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Stable Noncyclic Singlet Carbenes

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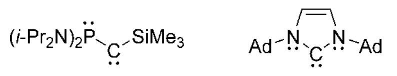
1. Introduction

Carbenes are neutral compounds featuring a divalent carbon atom. Their rich reactivity both as naked species and within complexes of transition metals has allowed for spectacular synthetic developments following the pioneering contributions of Doering and Fischer.[1] Carbenes were long considered only as fleeting intermediates. Therefore, the preparations of the distillable phosphinosilylcarbene **Ia**[2] and the crystalline imidazol-2-ylidene **1a**[3] in 1988−1991 by Bertrand and Arduengo (Figure 1) represented major breakthroughs.[4] These species are stabilized by the presence of two heteroatoms interacting with the carbene center, and their "true" carbene nature has been controversial and debated. About 20 years later, whatever the extent of carbene perturbation of these species, it is clear that the isolation of **Ia** and **1a** has opened a new, rapidly developing area in carbene chemistry, and numerous research groups from all over the world are actively working in this field. These studies are directed to the fundamental issues related to the stabilization modes and degree of carbene perturbation, as well as to the development of synthetic applications. In this respect, stable carbenes have already proved valuable models for their transient congeners, extremely powerful ligands for transition metals,[5] and very efficient organo-catalysts.[6] New perspectives have also recently emerged regarding their reactions with small molecules.[7]

This review focuses on the main achievements reported up until the year 2008 for stable or at least persistent noncyclic singlet carbenes.[4b,8] These carbenes differ from their cyclic analogues in the absence of geometric constraint, resulting in a broader variation of the carbene bond angle (from strongly bent to quasi-linear) and in free orientation of the substituents susceptible to interact with the carbene center (typically lone pairs and π^* or σ^* orbitals). Thanks to better synthetic accessibility, the variety of noncyclic



Ia **1a**

Figure 1. First "bottleable" singlet carbenes.

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Joan Vignolle was born in Biarritz (France) in 1979. He studied biology at the Université de Pau (France) and chemistry at the Université de Toulouse (France). He then started a Ph.D. (2003−2006), working under the supervision of Pr. G. Bertrand and Dr. D. Bourissou both at the University of Toulouse and at the University of California, Riverside. He is presently a Research associate with Pr. T. D. Tilley at the University of California, Berkeley, working on the synthesis and self-assembly of nanoparticles.

Xavier Cattoën was born in Poitiers in 1978. He studied chemistry at the Ecole Normale Supérieure de Cachan from 1997 to 2000 and then completed his Ph.D. (2004) under the supervision of Pr. G. Bertrand and Dr. D. Bourissou, carrying out his research both at the University of Toulouse and at the University of California, Riverside. After a postdoctoral stay at ICIQ (Tarragona, Spain), he moved to the Institut Charles Gerhardt in Montpellier (France) where he is presently working as a Chargé de Recherches CNRS on the structuring of hybrid materials for applications in optics and catalysis.

carbenes largely surpasses that of cyclic ones. The known stable noncyclic carbenes can be classified as phosphino- or amino carbenes depending on the predominant stabilizing substituent, and to date, the second substituent has been varied from silyl, phosphonio, amino, hydrazino, thio, oxy, aryl, alkyl, and phosphino. All of these carbenes are included in this review, but not the sulfinylcarbenes $F_3S{-}\ddot{C}{-}R$ and masked analogs of diborylcarbenes $R_2B{-}\ddot{C}{-}BR_2$ that have been recently reviewed extensively.[9]

The synthesis and electronic structure of the various stable noncyclic singlet carbenes will be discussed first. Subsequently, their reactivity will be presented, including typical carbene and unusual reactivity, as well as coordination to transition metals. Special attention has been devoted to the mechanistic and bonding issues, and whenever appropriate, comparisons have been made with cyclic carbenes.

Didier Bourissou, born in Nice (1972), studied chemistry at the Ecole Normale Superieure in Paris from 1992 to 1994 and obtained his Ph.D. degree in 1998 under the supervision of G. Bertrand in Toulouse (Dina Surdin Award in 2000). He then joined F. Mathey's team at the Ecole Polytechnique in Palaiseau as a research associate. He is currently CNRS Director of Research at the Laboratoire Hétérochimie Fondamentale et Appliquée in Toulouse (University Paul Sabatier, CNRS) and Associate Professor at the Ecole Polytechnique in Palaiseau. His research is mainly focused on (1) novel coordination chemistry, including fundamental studies on ambiphilic (bifunctional donor−acceptor) ligands, (2) highly reactive species (carbenes, 1,3-diradicals,...), and (3) biodegradable polymers (new monomers, organo-catalyzed ring-opening polymerization, applications in drug delivery systems). He was recently awarded the Bronze Medal of the CNRS (French National Research Council) and the Clavel Lespiau Distinction (French Academy of Sciences) in recognition of this work.

