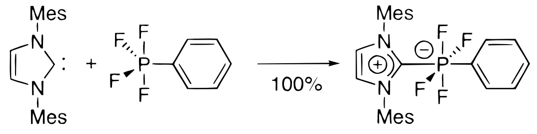
Apart from carbene−phosphinidene adducts which have been described in section V.2.2, only two carbene−group 15 element adducts have been reported. Reaction of the imidazol-2-ylidene **IIIi** with chlorodiphenylphosphine leads to the corresponding phosphino−imidazolium salt **114a**, which has been structurally characterized as **114b** after treatment with aluminum trichloride (eq 47a).[190a] On the other hand, phosphoranide **115** has been obtained in quantitative yield by treatment of the imidazol-2-ylidene **IIIl** with phenyltetrafluorophosphorane in THF solution (eq 47b).[190b] The crystallographic analysis for **115** reveals the expected octahedral geometry at the phosphorus center and a very long P−C bond (1.91 Å). As a whole, the structural and NMR data support the depiction of the valence bond structure of **115** as zwitterionic.



(47a)

IIIi

114a: X = Cl
114b: X = AlCl$_4$

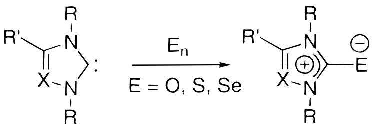


(47b)

IIIl **115**

V.5.5. Carbene–Group 16 Element Adducts

The imidazol-2-ylidenes **IIIi**−**l**,**q** readily react with elemental selenium and tellurium to afford the stable adducts **116a**−**h** in high yields (eq 48).[54,191−192] Interestingly, these reactions are opposite to those used for the synthesis of **IIIi**−**k** (reduction of the corresponding imidazol-2(3*H*)-thiones, see eq 6).[47] The ylidic nature of the chalcogen−carbon bond is revealed by both NMR and X-ray analyses and implies that derivatives **116** can be considered as imidazolium chalcogenides. It has been reported that the 1,2,4-triazol-5-ylidene **IVa** similarly reacts with oxygen, sulfur, and selenium giving **116i**−**k** (eq 48).[48,170f]

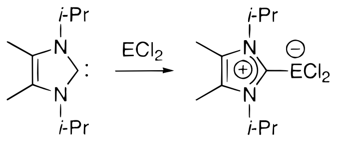


(48)

IIIi-l,q, IVa **116a-k**

	X	R'	R	E	Yield
a	CMe	Me	Me	Se	84%
b	CMe	Me	Et	Se	88%
c	CMe	Me	*i*-Pr	Se	85%
d	CMe	Me	Me	Te	91%
e	CMe	Me	Et	Te	90%
f	CMe	Me	*i*-Pr	Te	94%
g	CH	H	Mes	Te	100%
h	CCl	Cl	Mes	Te	100%
i	N	Ph	Ph	O	30%
j	N	Ph	Ph	S	100%
k	N	Ph	Ph	Se	

The imidazol-2-ylidene **IIIi** also reacts with sulfur dichloride and thionyl chloride giving the hypervalent sulfur derivatives **117a**,**b** (eq 49).[193]



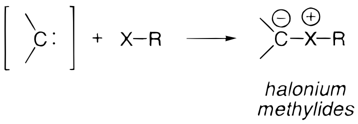
a E = S (30%)
b E = S=O (66%)

(49)

IIIi **117a**,**b**

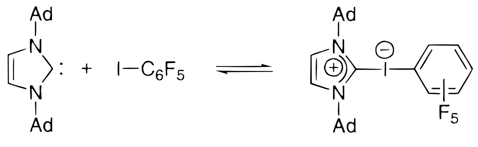
V.5.6. Carbene–Group 17 Element Adducts

With halogen centers, transient electrophilic carbenes typically form halonium methylides with a characteristically small C−X−C angle (eq 50a).[194,195]



(50a)

In the presence of iodopentafluorobenzene, the imidazol-2-ylidene **IIIc** is in equilibrium with the corresponding adduct **118** in THF solution (eq 50b).[196]



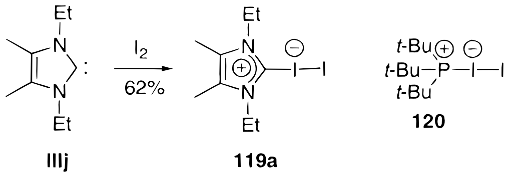
(50b)

IIIc **118**

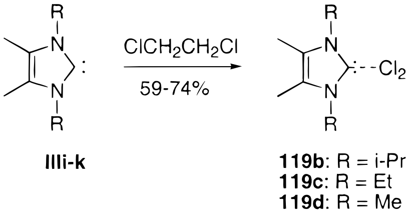
Compound **118**, which was the first isolated adduct between an aminocarbene and a Lewis acid, crystallized from THF and is stable in the solid state. In contrast to classical halonium methylides, derivative **118** features an almost linear C−I−C framework (178.9°), consistent with a 10e−I−2c (hypervalent) bonding at the iodine center and a *reverse ylide* nature. This is confirmed by the slightly increased π

delocalization in the imidazole ring of **118**, compared to that of **IIIc**.

With iodine, the imidazol-2-ylidene **IIIj** forms the stable adduct **119a** (eq 51a),[197a] in which the carbene acts as a σ donor with a pronounced basic character, just like a tertiary phosphine. Interestingly, the molecular structure of **119a** may be considered as an isolated transition state which models the nucleophilic attack of the carbene on the iodine molecule. The hypervalency caused at the central iodine atom is revealed by its geometry (C−I−I, 176.0°) and by the significant lengthening of the iodine−iodine bond (334.8 pm). In fact, the structure of **119a** is analogous to the isolable phosphine−iodine adduct **120** (P−I−I, 177.6°; I−I, 332.6 pm).[198] Related chlorine adducts **119b**−**d** have been obtained by reaction of the imidazol-2-ylidenes **IIIi**−**k** with 1,2-dichloroethane (eq 51b).[197b] The precise structure of derivatives **119b**−**d** is not known; however, these compounds have been used as chlorinating and chloride donor reagents.

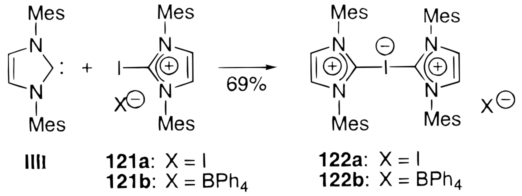


(51a)

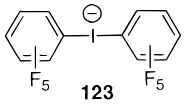


(51b)

The reaction of the 2-iodoimidazolium salts **121** with the imidazol-2-ylidene **IIIl** leads to the symmetrical compounds **122** in 69% yield (eq 52).[199a] The X-ray diffraction study carried out on **122b** revealed an almost linear C−I−C framework (177.5°), with a small difference between the two C−I distances (228.6 and 236.3 pm). These data are very similar to those observed for other symmetrical 10e−I−2c iodanides such as **123** (C−I−I, 175.2°; C−I, 233.1 and 240.3 pm).[199b]

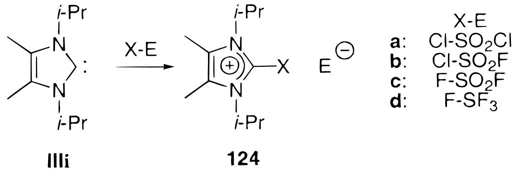


(52)



123

Halogen abstraction from hypervalent sulfur halides has also been reported for the imidazol-2-ylidene **IIIi**. This reaction gives a nice example of the synthetic utility of N-heterocyclic carbenes. Indeed, **124a** is the first structurally characterized derivative featuring the chlorosulfite ion (SO_2Cl^-).[200a] Moreover, the versatility of the related chloroimidazolinium salts for dehydration, chlorination, oxidation, reduction, and rearrangement reactions has recently been pointed out.[200b]

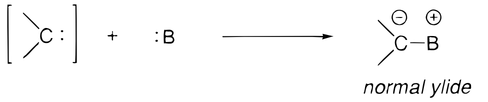


(53)

A very intriguing and original reaction between the imidazol-2-ylidene **IIIl** and carbon tetrachloride has been observed by Arduengo.[53b] This yields a new stable carbene **IIIq**, which formally results from the substitution of the ring protons by chlorine atoms (Scheme 26). The authors believe that the process begins by the chlorination of the imidazole with liberation of the trichloromethyl anion. This anion would then react with the imidazolium salt by deprotonation at the 4 position to produce chloroform and 2-chloroimidazolium-4-ate. The latter could react with additional CCl_4 to chlorinate the 4 position and produce another trichloromethyl anion. This deprotonation/chlorination process would be repeated for the 5 position to afford the 2,4,5-trichloroimidazolium ion. Finally, the 2 position of this ion would be dechlorinated by reaction with **IIIl** or CCl_3^- to produce **IIIq** (Scheme 26).

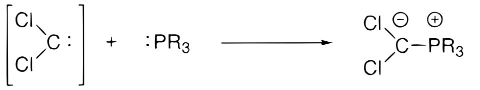
V.6. Carbene−Lewis Base Adducts

Transient electrophilic carbenes are known to react with Lewis bases to give *normal ylides* (eq 54). For



(54)

example, carbene−pyridine adducts have been spectroscopically characterized and used as a proof for the formation of carbenes.[17a,201] The reaction of transient dihalogenocarbenes with phosphines is even a preparative method for *C*-dihalogeno phosphorus ylides (eq 55).[202] Moss et al. have shown that

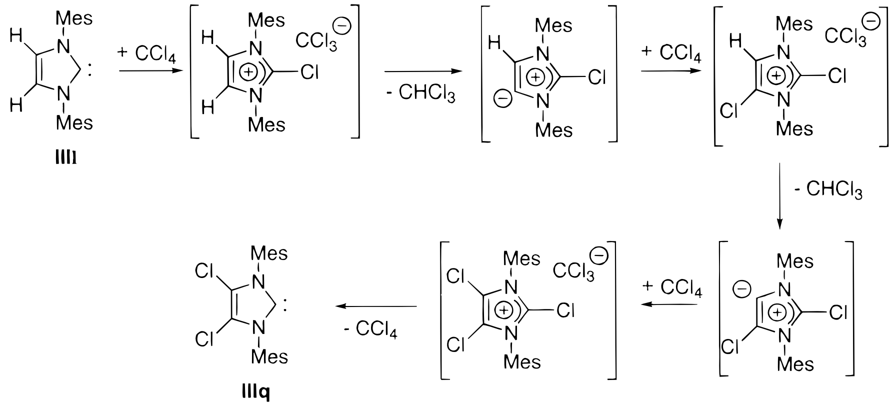


(55)

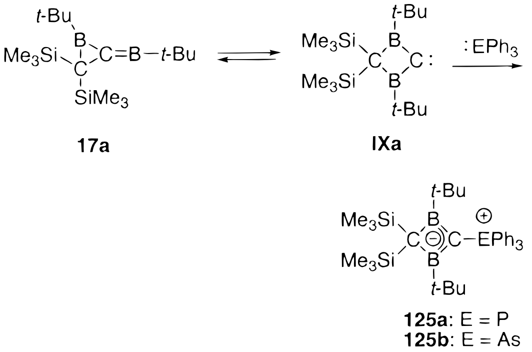
in contrast to dialkoxycarbenes, carbenes featuring only a weak π-donor substituent, such as acetoxyphenylcarbene, give carbene−Lewis base adducts.[203]

So far, there are only very few examples of Lewis base adducts involving stable carbenes. Berndt has found that addition of triphenylphosphine and -arsine to the boriranylideneborane **17a** led to the corre-

Scheme 26

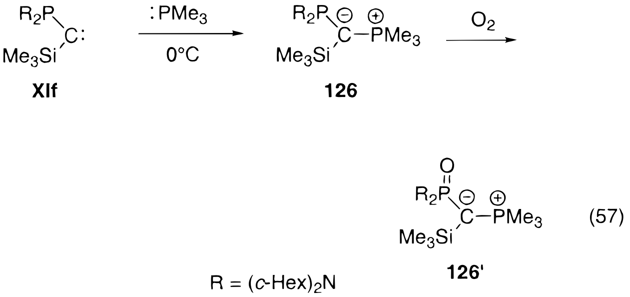


sponding ylides **125a** and **125b**, respectively (eq 56).[204] These results are not surprising since the



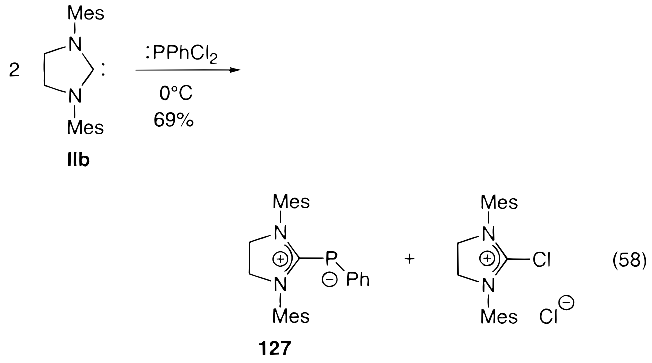
carbene **IXa** is strongly electrophilic.