2. Synthesis and Stabilization Modes

All of the singlet carbenes considered in this review feature an in-plane lone pair (referred to as n_σ) and an out-of-plane formally vacant orbital (referred to as p_π) and adopt the σ^2 electronic configuration in the ground state (Figure 2). As discussed previously in detail,[9] the substituents influence the electronic structure of carbenes both sterically (via kinetic protection and modulation of the carbene bond angle) and electronically (via mesomeric and inductive effects). These substituent effects govern the energetic positions of the frontier orbitals n_σ and p_π and, thus, dictate the singlet−triplet energy gap.

All of the noncyclic singlet carbenes isolated to date feature at least one phosphino or amino group stabilizing the carbene through π interaction (the lone pair of the heteroelement interacts with the vacant p_π orbital of the carbene). Note that the trivalent nature of group 15 elements ensures higher steric protection than alternative π-donating groups, such as those derived from divalent group 16 elements. The electronic properties and chemical reactivity of stable noncyclic carbenes intimately depend on the nature of the predominant π-donating substituent (phosphino or amino), leading to two rather different and complementary types of carbenes, namely, phosphino- and aminocarbenes. This dichotomy between phosphino- and

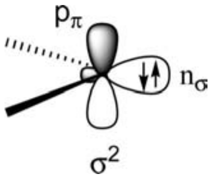


Figure 2. Electronic configuration of the noncyclic singlet carbenes considered in this review.

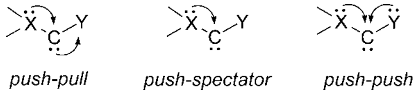
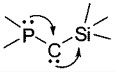
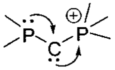
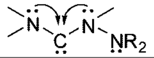
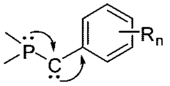
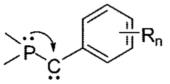
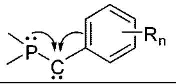
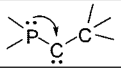
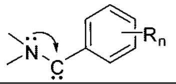
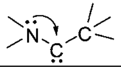
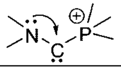
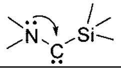
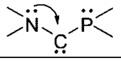


Figure 3. Schematic representation of the three stabilization modes evidenced among stable noncyclic singlet carbenes (X = P or N).

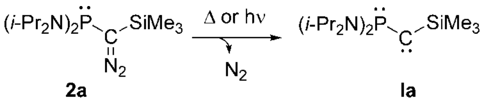
aminocarbenes also holds true for their preparation, with the first ones typically being prepared by irradiation of the corresponding diazo compounds while the latter are usually generated by deprotonation of iminium salts. The pronounced difference between phosphorus and nitrogen in terms of π donation stems from the energetic cost required to achieve planar environment (~30−35 kcal/mol for phosphorus versus ~5 kcal/mol for nitrogen as a result of the reluctance of heavier main group elements to s-p hybridize).[10] As a consequence, phosphino groups are significantly weaker π donors than amino groups,[11] and the smaller stabilizing effect of phosphorus versus nitrogen results in less electronic perturbation of the carbene with phosphorus than with nitrogen.

In addition, the group of Bertrand demonstrated in the early 2000s that a single phosphino or amino group is sufficient to isolate a carbene, opening access to a significantly broader variety of substitution patterns. Accordingly, the second substituent (referred to as Y in Figure 3) was varied extensively among heteroatomic substituents (silyl, phosphonio, amino, hydrazino, thio, oxy, phosphino) and even carbon-based groups (aryl, alkyl) (Table 1). The various phosphino- and aminocarbenes **I**−**XIII** reported over the past few years can be classified according to the mesomeric role of the second substituent, leading to three possible stabilization modes, namely, push−pull, push−spectator, and push−push. The degree of carbene perturbation, which largely dictates the electronic properties and reactivity, depends on their stabilization mode as well as on the heteroelement (phosphorus or nitrogen) involved in the main interaction with the carbene center. For example, on the one hand, phosphinoalkylcarbenes such as $(c\text{-Hex}_2N)_2P{-}\ddot{C}{-}CF_3$ **VIIIa** are only weakly perturbed and their reactivity matches that of transient carbenes. On the other hand, diaminocarbenes such as $i\text{-Pr}_2N{-}\ddot{C}{-}Ni\text{-Pr}_2$ **IIIa** are strongly stabilized by π donation from the two nitrogen atoms and appear as new types of neutral strong Lewis bases that open promising perspectives in synthesis.

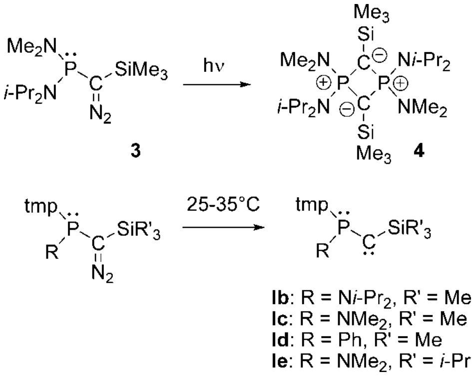
Table 1. Stable Noncyclic Carbenes: Substitution Patterns and Stabilization Modes

			predominant π donor substituent	stabilization modes
I	phosphino-silyl		P	push-pull
II	phosphino-phosphonio		P	push-pull
III	diamino		N	push-push
IV	amino-hydrazino		N	push-push
V	amino-thio		N	push-push
VI	amino-oxy		N	push-push
VII	phosphino-aryl	  	P	push-pull push-spectator push-push
VIII	phosphino-alkyl		P	push-spectator
IX	amino-aryl		N	push-spectator
X	amino-alkyl		N	push-spectator
XI	amino-phosphonio		N	push-spectator
XII	amino-silyl		N	push-spectator
XIII	amino-phosphino		N	push-spectator

Scheme 1



Scheme 2



2.1. Phosphinosilyl- and Phosphinophosphonio Carbenes

Phosphinosilylcarbenes **I** and phosphinophosphoniocarbenes **II** are the prototypes of push−pull stabilized carbenes, thanks to the π-donor ability of the phosphino group and the σ^*-withdrawing effect of the silyl/phosphonio substituents (negative hyperconjugation).

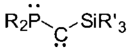
2.1.1. Phosphinosilyl Carbenes

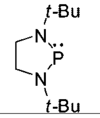
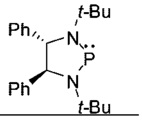
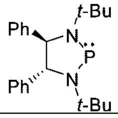
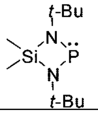
In 1988, Bertrand and co-workers isolated the first phosphinosilylcarbene ($(i\text{-Pr}_2N)_2P{-}\ddot{C}{-}SiMe_3$) **Ia**.[2] Carbene **Ia** is stable for weeks in solution at room temperature and can even be distilled at 75−80 °C under vacuum (10^{-2} mmHg). It is obtained by nitrogen elimination from the corresponding diazo precursor **2a**,[12] via flash vacuum pyrrolysis (250 °C, 10^{-2} mmHg) or low-temperature photolysis (−50 °C, 300 nm) (Scheme 1).

Soon after this pioneering result, the influence of the substitution pattern at phosphorus and silicon was investigated (Table 2).[13,14] In this respect, steric factors play a major role, as indicated by the isolation of the carbene head-to-tail dimer **4** upon photolysis of the diazo compound **3**, which features a dimethylamino group at phosphorus (Scheme 2). With a 2,2,6,6-tetramethylpiperidino (tmp) substituent at phosphorus, the steric demand of the second substituent can be decreased to a dimethylamino or even phenyl group (carbenes **Ic** and **Id**, respectively). Comparatively, the replacement of the methyl groups at silicon for isopropyl groups has negligible impact, with the two carbenes **Ic** and **Ie** being similarly stable for weeks in solution at 25 °C. Note that the formation of the tmp-substituted phosphinosilylcarbenes **Ib**−**e** from the corresponding diazo compounds proceeds under remarkably mild conditions (25−35 °C).