We have recently shown that instantaneous and quantitative formation of the phosphorus ylide **126** occurred when 1 equiv of trimethylphosphine was added at 0 °C to a pentane solution of the carbene **XIf.** The *C*-phosphino phosphorus ylide **126** is highly oxygen sensitive, and attempted recrystallizations led to the corresponding phosphine oxide **126′**, which was isolated in 90% yield (eq 57).[205]



The formation of the ylides **125** and **126** is of particular significance since it is certainly the most striking evidence for the presence of an accessible vacant orbital at the carbene center of the electrophilic diborylcarbenes **IX** and nucleophilic phosphinosilylcarbenes **XI**.

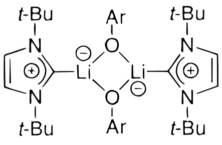
It is interesting to note that imidazolidin-2-ylidene **IIb** reacts with phenyldichlorophosphine affording the carbene−phosphinidene adduct **127** along with 2-chloroimidazolidinium chloride (eq 58).[129b]



V.7. Carbene−Metal Adducts

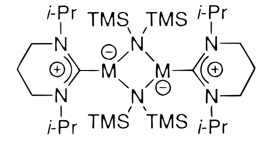
V.7.1. Carbene−Alkali Metal Adducts

The imidazol-2-ylidene **IIIp** and tetrahydropyrimid-2-ylidene **II′a** react with alkali (2,4,6-trimethyl)phenolate and bis(trimethylsilyl)amide to give the dimeric carbene−alkali adducts **128a**[206] and **128b**,[50] respectively. The X-ray crystal structure determination of **128a** revealed that the N−C̈ bond lengths and N−C̈−N bond angle are essentially the same as in **IIIp**. Thus, coordination of a lithium atom has only a marginal influence on the structure of the imidazol-2-ylidene. A similar feature has been observed with the dimeric *N*-borane imidazol-2-ylidenelithium complex **128c**.[113]



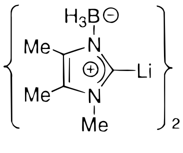
128a

Ar = 2,4,6-Me$_3$C$_6$H$_2$



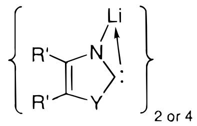
128b

M = Li, Na, K



128c

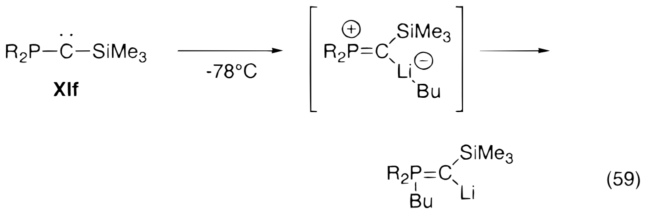
3-Lithiated imidazol-2-ylidenes and thiazol-2-ylidenes **129a** and **129b,** respectively, have been isolated as dimers or tetramers and structurally characterized.[207] In these derivatives, the lithium linked



129a: Y = NR
129b: Y = S

to the nitrogen atom is also bonded to the carbene center. Note that, despite this three-center interaction, there are some similarities between these acyl anion equivalents **129** and the related N-heterocyclic carbenes.[207]

Butyllithium instantaneously reacts at −78 °C with **XIf** to afford the α-(lithiomethylene)phosphorane **130**, which has been isolated in a nearly quantitative yield (eq 59).[208] Most probably, after coordination of the carbene center to the metal, the butyl group attacks the electrophilic phosphorus atom. This result clearly illustrates the synthetic utility of stable carbenes. Derivative **130** is the only known phosphonium yldiide[209,210] that has been fully characterized. So far, a promising synthetic application[211] of this type of carbodianion has been hampered by the difficulties associated with their synthesis.[212−214]



XIf

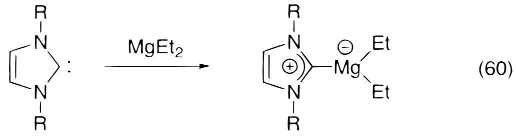
130

(59)

R = (c-Hex)$_2$N

V.7.2. Carbene–Alkaline Earth Metal Adducts

The imidazol-2-ylidenes **IIIc**,**l** react with diethylmagnesium to afford the corresponding 1:1 adducts **131a**,**b** in good yields (eq 60).[215] Derivative **131a** is monomeric, while **131b** is dimeric with bridging ethyl groups. This has been rationalized in terms of the relative steric hindrance imposed by the two R substituents.

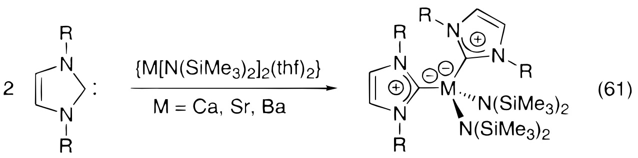


(60)

IIIc: R = Ad
IIIl: R = Mes

131a: R = Ad (79%)
131b: R = Mes (62%)

With the bis(amido) derivatives of calcium, strontium, and barium {M[N(SiMe$_3$)$_2$]$_2$(THF)$_2$}, the 2:1 adducts **132** have been prepared from **IIIo**,**p** (eq 61).[216] Both complexes **131** and **132** feature predominantly ionic metal−carbene bonds; the heavier the alkaline earth metal, the more labile the carbene ligand. A dissociative equilibrium has even been observed for **132e**,**f**.

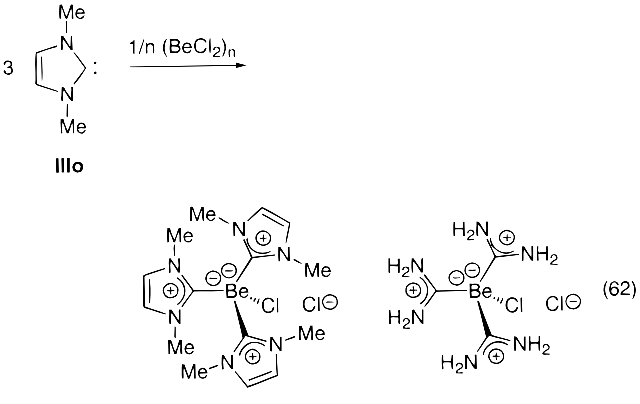


(61)

IIIo: R = Me
IIIp: R = t-Bu

	M	R
132a	Ca	Me
132b	Ca	t-Bu
132c	Sr	Me
132d	Sr	t-Bu
132e	Ba	Me
132f	Ba	t-Bu

The 3:1 carbene−beryllium adduct **133** has been prepared in 73% yield by treatment of beryllium chloride with 3 equiv of the imidazol-2-ylidene **IIIo** in toluene solution (eq 62).[217] In this reaction, the polymeric structure of BeCl$_2$ is destroyed, which emphasizes the pronounced nucleophilicity of **IIIo**. Moreover, quantum chemical ab initio calculations performed on the model compound **133*** clearly established that the carbene ligands act as pure σ-donors toward the highly Lewis acidic beryllium atom.[218]



IIIo

133 (73%)

133*

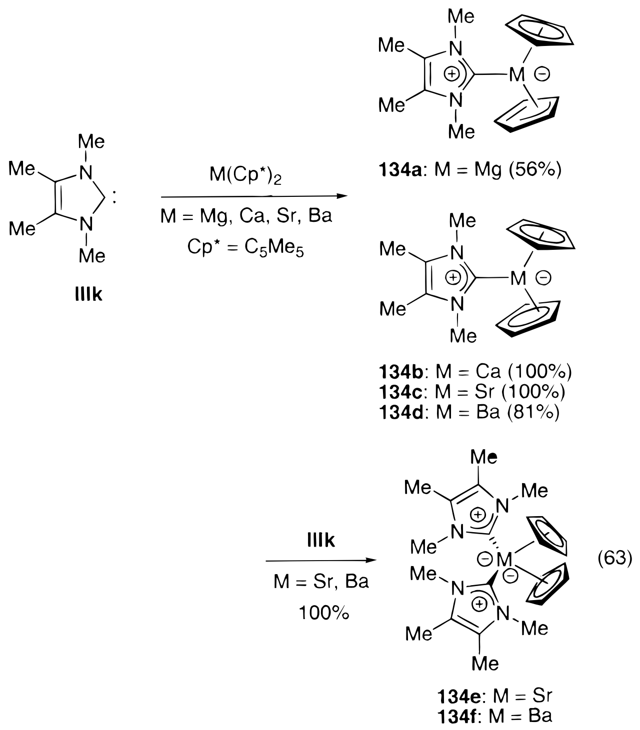
(62)

The tetramethylimidazol-2-ylidene **IIIk** reacts smoothly with bis(pentamethylcyclopentadienyl)magnesium, -calcium, -strontium, and -barium to give the all-carbon-ligated 1:1 adducts **134a**−**d** (eq 63).[219] For compounds **134b**−**d**, the two Cp* rings are η^5-coordinated to the metallic center, while in **134a**, one of the Cp* rings is coordinated in a η^5-fashion and the second exhibits a “slipped” geometry. As observed for **131** and **132**, the ligther the alkaline earth metal, the stronger the metal−carbene interaction, as evidenced by the relative M−C bond distances and ^{13}C chemical shifts of the ligating carbon atom. Addition of a second equivalent of carbene **IIIk** to the heavier metal complexes **134c**,**d** leads to the corresponding 2:1 adducts **135c**,**d**, in which the two carbene ligands are weakly σ-coordinated to the metal center.[219]

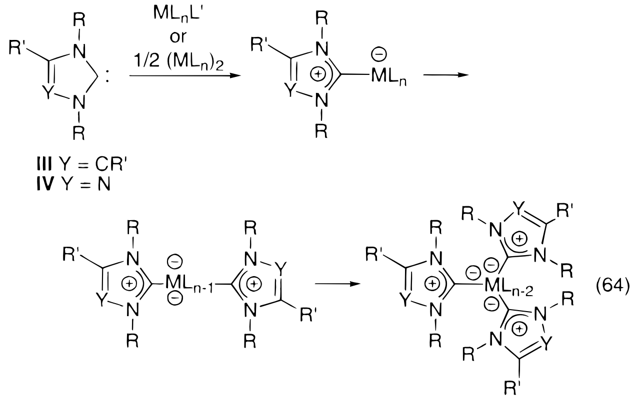
V.7.3. Carbene–Transition Metal Adducts

Amino- as well as phosphinocarbene transition metal complexes have been described, but their synthesis, electronic structure, and synthetic interest are totally different; therefore, they will be discussed in two separate sections.

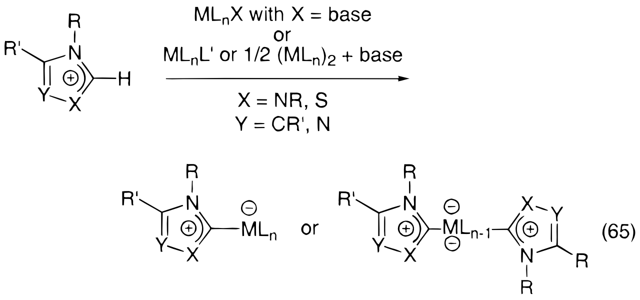
V.7.3.1. Aminocarbene Complexes. *a. Synthesis.* Transition metal complexes of N-heterocyclic car-



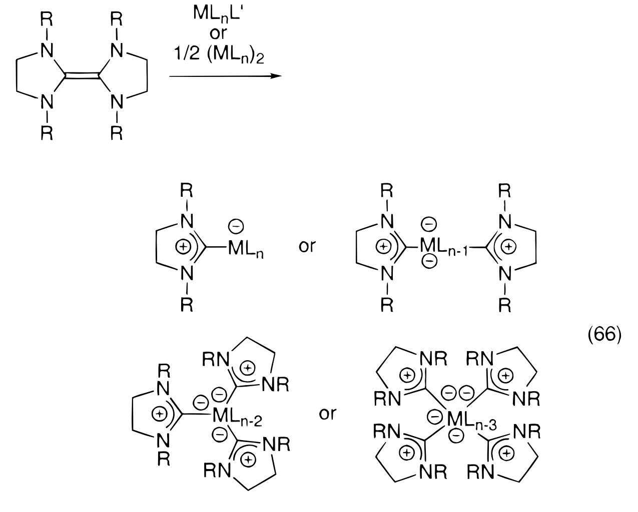
benes are accessible by six different routes (eqs 64–69). Imidazol-2-ylidenes **III** and triazol-2-ylidenes **IV** react with a broad variety of organometallic precursors ML$_n$L′ to afford the corresponding complexes after replacement of a two-electron donor[220–222] (such as tetrahydrofuran, carbon monoxide, nitriles, phosphines, or pyridine). In some cases, further ligand substitution can occur to give bis- and triscarbene complexes.[223] For example, one or two molecules of carbon monoxide are displaced from carbonyl complexes M(CO)$_n$ (M = Cr, Mo, W, Fe, Ni),[220] and further substitution requires photolytic conditions.[223] Dinuclear precursors featuring halo or acetato bridges (ML$_n$)$_2$ are smoothly split by N-heterocyclic carbenes to give the corresponding mononuclear complexes in excellent yields (eq 64).[46a]



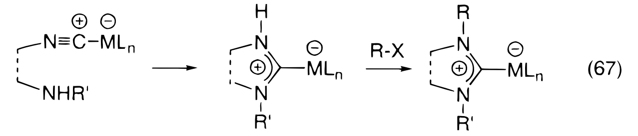
N-Heterocyclic carbene complexes can also be obtained by deprotonation of the corresponding azolium salts in the presence of organometallic fragments ML$_n$X or ML$_n$L′ (eq 65). A basic ligand X (such as hydride,[224] alkoxide,[225] or acetate[226]) of a ML$_n$X complex can deprotonate the azolium salt, or alternatively, an organic base (such as triethylamine[227]) can be used with ML$_n$L′ or (ML$_n$)$_2$ fragments. This synthetic strategy was recognized as early as 1968 by Öfele,[224] and because of the broad variety of CH-acidic heteroaromatic compounds, it is much more general than the previous method starting from isolated carbenes. It has been applied, for example, to mono- and biscarbene complexes of group 6 metals.[228]



Imidazolidin-2-ylidene complexes are accessible by reaction of the corresponding electron-rich olefin dimers with mononuclear or bridged dinuclear organometallic fragments (eq 66). Accordingly, mono-, bis-, tris-, and even tetrakiscarbene complexes of various metals have been prepared.[229]



Complexes of acyclic as well as cyclic diheteroatom-substituted carbenes can be generated by transforming other C-bound ligands (eq 67). In particular, inter- or intramolecular addition of N-nucleophiles to coordinated isocyanides is one of the most general synthetic approaches to diaminocarbene transition metal complexes.[230]



Carbene transfer reactions between transition metals have been recently reported (eq 68).[231] So far,

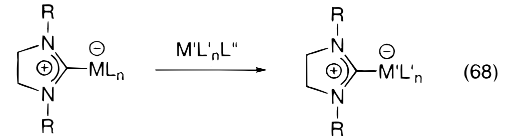
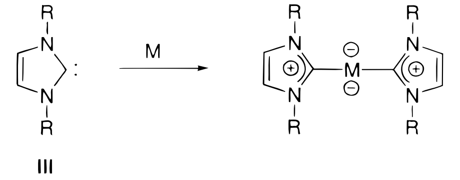


Table 8. N-Heterocyclic Carbene−Transition Metal Complexes (Formal Oxidation State in Parentheses, References in Italic

Ti (IV) *221,233*	**V** (IV) *221*	**Cr** (0) *220,223,224a,230, 234-236,238* **Cr** (I) *235* **Cr** (II) *237* **Cr** (III) *237a*	**Mn** (I) *113,248*	**Fe** (-II) *248* **Fe** (0) *220,224b,248,250-252* **Fe** (I) *248,251,253,254* **Fe** (II) *248,251* **Fe** (III) *255*	**Co** (-I) *248,265* **Co** (I) *266* **Co** (II) *266* **Co** (III) *266*	**Ni** (0) *220,232,246-248, 256,285* **Ni** (I) *286* **Ni** (II) *248,277,281b,282,287*
Zr (IV) *221*	**Nb** (IV) *221*	**Mo** (0) *44b,220,223,230, 235,236,238-242* **Mo** (II) *240,243,244*	**Tc**	**Ru** (-II) *256* **Ru** (0) *238,248,256* **Ru** (II) *46,222,227,256-264*	**Rh** (I) *46,225,231,246,247, 261,264,265,267-281* **Rh** (III) *227,274,276*	**Pd** (0) *232,288,289* **Pd** (II) *46a,226,231, 280-282,289-294*
Hf (IV) *221*	**Ta** (IV) *221*	**W** (0) *46b,54,220,223,230, 235,236,238,244-247* **W** (II) *239a,244*	**Re** (I) *230,249* **Re** (VII) *221*	**Os** (II) *46a,256,257c*	**Ir** (I) *46a,225,276,279,282* **Ir** (III) *276,283,284*	**Pt** (0) *232,285,288* **Pt** (II) *231,240,277,282, 289-291,295-297*

this promising strategy has allowed the preparation of groups 9 and 10 metal−imidazolidin-2-ylidene complexes from the corresponding group 6 metal complexes.

Last, two-coordinate homoleptic metal carbene complexes have been obtained by co-condensation of group 10 metal vapor with imidazol-2-ylidenes **III**.[232] This synthetic route is straightforward but limited by the experimental conditions.



(69)

The broad variety of N-heterocyclic carbene−transition metal complexes prepared following these six strategies is illustrated in Table 8.

b. Electronic Properties. So far, carbene complexes have been divided into two types according to the nature of the formal metal−carbon double bond (Figure 18).[298] The metal−carbon bond of Fischer-type carbene complexes is a donor−acceptor bond and formally results from the superposition of carbene to metal σ-donation and metal to carbene π-back-donation (Figure 18a). In contrast, the metal-carbene bond of Schrock-type complexes is essentially covalent and formally results from the interaction of a triplet carbene with a triplet metal fragment (Figure 18b). In relation to these different bonding situations, Fischer complexes are generally formed with a low-valent metal fragment and a carbene bearing at least a π-donor group, whereas Schrock complexes are usually formed with metals in a high oxidation state and carbene ligands bearing alkyl substituents.

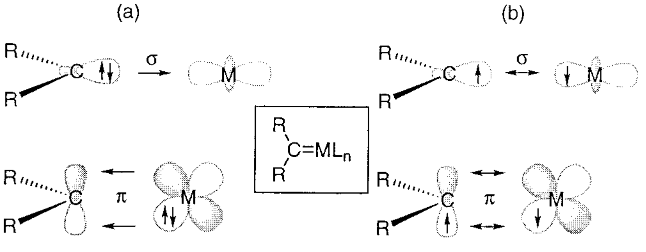
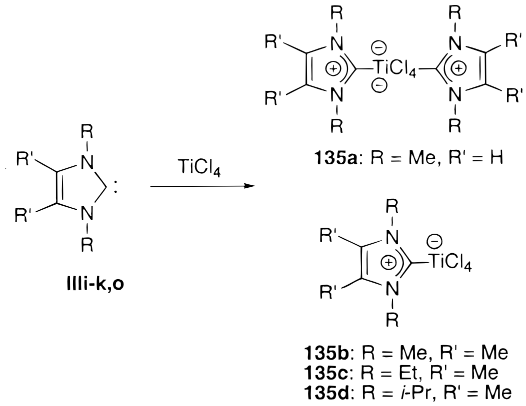


Figure 18. Schematic representations of (a) donor−acceptor bonding in Fischer carbene complexes and (b) covalent bonding in Schrock carbene complexes.

Due to the presence of two π-donor substituents at the carbene center, the N-heterocyclic carbene complexes may be classified, at a first glance, as Fischer-type compounds. However, in contrast to usual Fischer-type complexes, N-heterocyclic carbenes and especially imidazol-2-ylidenes **III** and imidazolidin-2-ylidenes **II** bind to transition metals only through σ donation, π-back-bonding being negligible. Photoelectron spectroscopy coupled with density functional calculations have demonstrated that even for group 10 metals, bonding occurs very predominantly through σ donation from the carbene lone pair.[288] These peculiar binding properties are easily understandable since the energy of the vacant p_π orbital at the carbene center is considerably increased by the strong $N \rightarrow \ddot{C}$ π donation (see section II.1.1.2). The CO stretching frequencies of mixed carbene−carbonyl complexes also afford interesting information about the electronic properties of N-heterocyclic carbene ligands.[7a] The ratio of σ donation to π back-donation for $Fe(CO)_4$-bonded heteroatom-substituted carbenes increases in the order :C(OR)R < :C(NR_2)R < :C(NR_2)$_2$ ≈ imidazolidin-2-ylidenes ≈ imidazol-2-ylidenes. The π-acceptor ability of diaminocarbenes

II−**IV** and **VI** lies between that of nitriles and pyridine. On the basis of solution calorimetric investigations, a relative enthalpy scale has been established for a series of sterically demanding nucleophilic carbene ligands coordinated to the Cp*RuCl moiety.[258] Imidazol-2-ylidenes **III** ligands behave as better donors than the best phosphine donor ligands with the exception of the sterically demanding 1,3-di(1-adamantyl)imidazol-2-ylidene **IIIc**.