Stable phosphinosilylcarbenes have also been obtained with two dicyclohexylamino groups or a *N*,*N′*-di-*tert*-butyl-1,2-ethanediamino moiety at phosphorus (carbenes **If**[15] and **Ig**−**h**,[16] respectively) (Table 2). The presence of *tert*-butyl groups at nitrogen was found critical to the stability of

Table 2. Phosphinosilyl Carbenes Ia−i



compound[a]	R_2P[b]	$\delta^{13}C_{carbene}$ in ppm ($^1J_{CP}$ in Hz)	$\delta^{31}P$ in ppm	Stability	Ref
Ia	$(i\text{-}Pr_2N)_2P$	142.7 (159)	− 40.0	b.p. 75-80°C (10^{-2} mm Hg)	2
Ib	$(tmp)(i\text{-}Pr_2N)P$	145.5 (203)	− 49.7	weeks at rt	13
Ic	$(tmp)(Me_2N)_2P$	133.5 (147)	− 24.1	weeks at rt	13
Id	(tmp)PhP	136.9 (147)	− 38.1	weeks at -20°C few hours at rt	13
Ie	$(tmp)(Me_2N)_2P$	120.7 (181)	− 27.8	weeks at rt	13
If	$(c\text{-}Hex_2N)_2P$	139.3 (160)	− 31.4	weeks at rt	15
Ig		-	− 36.0	oil, stable at rt	16
(*S*,*S*)-**Ih**		-	− 32.7	stable in toluene solution at rt	16
(*R*,*R*)-**Ih**					
Ii		77.6 (153)	− 26.7	m.p. 122°C	17

[a] R′ = Me except for **Ie** (R = *i*-Pr). [b] tmp = 2,2,6,6-Tetramethylpiperidino.

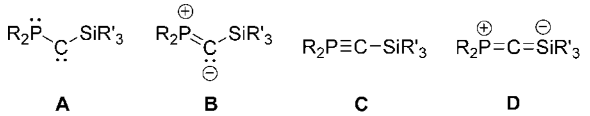


Figure 4. Four possible structures of phosphinosilylcarbenes **I**.

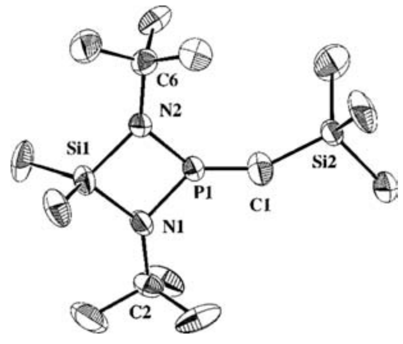


Figure 5. Molecular structure of the phosphinosilylcarbene **Ii**, as determined from X-ray diffraction analysis. Reprinted with permission from ref 17. Copyright 2000 American Chemical Society.

carbenes **Ig**−**h**, head-to-tail dimerization, or carbene−diazo coupling reactions being observed with isopropyl groups (see sections 3.1.1.1 and 3.1.1.5). Note that carbene **Ih** was prepared in optically pure (*R*,*R*) and (*S*,*S*) forms, and it is the only enantiomerically pure stable noncyclic carbene reported to date. Finally, the quest for a crystalline stable phosphinosilylcarbene became a reality in 2000 with the incorporation of the phosphorus atom in a four-membered NSiNP skeleton (carbene **Ii**).[17]

Phosphinosilylcarbenes **I** were found early on to exhibit reactivity typical for carbenes as well as PC multiply bonded species (see section 3), raising the question of their true electronic structure. Depending on the nature and extent of interaction between the carbene center and its two heteroatomic substituents, the four limiting structures **A**−**D** can be conceived (Figure 4). Until the structural characterization of **Ii** in 2000, theoretical calculations were the only sources of information regarding the electronic structure of phosphinosilylcarbenes. First, the parent phosphinocarbene $H_2P-\ddot{C}-H$ was shown to have a singlet ground state. π interaction between the phosphorus lone pair and the carbene vacant orbital p_π was apparent from the short $PC_{carbene}$ bond and the planar environment around phosphorus.[18] The λ^5-phosphaacetylene form **C** is only the transition structure for the inversion at the carbene center, located about 10 kcal/mol higher in energy than structure **B**. Similar conclusions were drawn from the more realistic model $(H_2N)_2P-\ddot{C}-SiH_3$.[19] However, significantly wider carbene bond angles were predicted (up to 138−151°). The presence in the ELF analysis[17] of a $PC_{carbene}$ double bond and a lone pair at carbon pointing away from both phosphorus and silicon further supported form **B** as the best formulation for carbenes **I**. Consistently, recent calculations carried out on the actual carbene $(i\text{-}Pr_2N)_2P-\ddot{C}-SiMe_3$[19b] led to $PC_{carbene}$ and $C_{carbene}Si$ bond orders of 2.1 and 0.8, respectively, associated with an atomic charge of −1.4 at the carbene center. The remarkable shortness of the $PC_{carbene}$ (1.570 Å) and $C_{carbene}Si$ (1.817 Å) bonds, attributable to negative hyperconjugation between the carbene lone pair and σ^* orbitals centered at phosphorus and silicon, suggests nevertheless some modest contribution of structures **C** and **D**. The stabilization of phosphinosilylcarbenes thus combines strong donation from the phosphorus and weak withdrawal from the silicon, resulting overall in a push−pull system.

The X-ray diffraction analysis performed on the carbene **Ii** unambiguously confirmed this bonding situation (Figure 5).[17] The whole Si1N2C6N1C2P1C1Si2 skeleton is planar, the $PC_{carbene}$ bond length is extremely short [1.532(3) Å], and the $PC_{carbene}Si$ framework is bent [152.6(3)°]. All these features support once again form **B** as the best formulation of **Ii**, as the result of strong $P \rightarrow C_{carbene}$ π interaction. In addition, some withdrawing effect of the silyl substituent at the carbene center is apparent from the short $C_{carbene}Si$ bond distance [1.795(3) Å].

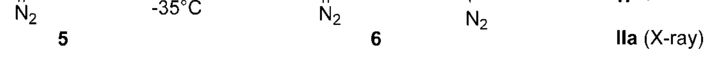
From a spectroscopic viewpoint, the ^{31}P NMR chemical shifts for phosphinosilylcarbenes **Ia**−**i** range from −50 to −24 ppm (Table 2), shifted upfield by 60 to 160 ppm compared to their diazo precursors. The ^{29}Si NMR chemical shifts lie between −20 and 0 ppm, while the ^{13}C NMR signals for the carbene center typically appear as doublets with large coupling constants ($^1J_{PC}$ = 150−200 Hz) and chemical shifts around 130−150 ppm (with the exception of Ii: $\delta^{13}C_{carbene} = 78$ ppm).

2.1.2. Phosphinophosphoniocarbenes

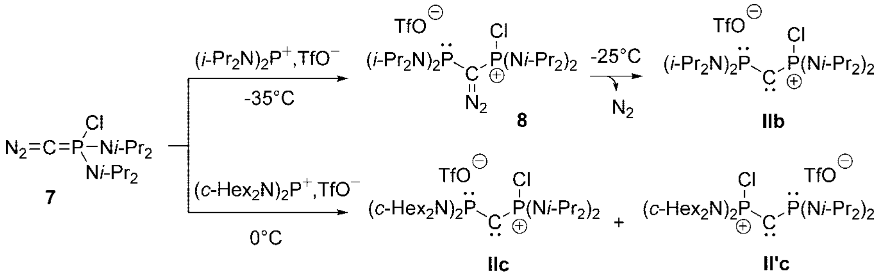
Soon after the isolation of the first phophinosilylcarbene **Ia**, it was envisaged to replace the silyl group by an isoelectronic and isovalent phosphonio moiety. The phosphinophosphoniocarbene **IIa** was readily prepared by reacting the corresponding α-bis(phosphino)diazomethane **5** with trifluoromethanesulfonic acid (Scheme 3).[20] The *P*-protonated diazo compound **6** was characterized spectroscopically at low temperature and found to rapidly eliminate N_2 above −25 °C. The ensuing carbene **IIa** was isolated as yellow crystals (melting point (mp) = 88 °C, 76% yield) stable for months at room temperature in the solid state. The dissymmetrization of the two phosphorus atoms was clearly apparent from ^{31}P NMR spectroscopy (AX system), with the large $^1J_{PH}$ coupling constant (530 Hz) indicating the presence of a direct PH linkage. The ^{13}C NMR signal for the carbene center appears as a doublet of doublet at 99 ppm with $^1J_{PC}$ coupling constants of 143 and 158 Hz.

Despite some disorder on the phosphonium part, the X-ray diffraction analysis performed on **IIa**[20] unambiguously confirmed its ionic character and provided valuable information regarding its stabilization mode. In particular, the planar environment around the σ^3-phosphorus atom and the shortness of the associated $PC_{carbene}$ bond [1.548(4) Å] indicate strong π interaction. The σ^4-$PC_{carbene}$ bond length [1.605−1.615(5) Å] is noticeably shorter than anticipated for a single bond and more in the range typical for phosphorus ylides. Along with the rather large carbene bond angle [$PC_{carbene}P$ =

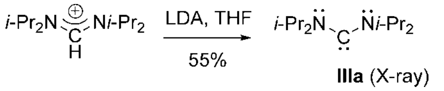
Scheme 3



Scheme 4



Scheme 5



164.1−165.1(4)°], this suggests significant C → σ^4-P negative hyperconjugation. Calculations carried out on the complete carbene (i-Pr$_2$N)$_2$P−C̈−PH(Ni-Pr$_2$)$_2^+$ nicely reproduced the experimental geometric features and predicted atomic charges of +0.6, −0.8, and +1.0 for the σ^3-phosphorus, carbene, and σ^4-phosphorus centers, respectively. In addition, some delocalization of the carbene lone pair into phosphorus-centered σ* orbitals was apparent in the molecular orbitals.[21] Phosphinophosphoniocarbenes thus benefit from push−pull stabilization involving the two phosphorus atoms.