Given these statements, it is not surprising that N-heterocyclic carbene complexes of almost all the transition metals have been prepared (Table 8). In particular, metals incapable of π back-donation such as titanium were only involved in Schrock carbene complexes until the stable Fischer-type complexes **135a**−**d** were prepared from $TiCl_4$ and the imidazol-2-ylidenes **IIIi**−**k**,**o** (eq 70a).[221,233] The electronic properties of these N-heterocyclic carbenes are also well illustrated in metallocene chemistry: (i) the 14-electron chromium(II) complexes **136a**,**b** have been isolated,[237] (ii) the displacement of a Cp ligand of chromocene and nickellocene can be achieved by imidazol-2-ylidenes, giving the biscarbene complexes **136d**,**e**[237b] (eq 70b).

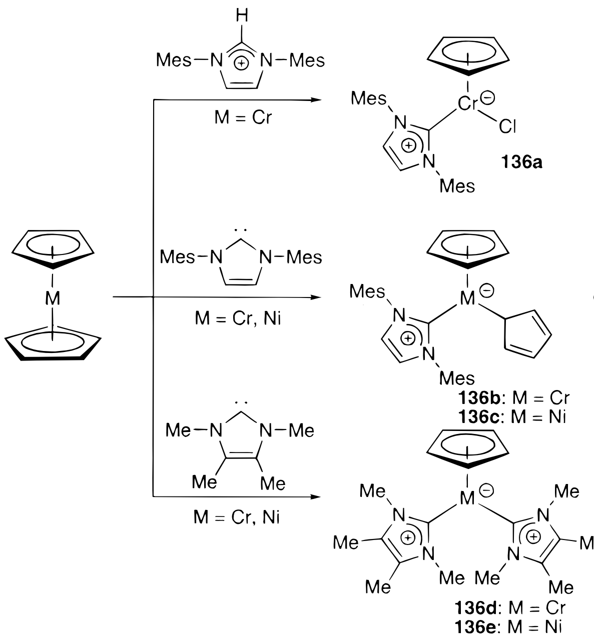


IIIi-k,o

135a: R = Me, R' = H

(70a)

135b: R = Me, R' = Me
135c: R = Et, R' = Me
135d: R = *i*-Pr, R' = Me



136a

(70b)

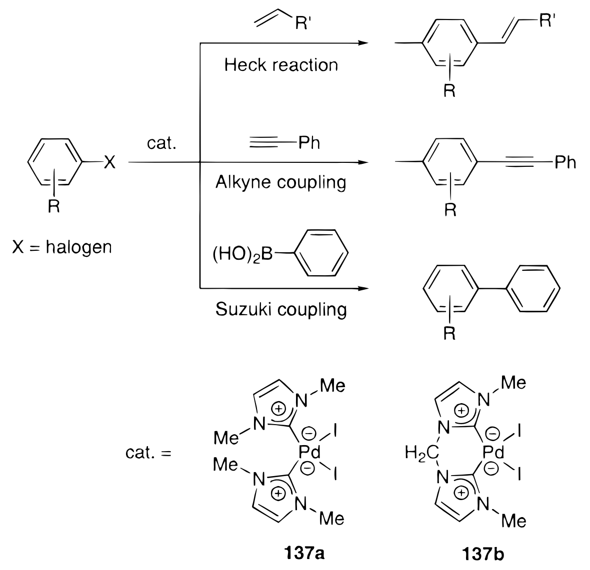
136b: M = Cr
136c: M = Ni

136d: M = Cr
136e: M = Ni

The X-ray diffraction studies performed on many complexes also reveal the pure σ-donor character of the N-heterocyclic carbenes. Indeed, elongated single M−C bonds are generally observed. At the same time, the internal ring angle at the carbon atom is slightly larger in coordinated than in free carbenes, although not as large as that in the related imidazolium salts. Similarly, the C−N bond distances lie between those of the free carbenes and imidazolium salts. These data as a whole suggest that the three- and five-center π-delocalization in the imidazolidin-2-ylidenes **II** and imidazol-2-ylidenes **III**, respectively, is increased by coordination of the carbene center.

c. Catalytic Properties. Due to their remarkable stability, diaminocarbene complexes appeared as promising catalysts for various organic reactions. Over the last two decades, the catalytic activity of imidazolidin-2-ylidene and imidazol-2-ylidene complexes have been investigated and compared to that of the commonly used phosphine complexes. Enantiomerically pure complexes featuring either chiral substituents at the nitrogen atoms,[229,246,247,281a,293] a chiral ring framework,[229] a chiral metal center,[227] or alternatively a chiral backbone[281b] have even been prepared (Scheme 27) and tested in asymmetric catalysis.

Heck-type reaction. Herrmann et al. prepared complexes **137a**,**b**[226] from the corresponding imidazolium salts and palladium(II) acetate (according to eq 65) and investigated their activity in palladium-catalyzed reactions (eq 71). These new catalysts are exceptionally stable toward heat, oxygen, and moisture; moreover, carbene dissociation has never been detected. All these properties make these palladium−carbene complexes suitable for the Heck reaction (eq 71a), particularly for the activation of chloroarenes.[226] Promising results have also been obtained for alkyne (eq 71b) and Suzuki (eq 71c) coupling reactions.[226b]

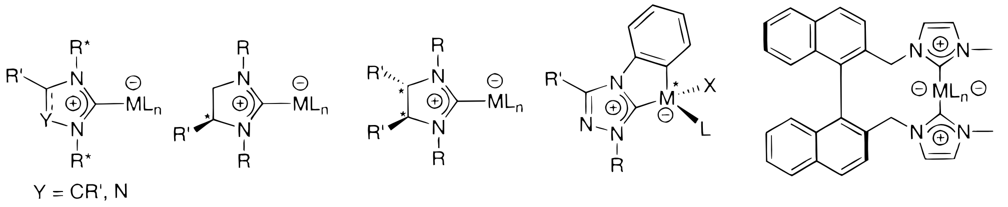


(71a)
(71b)
(71c)

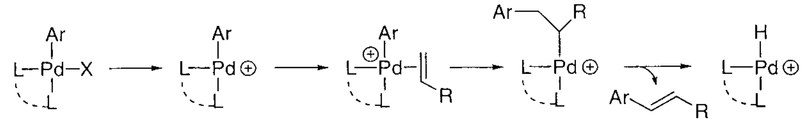
137a **137b**

Recently, Enders et al. prepared the related palladium complexes **138** and **139** featuring two chiral 1,2,4-triazol-5-ylidene ligands, but their use in asym-

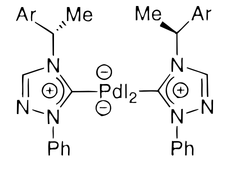
Scheme 27



Scheme 28



metric Heck reactions has not yet resulted in significant optical induction (ee < 8%).[293]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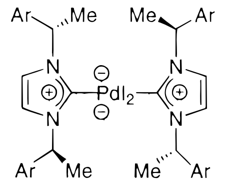
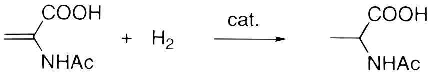

139

The crucial steps of these Heck-type reactions, insertion of the olefin in the palladium–aryl bond and β-hydride elimination, have been experimentally[289a–c] and theoretically[289d] investigated. All the results suggest an ionic pathway starting with the cleavage of the Pd–halide bond (Scheme 28).

Hydrogenation of olefins. Rhodium(I)– and ruthenium(II)–carbene complexes **140** are efficient catalysts for the hydrogenation of olefins such as dehydro-α-amino acids (eq 72).[272,299] Preliminary studies have demonstrated that the best results are obtained by combining a carbene ligand with less σ-donor and more π-acceptor ligands such as phosphines. With these mixed systems, the electron density at the metal center is decreased compared to the biscarbene complexes and therefore the activation of H_2 is favored.



(72)

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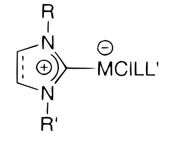
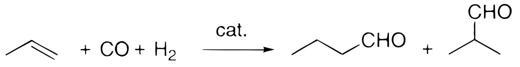


140
M = Rh, Ru
L, L' = PR''$_3$, CO

Hydroformylation of olefins. Rhodium(I)–N-heterocyclic carbene complexes have also been tested for the hydroformylation of olefins (eq 73).[300] Complexes such as [RhCl(COD)(carbene)] **141a**, [RhCl(PPh$_3$)$_2$(carbene)] **141b**, [RhCl(CO)(PPh$_3$)(carbene)] **141c**, or [RhCl(CO)(carbene)$_2$] **142** can be used without an excess of carbene since this ligand does not dissociate. However, the electron density at the metal center is significantly increased by the highly nucleophilic N-heterocyclic carbenes, and thus, the rhodium(I)–carbene complexes **141a** and **142** are less active than the more commonly used triphenylphosphine complex RhH(CO)(PPh$_3$)$_3$. Here also the mixed rhodium(I) complexes **141b**,**c** confer a combination of high activity with long-term stability.



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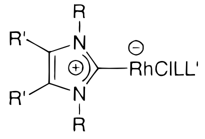
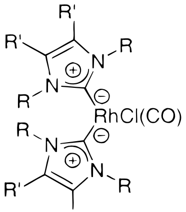


141a: LL' = *cis*-COD
141b: L = L' = PPh$_3$
141c: L = PPh$_3$, L' = CO



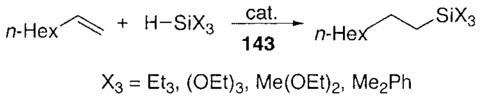
142

Hydrosilylation reactions. Various rhodium– and ruthenium–carbene complexes **143**–**145** have been tested in the hydrosilylation of terminal alkenes and alkynes, as well as ketones (eq 74–79).

Rhodium complexes such as the readily available [RhCl(COD)(carbene)], [RhCl(PPh$_3$)$_2$(carbene)], and [RhCl(CO)(PPh$_3$)(carbene)] **143** are better catalysts than [RhCl(PPh$_3$)$_3$] for the anti-Markovnikov addition of silanes to terminal alkenes (eq 74).[301] With alkynes, mixtures of cis and trans silylated alkenes are generally obtained but cis to trans isomerization is completely achieved by further heating (eq 75).[261,301]

Hydrosilylation is a mild way to reduce ketones to the corresponding secondary alcohols (eq 76).[261] Rhodium(I)–carbene complexes **143** and especially the mixed phosphine–carbene systems [RhCl(PPh$_3$)$_2$(carbene)] proved to be efficient catalysts for the reaction of triethylsilane with acetophenone, the tetrakis(carbene)–ruthenium(II) complexes **144** being less reactive. Again, all these catalysts have remarkably long lifetimes, no signs of decomposition being observed after reaction times in excess of 2 weeks.