A related phosphinophosphoniocarbene **IIb** was synthesized by reaction of the *P*-chlorodiazomethylenephosphorane **7**[22] with the bis(diisopropylamino)phosphenium trifluoromethanesulfonate (Scheme 4).[23] The resulting diazo compound **8**, spectroscopically characterized at low temperature, decomposed above −25 °C with elimination of N$_2$. The structure of the ensuing carbene **IIb** was unambiguously established by ^{31}P (δ = 52 and 35 ppm, $^2J_{PP}$ = 71 Hz) and ^{13}C (δ = 104 ppm, $^1J_{CP}$ = 128 and 154 Hz) NMR spectroscopy. This synthetic pathway also enabled the formation of unsymmetrical phosphinophosphoniocarbenes upon reaction of **7** with the bis(dicyclohexylamino)phosphenium trifluoromethanesulfonate. The formation of a 4:1 mixture of the two regioisomers **IIc** and **II′c** suggests facile migration of the chlorine atom between the two phosphorus centers.

2.2. Diamino-, Aminohydrazino-, Aminothio-, and Aminooxycarbenes

The presence of two strong π-donating substituents at the carbene center may also result in stable species. Diaminocarbenes **III** are the prototypes of such push−push stabilized carbenes. One amino group can be replaced by an hydrazino-, thio-, or oxy-susbtituent, leading to stable or at least persistent carbenes **IV**−**VI**.

2.2.1. Diamino- and Aminohydrazinocarbenes

The first acyclic diaminocarbene **IIIa** was reported by Alder et al. in 1996 (Scheme 5).[24] Bis(diisopropylamino)carbene **IIIa** is a crystalline compound, stable both in solution and in the solid state. Its ^{13}C NMR signal appears at 255 ppm, shifted downfield by 10−20 ppm compared to cyclic imidazolidin-2-ylidenes (235−245 ppm) and by 30−50 ppm compared to imidazol-2-ylidenes (207−221 ppm), but in the same range as seven-membered cyclic diaminocarbenes (250−260 ppm). As their cyclic analogues, carbene **IIIa** is prepared by deprotonation of its conjugated acid, namely, the tetraisopropylformamidinium salt. The reaction can be achieved with lithium diisopropylamide in tetrahydrofuran[24] or sodium hydride in liquid ammonia.[25]

Soon after, the bis(piperidino)carbene **IIIb**[26] was characterized by ^{13}C NMR (δ = 236.8 ppm) in solution at room temperature. More recently, the bis(pyrrolidino)carbene **IIIc**,[27] the bis(4-methylpiperidino)carbene **IIId**,[28] and the (diisopropylamino)(*cis*-2,6-dimethylpiperidino)carbene **IIIe**[29] were isolated as solids (Table 3). The stability of diaminocarbenes increases with the steric demand of the substituents. However, even the bis(dimethylamino)carbene **IIIf**, generated by deprotonation with lithium diisopropylamide (LDA) or lithium tetramethylopiperdine TMPLi, is relatively stable in toluene solution at room temperature (δ ^{13}C = 238.4 ppm).[30]

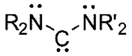
Compared to **IIIa** and **IIIe**, the ^{13}C NMR chemical shifts of diaminocarbenes **IIIb**−**d**,**f** are shifted to a lower frequency by ~20 ppm, suggesting that **IIIb**−**d**,**f** are not obtained as free carbenes but rather as lithium complexes because of reduced steric protection. This was recently confirmed with the bis(diethylamino)carbene **IIIg**.[31] Upon addition of a cryptand, the lithium adduct **IIIg**−**Li** was converted to the naked carbene **IIIg**, inducing a significant downfield shift of the ^{13}C NMR signal from 244 ppm in **IIIg**−**Li** to 252 ppm in naked **IIIg**) (Scheme 6).