With chiral complex **145**, optical inductions higher than 30% were achieved for the reaction of acetophenone with diphenylsilane (eq 77).[246] This was the first example of asymmetric catalysis using chiral carbene



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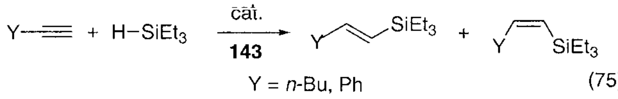

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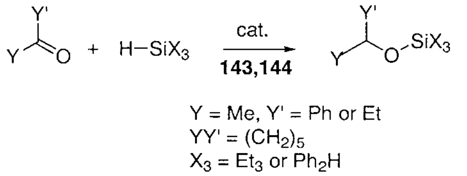

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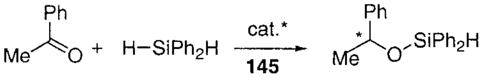

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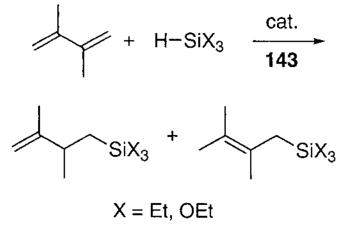

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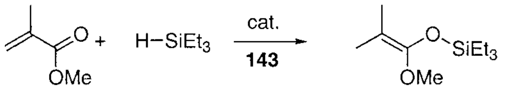

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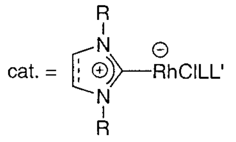
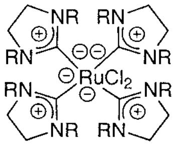


143
L, L' = CO, PPh3
or LL' = *cis*-COD



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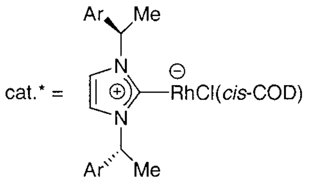
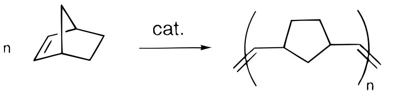


145a: Ar = Ph
145b: Ar = α-Naph

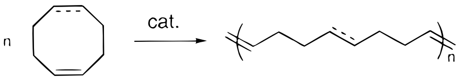
complexes. Although the enantiomeric excess clearly needs to be improved, this result is very promising.

Catalytic hydrosilylation of dienes with rhodium complexes **143** yields the corresponding 1/1 diene/silane adducts in moderate to good yields (eq 78). The ratio of 1,2- versus 1,4-addition products depends on the nature of the nitrogen substituents R. The 1,4-adduct is generally the major product (up to 95%).[301] Interestingly, only the 1,4-adduct is obtained in the reaction of methylacrylate with triethylsilane in the presence of **143** (eq 79).[301]

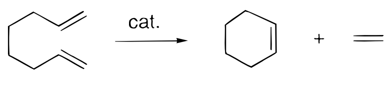
Olefin metathesis. The catalytic properties of ruthenium(II)–carbene complexes for olefin metathesis have recently been investigated.[222,258a,259] The bond between ruthenium and the N-heterocyclic carbene is so strong that the polymerization of cyclic olefins such as norbornene cannot be achieved with complexes such as [Ru(p-cymene)Cl_2(carbene)]. In contrast, the original ruthenium(II) catalysts **146** are extremely active for ring-opening (eq 80) as well as ring-closing olefin metatheses (eq 81). So far, the best catalysts are the mixed complexes **146b**[222b–d,258a,259] (featuring an alkylidene group, an imidazol-2-ylidene ligand, and a phosphine) and dinuclear complexes **146c**[222b–d] (featuring an alkylidene group and an imidazol-2-ylidene ligand). Of special interest, these catalysts are effective for the formation of tri- and even tetrasubstituted cycloalkenes of medium or even large ring size. A striking feature for the catalytic polymerization of cyclooctene is the pronounced dependence on the nitrogen substituents R, suggesting that subtle steric effects could be exploited to tune the catalytic performance much precisely than with the known phosphine systems.



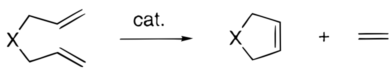
(80a)



(80b)

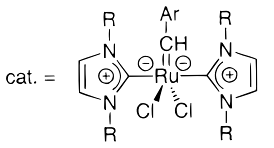


(81a)

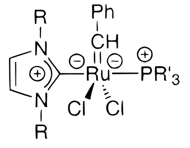


(81b)

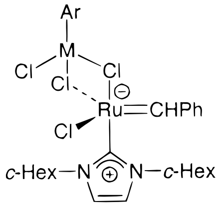
X = $C(CO_2Et)_2$, NTs...



146a
R = *i*-Pr, *c*-Hex, CHMePh, CHMeNaph
Ar = p-C_6H_4-X with X = H, Cl



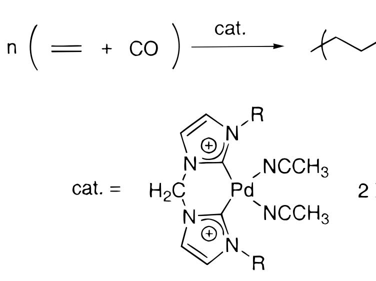
146b
R = *t*-Bu, *c*-Hex, Mes, CHMePh, CHMeNaph
R' = *c*-Hex, Ph



146c
M = Os, Ir, Ru, Rh
Ar = η^6[1-(i-Pr),4-Me-C_6H_4]
η^5[1,3-(t-Bu)$_2C_5H_3$], η^5(C_5Me_5)

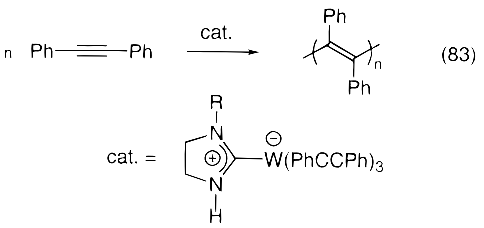
Copolymerization of ethylene and CO. Herrmann et al. recently reported that the dicationic N-heterocyclic carbene chelates **147a**,**b** catalyze the copolymerization of ethylene and carbon monoxide to give high molecular weight and strictly alternating poly(C_2H_4-*alt*-CO) under mild conditions and low pressures (eq 82).[294]

Polymerization of alkynes. The tungsten complexes **148**, two of the few known carbene complexes with



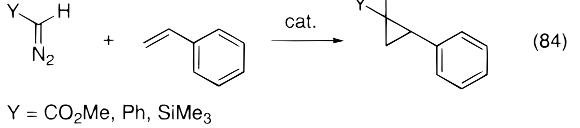
147a: R = Mes, X = PF_6
147b: R = Me, X = BF_4

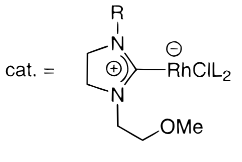
coordinated alkyne ligands, catalyze the polymerization of diphenylacetylene (eq 83).[245] The corresponding polymer is obtained in 66% yield (based on the amount of alkyne consumed), with only minor traces of hexaphenylbenzene (3.7%).



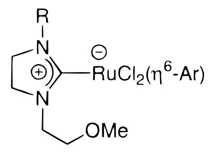
148
R = H, Et

Cyclopropanation of olefins. Dixneuf et al. showed that rhodium(I) and ruthenium(II) complexes, **149a**−**c** and **149d**−**g**, respectively, are efficient catalysts for the cyclopropanation of olefins with diazoalkanes (eq 84).[264] In these complexes, the metal is ligated strongly by the N-heterocyclic carbene and reversibly by one or two pendant functional groups. From these results, it is clear that this type of hemilabile ligands deserves further study, especially because they are now readily available in the imidazolidin- and imidazol-2-ylidene series.



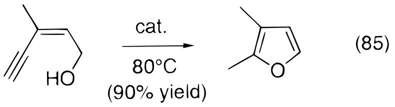


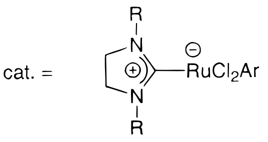
149a: R = Me, L = PPh_3
149b: R = CH_2CH_2OMe, L = PPh_3
149c: R = CH_2CH_2OMe, L_2 = *cis*-COD



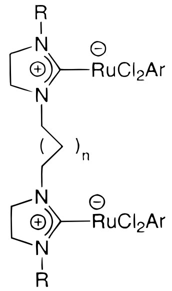
149d: R = Me, Ar = C_6Me_6
149e: R = CH_2CH_2OMe, Ar = C_6Me_6
149f: R = Me, Ar = cymene
149g: R = CH_2CH_2OMe, Ar = cymene

Furan synthesis. To be comprehensive, note that imidazolidin- and imidazol-2-ylidene complexes of ruthenium(II) **150** have been used as catalysts in the synthesis of the 2,3-dimethylfuran from (*Z*)-3-methylpent-2-en-4-yn-1-ol (eq 85).[263]



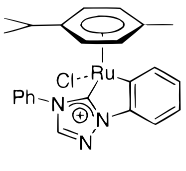


150a
R = Me, Et, CH_2CH_2OMe
Ar = C_6Me_6, *p*-MeC_6H_4(*i*-Pr)

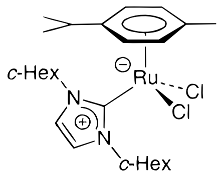


150b (n=0) and **150c** (n=1)
R = Et
Ar = *p*-MeC_6H_4(*i*-Pr)

Atom transfer radical polymerization (ATRP) of vinyl monomers. Last, Demonceau et al. recently studied the scope and limitations of stable ruthenium carbene complexes such as **151a**,**b** as potential catalysts for the ATRP of vinyl monomers.[260] According to preliminary results, these carbene complexes are less active and give broader polydispersities than the related phosphine complexes.



151a

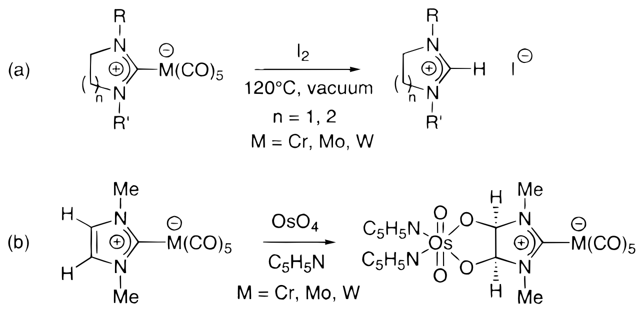


151b

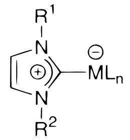
d. Concluding Remarks. N-Heterocyclic carbenes are promising alternative ligands to the commonly used phosphines and phosphites. The major advantage for diaminocarbene-based organometallic catalysts is undoubtedly their remarkable stability. Dissociation of the carbene ligands has only been observed in very oxidative conditions (iodine at 120 °C under vacuum),[302] and therefore, no ligand excess is required (Scheme 29a). The carbene−metal bond is even retained when imidazol-2-ylidene-M$(CO)_5$ complexes (M = Cr, Mo, W) are treated with osmium tetroxide (Scheme 29b).[303]

Aminocarbenes are strong σ-donor and weak π-acceptor ligands. They considerably increase the electron density at metal centers, and therefore, the most effective catalysts generally combine carbene and phosphine ligands. In asymmetric catalysis, the use of chiral carbene ligands merits further study. Recent developments of these new systems not only concern water-soluble carbene−metal complexes such as **152a**, but also functionalized imidazol-2-ylidene complexes

Scheme 29

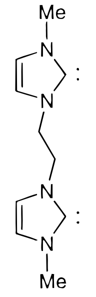


of type **152b**−**d** suitable for grafting to organic and inorganic polymers.[280a]

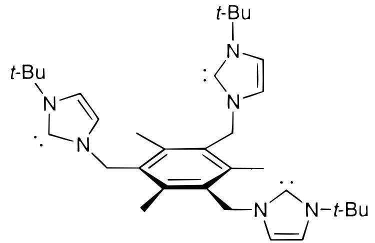


152a: $R^1 = R^2 = CH_2COOK$
152b: $R^1 = (CH_2)_3COOK$, $R^2 = CH_3$
152c: $R^1 = R^2 = CH_2COOEt$
152d: $R^1 = R^2 = CH_2CH_2OH$

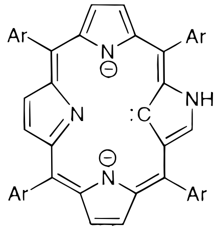
Note that bis- and tris-N-heterocyclic carbenes, **IIIh**[46] and **IIIu**,[304a] respectively, have been prepared, and their coordination properties are currently under investigation.[255] Finally, the connection between N-confused porphyrins **IIIv** and aromatic singlet carbenes has been drawn.[304b−e]



IIIh



IIIu



IIIv

V.7.3.2. Phosphinocarbene Complexes. Due to the presence of the phosphorus lone pair next to the carbene center, phosphinocarbenes can potentially act either as 2- or 4-electron donors. Although direct complexation of free phosphinocarbenes has not yet been achieved, a few complexes featuring a phosphinocarbene ligand have been described and, indeed three different coordination modes **A**, **B**, and **C** have been evidenced (Figure 19).

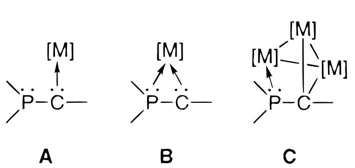
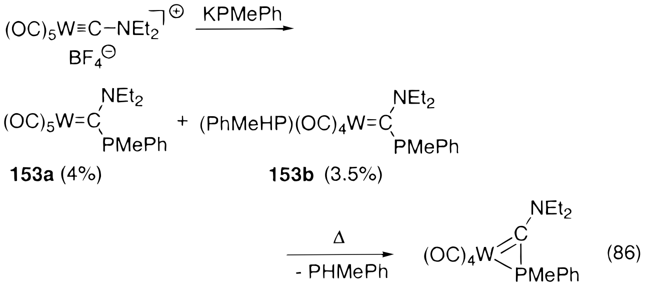


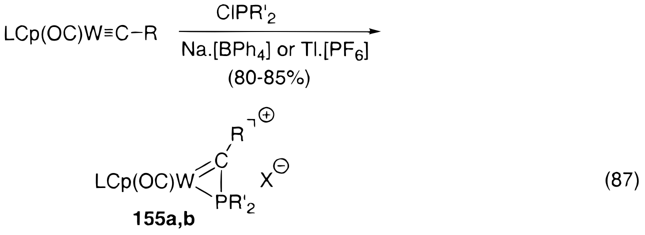
Figure 19. Coordination modes for phosphinocarbenes.

In complexes **153a**,**b**, phosphinocarbenes simply act as 2-electron donors via the carbene center (coordination mode **A**). They have been obtained as byproducts in 4% and 3.5% yield, respectively, by addition of potassium methylphenylphosphide to the cationic carbyne complex $[(OC)_5WCNEt_2]BF_4$ (eq 86).[305a] The analogous arsinocarbene complexes can be prepared using the same synthetic strategy.[305b] Interestingly, complexes **153a**,**b** feature phosphinoaminocarbene ligands.



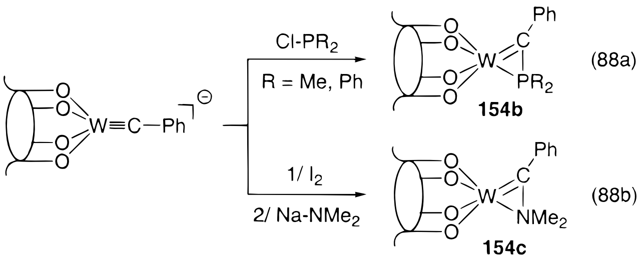
On warming a solution of **153b**, the phosphine ligand dissociates to afford the new complex **154a**. An X-ray diffraction study of the latter complex indicates that the phosphinocarbene behaves as a 4-electron ligand (coordination mode **B**) (eq 86).[306]

Kreissl et al. developed several different strategies for the conversion of neutral carbyne complexes into cationic phosphinocarbene complexes of type **B**.[307,308] For example, the carbene complexes **155a**,**b** are prepared in one step by treatment of the corresponding carbyne derivatives with a chlorophosphine in the presence of a Lewis acid (eq 87).[308a−c]

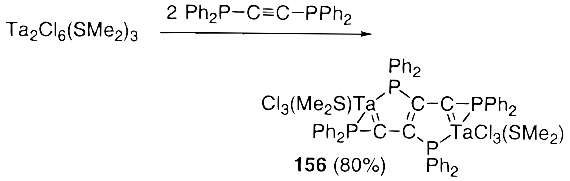


a: R = *p*-MeC_6H_4, R' = Me, L = CO
b: R = R' = Me, L = CO

η^2-Phosphinocarbene complexes **154b** can also be prepared from anionic carbyne complexes and chlorophosphines (eq 88a).[309] Interestingly, the analogous aminocarbene complex **154c** has also been obtained but by a two-step process (eq 88b).



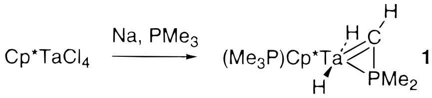
In 1982, Cotton et al. prepared the first phosphinocarbene tantalum complex **156** from the reaction of $Ta_2Cl_6(SMe_2)_3$ with bis(diphenylphosphino)acetylene. The most remarkable feature of this reaction is the formal dimerization of the alkyne moiety (eq 89).[310]



156 (80%)

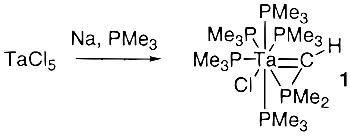
(89)

Some years later, Gibson and Green reported that Cp^*TaCl_4[311] and even $TaCl_5$[312] reacted with metallic sodium in neat trimethylphosphine to give the phosphinocarbene tantalum complexes **157a** and **157b**, respectively (eqs 90 and 91). These reactions are the



157a

(90)



157b (64%)

(91)

first examples of double activation of coordinated trimethylphosphine via oxidative cleavage of a substituent methyl C−H bond. A similar process was also observed in the reduction of tantalum pentabromide with magnesium turnings in the presence of dimethylphenylphosphine.[313]

X-ray diffraction studies of the η^2-(R_2PCR') complexes reported so far have revealed a metal−carbon distance within the range for a metal−carbon double bond (resonance form **B1**) (Figure 20). However, the phosphorus−carbon bond length is considerably shortened from that expected for a P−C single bond, which suggests a significant contribution from the resonance form **B2** in which the metallacycle may really be regarded as a coordinated λ^5-phosphaalkyne. Calculations performed by Gibson et al. have concluded that resonance form **B3** best describes this type of complex.[314] Typical for these complexes are the low-field methylidyne carbon ^{13}C resonance (170 to 244 ppm) and the high-field ^{31}P signal (−145 to −110 ppm) (Table 9).

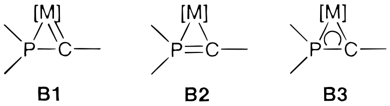


Figure 20. Resonance forms for the η^2-(R_2PCR') complexes.

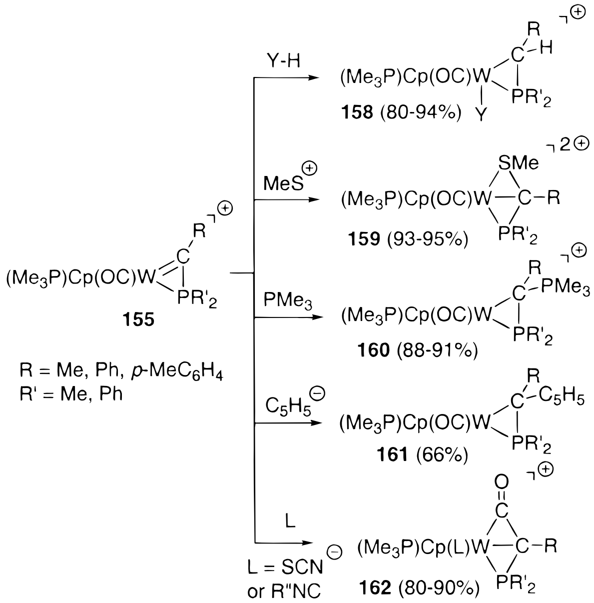
So far, no catalytic properties have been reported for the η^2-phosphinocarbene complexes; however, their reactivity is interesting. The tungsten complexes **155** show ambiphilic behavior (Scheme 30). Protic acids react with **155** affording the corresponding 1,2-adducts **158**.[315] With Lewis acids such as MeS^+, an electrophilic attack occurs at the metal−carbon double bond, affording the dicationic tungstaphosphathiabicyclo[1.1.0]butane complexes **159**.[316a,b] On the other hand, nucleophiles such as trialkyl phosphines and the cyclopentadienyl anion $C_5H_5^-$ add at the carbene center, affording the tungstaphosphacyclopropane complexes **160**[316b] and **161**,[316c] respectively. Last, a third reaction pathway is observed on reaction with the thiocyanate anion or isonitriles: cationic tungstaphosphabicyclo[1.1.0]butane complexes **162** are formed, the CO ligand now bridging the metal center and the C−R fragment.[317]

Table 9. Selected ^{13}C and ^{31}P NMR and X-ray Data for η^2-(R_2PCR') Complexes

	bond lengths (Å)			^{13}C NMR		^{31}P NMR	
complexes	MC	MP	PC	δ (ppm)[a]	J_{PC} (Hz)	δ (ppm)[b]	ref
154a	2.108	2.465	1.807				306
154b				249.6	37.9	−86.8	309
155a	2.032	2.377	1.737	243.9	39.5	−145.1	308b
156	2.018	2.471	1.683				310
157	2.005	2.480	1.714	191.2		−114.3	311
158				187.8	73	−136.9	312c
166	2.015	2.516	1.716	193.5	78	−135.2	312a,b
167	2.026	2.495	1.704	173.1	50	−118.2	312c
168				170.0		−124.0	312c

[a] Chemical shift for the methylidyne carbon in ppm relative to TMS. [b] Chemical shift for the phosphorus atom of the metallacycle in ppm relative to H_3PO_4.