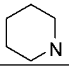
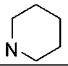
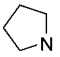
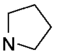
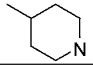
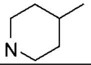
To avoid the formation of complexed carbenes, an alternative method was developed by Bertrand and coworkers. *C*-Chloroformamidinium chlorides were readily reduced by bis(trimethylsilyl)mercury to afford free diaminocarbenes along with mercury and chlorotrimethylsilane (Scheme 7).[32] The validity of this approach was first demonstrated with the preparation of **IIIa** and then exploited to access the salt-free bis(dimethylamino)carbene **IIIf**. In naked form, carbene **IIIf** exhibits a ^{13}C NMR signal at 259.7 ppm (versus 238.4 ppm for its lithium adduct **IIIf**−**Li** prepared by the deprotonation route) and survives for only a few hours at 0 °C in THF solution[32] (while **IIIf**−**Li** is stable for days at room temperature in toluene solution). Note that decomplexation of the lithium from the adduct did not lead to dimerization but only to decomposition in this case.[33]

Another interesting route to diaminocarbenes relies on nucleophilic substitution at the carbene center of aminophosphoniocarbene **XII** (see section 3.4.4). The unsymmetrical diisopropylaminodiphenylaminocarbene **IIIh** prepared via this method (Scheme 8) proved persistent in tetrahydrofuran solution at room temperature and stable in the solid state (mp = 75 °C).[34]

The symmetrical diaminocarbene **IIIi** featuring one aryl group at each nitrogen atom has also been recently prepared by Bielawski et al. (Scheme 9). Although no X-ray diffraction analysis could be performed, the ^{1}H NMR data suggest that

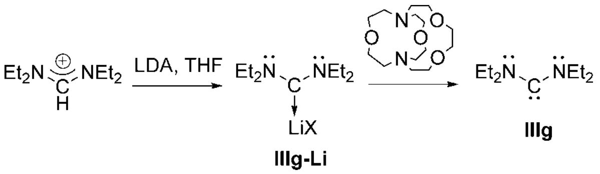
Table 3. Stable and Persistent Diaminocarbenes IIIa−i and Aminohydrazinocarbenes IVa−b



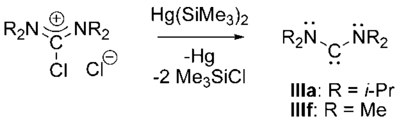
	R_2N	NR'_2	$\delta^{13}C_{carbene}$ (ppm)	Stability	Ref
IIIa	*i*-Pr_2N	N*i*-Pr_2	255.5	Stable solid m.p.: 51-55°C	24,32
IIIb			236.8	Stable in toluene solution > 24h	26
IIIc			241.9	Colorless crystalline solid	25
IIId			237.4	Colorless crystalline solid	25,28
IIIe	*i*-Pr_2N	2,6-dmp[a]	258.9	Stable solid m.p.: 37°C	29
IIIf.Li	Me_2N	NMe_2	238.4[b]	Stable in toluene solution for many days[c]	30
IIIf	Me_2N	NMe_2	259.7	Stable in THF solution for a few hours at 0°C	32
IIIg.Li	Et_2N	NEt_2	244[b]	-	31
IIIg	Et_2N	NEt_2	252	Stable in solution > 1 week	31
IIIh	*i*-Pr_2N	NPh_2	258.2	Stable solid m.p.: 75°C	34
IIIi	DIPP(Me)N[d]	N(Me)DIPP[d]	248.9	Yellow solid	35
IVa	*i*-Pr_2N	N(*i*-Pr)-NMe_2	228.9	$t_{1/2}$ ~ 20 min at -22°C in THF	37
IVb	*i*-Pr_2N	N(*i*-Pr)-Pip	228.0	$t_{1/2}$ ~ 2.5h at -5°C in THF	37

[a] dmp = *cis* 2,6-dimethylpiperidine. [b] Li complex generated from $LiN(SiMe_3)_2$ in toluene or $LiN(i\text{-}Pr)_2$ in THF. [c] As compared to a few hours in tetrahydrofuran (THF). [d] DIPP = 2,6-*i*-$Pr_2-C_6H_3$.