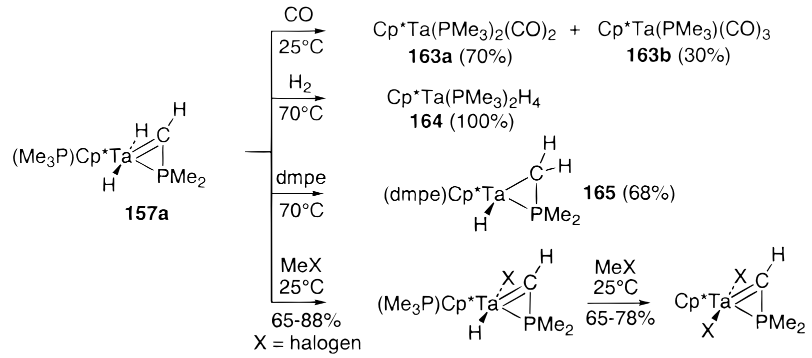
Scheme 30



In the case of the tantalum complex **157a**, reversible hydrogen migration may occur at room temperature in the presence of carbon monoxide or at 70 °C with dihydrogen or bis(dimethylphosphino)ethane to afford complexes **163**, **164**, and **165**, respectively.[311,314] In contrast, the phosphametallacycle remained intact when **157a** was treated with CH_3X (X = Cl, Br, I) (Scheme 31).[311,314]

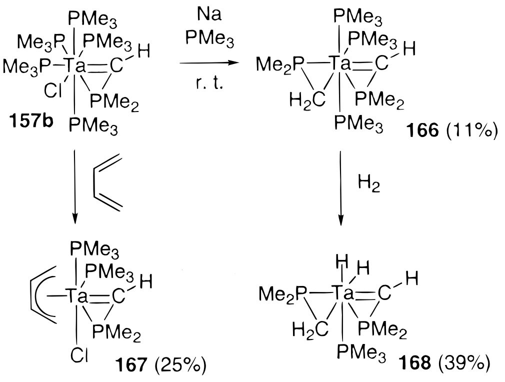
Green et al. observed that the tantalum complex **157b** is converted into the bicyclic complex **166** after prolonged exposure to sodium and trimethylphosphine.[312a,b] Two phosphine ligands of **157b** are easily displaced by butadiene, affording complex **167**, while

Scheme 31

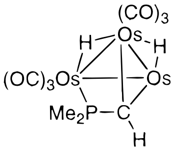


treatment of **166** with dihydrogen leads to the complex **168** by reduction of the metallic center. In both cases, the coordination mode of the carbene remains unchanged (Scheme 32).[312c]

Scheme 32



Last, a few phosphinocarbenes acting as 4-electron ligands in coordination mode **C** have been prepared by controlled pyrolysis of $Os_3(CO)_{11}(PMe_3)$ in high-boiling hydrocarbon solvents. Indeed, complex **169**, obtained in 60% yield, contains the Me_2PCH fragment bridging the three metal centers.[318]



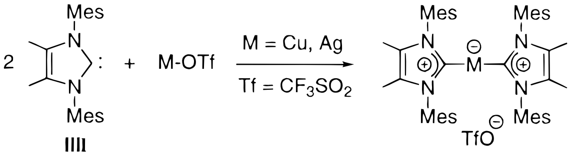
169

V.7.4. Carbene–Group 11 Metal Adducts

While carbene–gold complexes have been known since the early 1970s,[319,320] the first isolable complexes featuring a lighter group 11 element (copper and silver) were only reported in 1993,[321] 2 years after the discovery of the first stable free N-heterocyclic carbene.[45]

All the strategies developed for the preparation of carbene–transition metal complexes can be used for the synthesis of carbene-group 11 metal adducts.

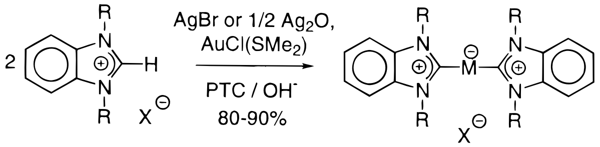
(a) Reaction of copper(I) and silver(I) triflate with 2 equiv of imidazol-2-ylidene **IIIl** gives the corresponding homoleptic complexes **170a**,**b** in high yields (eq 92).[321]



(92)

170a: M = Cu (92%)
170b: M = Ag (80%)

(b) Bis(benzimidazol-2-ylidene)silver(I) and -gold(I) complexes **171a**–**e** were prepared by treatment of the corresponding benzimidazolium salts with AgBr (or Ag_2O)[322] and $AuCl(SMe_2)$[323] under phase-transfer base catalysis (PTC/OH^-) (eq 93). Note that



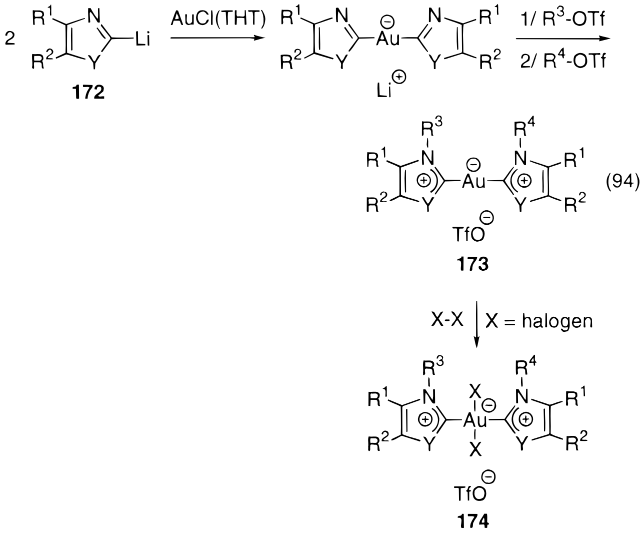
(93)

171a: M = Ag, R = Et
171b: M = Au, R = $C_{12}H_{25}$
171c: M = Au, R = $C_{14}H_{29}$
171d: M = Au, R = $C_{16}H_{33}$
171e: M = Au, R = Me

due to their four alkyl chains, compounds **171b**–**d** exhibit high thermal stability and relatively low temperatures for the transition into the liquid-crystalline phase.[323a] And due to its tendency to form weak intermolecular Au^I–Au^I interactions, derivative **171e** featuring four methyl groups luminesces in acetonitrile solution and in the solid state.[323b]

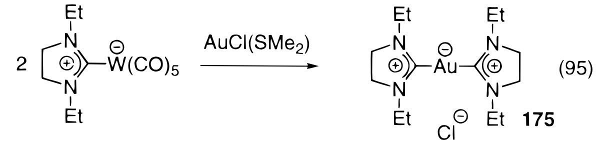
(c) Alternatively, gold(I) complexes have been obtained by transforming other C-bound ligands.[319,320,324,325] A representative example is the synthesis of bis(imidazolyl)- and bis(thiazolyl)gold complexes **173** by reaction of the lithiated heterocycles **172** with organometallic precursors such as AuCl(THT) and subsequent protonation or alkylation (eq 94).[324,325] Oxidative addition of halogens to these bis(carbene) complexes gives the corresponding gold(III) derivatives **174** in good yield.[326]

(d) Finally, Liu has recently prepared the bis(imidazolidin-2-ylidene) complex **175** by a carbene-



Y = S, NR
THT = tetrahydrothiophene

transfer reaction from the corresponding tungsten complex (eq 95).[231]



The X-ray diffraction study performed on complex **170b** revealed an essentially linear geometry around the metal, the two imidazole rings being twisted 39.7° from coplanarity.[321] Steric interactions as well as packing forces might dictate this twist angle, and values ranging from 0° to 50° have already been observed.[324a,327] Moreover, the proton-coupled ^{109}Ag NMR spectrum exhibit ^{1}H−^{107}Ag and ^{1}H−^{109}Ag coupling constants, suggesting that in contrast to that observed with many silver(I) complexes, no rapid ligand exchange occurs, at least on the NMR time scale.[321] This has been corroborated by ab initio calculations performed for the copper, silver, and gold chloride complexes of the parent imidazol-2-ylidene **III***.[328] Indeed, very high dissociation energies have been predicted at the CCSD(T) level of theory (67.4, 56.5, and 82.8 kcal/mol, respectively). As observed in the analogous transition metal complexes, the metal−ligand bonds have a strong ionic character (the π back-donation is much weaker than in classical Fischer carbene complexes).

Silver(I) complexes have been used in carbene transfer reactions, and accordingly, palladium(II) as well as gold(I) adducts **176** and **177**, respectively, have been obtained in nearly quantitative yields (Scheme 33).[322]

A N-heterocyclic bis(carbene)silver(I) polymer **179** has been prepared by treatment of the dicationic heterocycle **178** with 2 equiv of silver(I) acetate (Figure 21).[329] In this case, NMR studies suggest that rapid metal exchange reactions occur in solution. In the solid state, all the triazole rings are coplanar and due to the alternation in the orientation of the rings, the polymer is essentially one-dimensional. This result clearly shows that the use of 1,2,4-triazol-3,5-diylidenes and other biscarbenes as building blocks for organometallic polymers deserves further study.

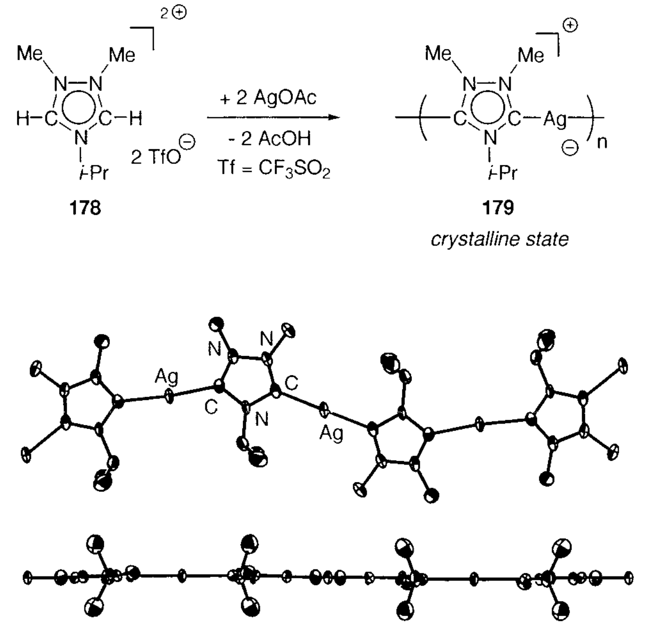
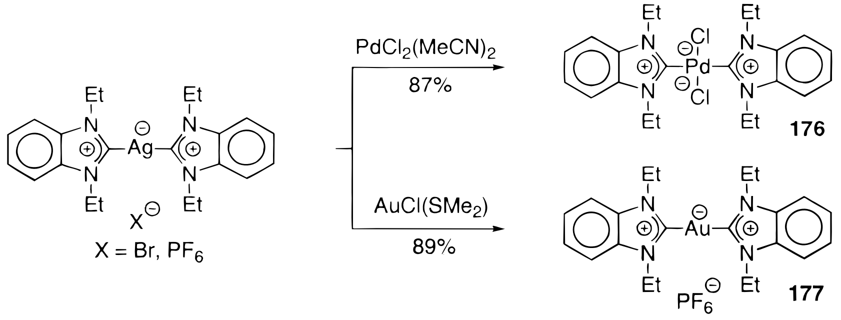


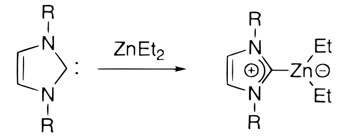
Figure 21. Synthesis and structure of the polymeric biscarbene−silver complex **179**.

V.7.5. Carbene–Group 12 Metal Adducts

The imidazol-2-ylidenes **IIIc**,**l** smoothly react with diethylzinc to afford the corresponding adducts **180a**,**b** in nearly quantitative yields (eq 96).[215] According to the X-ray diffraction study carried out for **180a**, the metal is in a rather unusual trigonal planar environment, the plane of the zinc coordination being twisted 81.6° with respect to the imidazole ring. The carbene−zinc distance is 209.6 pm, which is slightly

Scheme 33





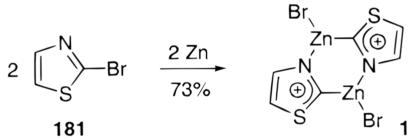
(96)

IIIc: R = Ad
IIIl: R = Mes

180a: R = Ad
180b: R = Mes

longer than the other two zinc−carbon distances (200.2 pm on average).

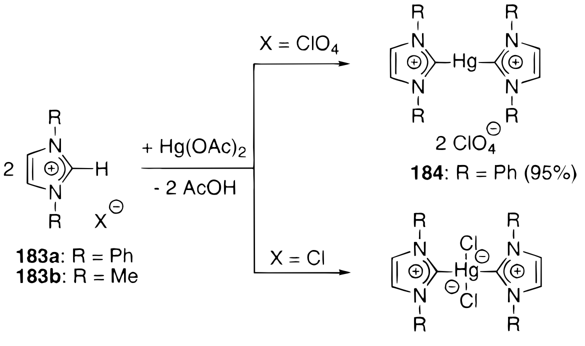
Treatment of the thiazole bromide **181** with zinc gives the dimeric 3-(zinc bromide)thiazol-2-ylidene **182** in 73% yield (eq 97).[207b] This compound is similar



181 **182** (97)

to the corresponding lithium complexes **129** (see section V.7.1).

Treatment of mercury(II) acetate with 2 equiv of the imidazolium salts **183a**,**b** leads to the bis(carbene) adducts **184** and **185** in high yields (eqs 98 and 99).[44b,330−332] The environment of the metal strongly



(98)

(99)

183a: R = Ph
183b: R = Me

2 $ClO_4^{\ominus}$
184: R = Ph (95%)

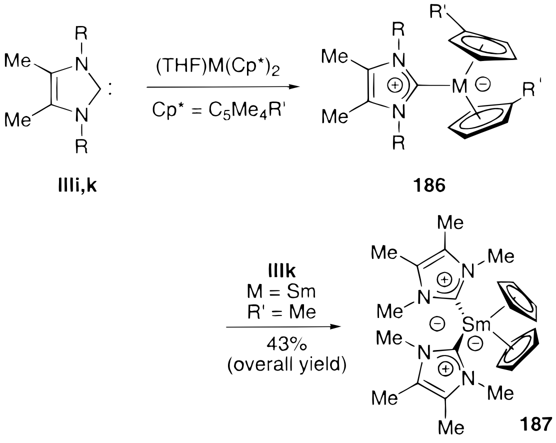
185a: R = Ph (63%)
185b: R = Me (90%)

depends on the nature of the imidazolium salt counteranions. A linear geometry was observed for the weakly nucleophilic perchlorate anions (C−Hg−C, 180°),[331] while a distorted tetrahedral arrangement results from the coordination of the two chlorides (C−Hg−C, 161.4°).[330] Note that analogous complexes featuring imidazol-2-ylidenes with pendant ferrocenyl substituents have been prepared and fully characterized.[333]

V.7.6. Carbene−Rare Earth Metal Adducts

With their 4f electrons lying deep inside the electron shell, lanthanoid metals are almost incapable of π-back-bonding. Therefore, they are acceptable coordination partners only for strong σ-donor ligands. Accordingly, imidazol-2-ylidenes **III** give very stable adducts with lanthanide(II) and -(III) complexes.[334]

By replacement of a THF ligand of suitable precursors, imidazol-2-ylidenes **IIIi**,**k** give the bis(cyclopentadienyl)samarium(II) and -ytterbium(II) complexes **186a**−**f** in good yields.[335,336] When the samarium−carbene complex **186a** is allowed to react with a second equivalent of the free carbene **IIIk**, the biscarbene adduct **187** is obtained in 43% overall yield (eq 100).[335] The X-ray diffraction studies per-

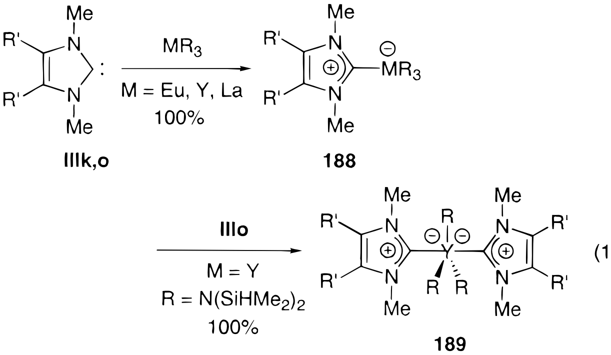


IIIi,k **186** **187** (100)

	M	R	R'	yield
a	Sm	Me	Me	33%
b	Sm	*i*-Pr	Et	75%
c	Yb	Me	Me	81%
d	Yb	*i*-Pr	Me	73%
e	Yb	Me	Et	80%
f	Yb	*i*-Pr	Et	78%

formed on **186c**[336a] and **187**[335] revealed extended single Yb− and Sm−C bonds (2.55 and 2.84 Å, respectively), which indicates the expected lack of Yb− and Sm−C π-back-bonding. Consequently, derivatives **186** and **187** have been considered as Fischer-type carbene adducts of organolanthanoid(II) compounds.

The lanthanoid(III)−carbene complexes **188a**,**b** have been quantitatively obtained by treatment of the imidazol-2-ylidene **IIIk** with tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium and -yttrium(III) (eq 101).[335] As determined by X-ray crystallography, the geometric environment at europium is essentially pentagonal bipyramidal and the Eu−C bond distance (2.66 Å) is similar to that observed in related Eu(III)−isonitrile complexes. Although the carbene−metal bond distances are far longer than those in related complexes of s-, p-, and d-block metals, the carbene ligand does not dissociate on the NMR time scale (a $^{89}Y-^{13}C$ coupling constant was

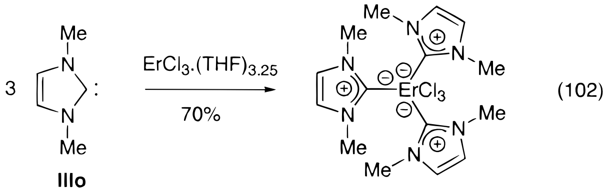


IIIk,o **188** **189** (101)

	R'	M	R
a	Me	Eu	thd
b	Me	Y	thd
c	H	Y	N(SiMe$_3$)$_2$
d	H	La	N(SiMe$_3$)$_2$
e	H	Y	N(SiHMe$_2$)$_2$

thd = 2,2,6,6-tetramethylheptane-3,5-dionato observed for the ^{13}C NMR signal of the ligating carbon atom).

Similar results have been obtained from **IIIo** and silylamide lanthanide(III) precursors, the corresponding complexes **188c**–**e** being obtained in quantitative yields (eq 101).[337] Since four-coordination in bis(silyl)amidelanthanide complexes is usually limited to small donor ligands, these results once more highlight the high nucleophilicity of imidazol-2-ylidenes **III**, which have been classified as hard donor ligands in Pearson's terminology.[337] Addition of a second equivalent of free carbene **IIIo** to **188e** even leads to the biscarbene adduct **189,** which adopts a trigonal bipyramidal coordination geometry in the solid state. Interestingly, the structural data for **188e** and **189** revealed that the N-heterocyclic carbene ligands affect the coordination mode of the bis(dimethylsilyl)amide counterligands by forcing them to form close β-Si–H–yttrium agostic contacts.[337] Finally, the imidazol-2-ylidene **IIIo** gives the stable tris(carbene) adduct **190** by THF displacement from $ErCl_3 \cdot (THF)_{3.25}$ (eq 102).[337]



IIIo **190** (102)

Interestingly, the geometry of the N-heterocyclic carbenes is almost unchanged by coordination to rare earth metals and the signal of the ligating carbon atom is only slightly shielded compared to that of the corresponding free carbene ($\Delta\delta \approx 10$ ppm).

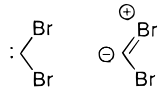
VI. Conclusion

From this review, it is clear that the common statement that carbenes only occur as reactive intermediates is no longer valid.

Although their crystallographic characterization has still to be achieved, persistent triplet carbenes with half-lives up to 16 s in room temperature solution and indefinitively stable in the solid state have been prepared.[31,34b] The synthesis of a triplet carbene that would be stable in room-temperature solution remains an exciting challenge which might in turn facilitate the processing of these derivatives into high-spin molecular clusters and organic paramagnets as well as ferromagnets.[41,338]

So far, two types of singlet carbene have been isolated. Following Pauling's predictions[12b] concerning the electronegativity of the carbene center, they feature either a push,push mesomeric–pull,pull inductive or a push,pull mesomeric substitution pattern. Although a pull,pull mesomeric–push,push inductive pattern should also bring electronic stabilization, singlet carbenes of this type, such as diborylcarbenes, have only been isolated in a masked form.[7b–c]

Due the nature of the substituents, all the stable singlet carbenes exihibit some carbon–heteroatom multiple bond character and for sometime their carbene nature has been a subject of controversy. One has to keep in mind that apart from dialkylcarbenes, all the transient singlet carbenes present similar electronic interactions. It is interesting to note that even as early as 1956, Skell drew the transient dibromocarbene **191** in its ylide form **191′** based on "*the overlap of the vacant p orbital of carbon with the filled p orbitals of the bromine atoms*".[143] In other words, the definition of carbenes as compounds featuring a neutral divalent carbon atom would exclude not only the known stable but also most of the transient singlet carbenes! A more suitable definition could be compounds with a neutral dicoordinate carbon atom featuring either two singly occupied nonbonding orbitals (triplet state) or alternatively both a lone pair and an accessible vacant orbital (singlet state).

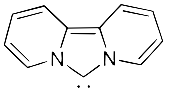


191 **191'**

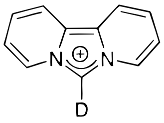
In aminocarbenes the vacant orbital is very high in energy due to the strong π-donation of the amino substituent. This is illustrated well by the structure of the radical anion **IVa**$^{\bullet-}$ obtained by reduction of the corresponding stable carbene **IVa**.[339] According to ESR spectroscopy and ab initio calculations, the additional electron is not located at the carbene carbon atom but delocalized into the PhCN fragment.

Consequently, aminocarbenes and especially N-heterocyclic carbenes are strong nucleophiles but very weak electrophiles. Toward transition metal centers, they behave as strong σ-donor ligands, their π-acceptor properties being negligible. These very peculiar properties have allowed for the synthesis of Fischer-type carbene complexes of almost all of the transition metals including those which are usually involved in Schrock-type carbene complexes; similarly, numerous rare earth metal complexes have been prepared. Due to the remarkable strength of the metal–carbene bond, they are promising alternative ligands to the more commonly used phosphines and phosphites for various catalytic reactions. Besides their interest in organometallic chemistry, the isolation of aminocarbenes has allowed for the synthesis of new classes of compounds such as carbene–group 13 element adducts, biscarbene–proton adducts featuring a C–H–C three-center four-electron interaction, and a variety of *reverse ylides*.

Interestingly, a recent paper by Weiss et al. indicates that the electronic properties of diaminocarbenes can be modified using a 2,2′-bipyridine framework. Indeed, since this fragment can accommodate a positive as well as a negative charge at the bridging carbon atom, the stable N-heterocyclic carbene **IIIw** leads to adducts of types **192a** (Arduengo-type adduct) but also **192b**, depending on the nature of electrophiles.[340]

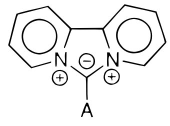


IIIw



192a

D = donor



192b

A = acceptor

In phosphinocarbenes, the LUMO remains accessible and the donation of the phosphorus lone pair is "reversible". Therefore, the reactivity of these species is quite similar to that observed for transient singlet carbenes; it is of particular interest that they retain an ambiphilic character. Striking examples are the reactions with trimethylsilyl trifluoromethanesulfonate and butyllithium which allowed for the preparation of the first methylene phosphonium salt and the first structural characterization of a phosphonium yldiide, respectively. Phosphinocarbenes also proved to be good precursors for various small heterocycles. So far, a few phosphinocarbene complexes have been prepared in the coordination sphere of transition metals but the coordination chemistry of the stable phosphinocarbenes has not been developed.

Although new knowledge has been accumulated over the last two decades, many challenges are still to be achieved in carbene chemistry. In the particular field of stable carbenes, the synthesis of mono- or even nonheteroatom-substituted singlet carbenes is an exciting and realistic goal. The preparation of a carbene that would be isolable in both the singlet and the triplet state would be a spectacular achievement,[341] but is it an inaccessible dream?

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