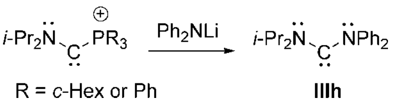
Scheme 6



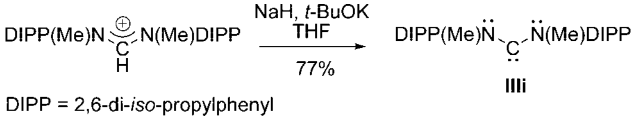
Scheme 7



Scheme 8



Scheme 9



carbene **IIIi** adopts conformation **G** with the *N*-aryl groups in distally opposed, pseudo-*trans* orientation about the diaminocarbene linkage (Figure 6).[35]

The variety of dinitrogen-subtituted carbenes has been recently extended to aminohydrazinocarbenes **IV**. Lassaletta et al. prepared a cyclic variant, namely, a bis-*N*-dialkylaminoimidazolin-2-ylidene, stable for several days in solution at room temperature.[36] Persistent acyclic versions have also been prepared and characterized by ^{13}C NMR spectroscopy (Scheme 10). The aminohydrazinocarbene *i*-$Pr_2N-\ddot{C}-N(i\text{-}Pr)-NMe_2$ **IVa**, related to the stable bis(diisopropylamino)carbene **IIIa**, survives only at low temperature in tetrahydrofuran solution ($t_{1/2}$ = 20 min at −22 °C).[37] The replacement of the dimethylamino group of **IVa** for a piperidino group induced a noticeable increase in stability ($t_{1/2}$ = 2.5 h at −5 °C for **IVb**), but the related carbenes

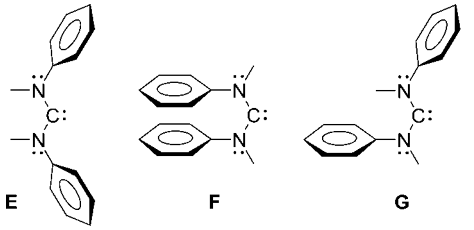
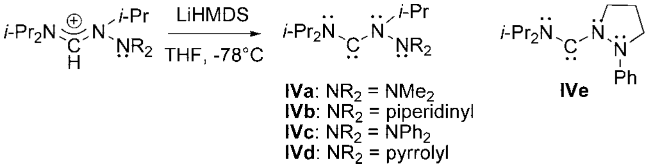


Figure 6. Schematic representation of the three possible conformations conceivable for **IIIi** (isopropyl groups were removed for clarity).

Scheme 10



IVc−e proved to be only transient species.[38] Because of the weakness of N−N single bonds, all of these acyclic aminohydrazinocarbenes undergo radical fragmentation reactions upon warm-up (see section 3.4.1).

The stabilization of diaminocarbenes results from π donation of the two nitrogen lone pairs to the carbene vacant orbital p$_\pi$, as represented by structures **J** and **K** and summarized by structure **L** (Figure 7). Experimentally, this has been substantiated crystallographically for the bis(diisopropylamino)carbene **IIIa** (Figure 8), the only acyclic diaminocarbene structurally characterized to date.[24] The molecule adopts approximate C_2 symmetry in the solid state. The nitrogen atoms are in trigonal planar environments (twisted to each other by 10−14°), and the NC$_{\text{carbene}}$ bond lengths are short [1.363(6) and 1.381(6) Å], indicating substantial multiple bond character. The substantial barrier to rotation around the NC$_{\text{carbene}}$ bonds determined by variable-temperature NMR experiments (12.7 kcal/mol for **IIIa**[24]) supports a similar situation in solution. The NC$_{\text{carbene}}$N bond angle [121.0(5)°] is at the upper limit of those observed in cyclic diaminocarbenes.[39] This probably results from severe steric repulsions in **IIIa** between the isopropyl groups at the nitrogen atoms [the C1N1C2 and C1N2C8 bond angles reach 133.5(4) to 135.1(4)°].

Density functional theory (DFT) calculations performed on the parent diaminocarbene **III*** and its permethylated analogue **IIIf** have further evidenced the push−push stabilization mode (Table 4).[40] The singlet ground-state features trigonal planar nitrogen atoms and short NC$_{\text{carbene}}$ bond lengths. The NC$_{\text{carbene}}$ bonds are elongated by ∼5 ppm in the corresponding triplet state because of electronic repulsion, and the geometry around the nitrogen atoms becomes pyramidal. Introduction of methyl substituents at the nitrogen atoms induces a substantial increase of the NC$_{\text{carbene}}$N bond angles (by >7°), as the result of steric effects. The S−T energy gaps predicted for both diaminocarbenes **III*** and **IIIf** (52.0 and 41.3 kcal/mol, respectively) are significantly larger than those computed for phosphinocarbenes (∼3−14 kcal/mol), consistent with the stronger π-donating character of the amino versus the phosphino groups.

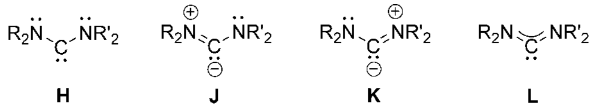


Figure 7. Possible representations for diaminocarbenes **III**.

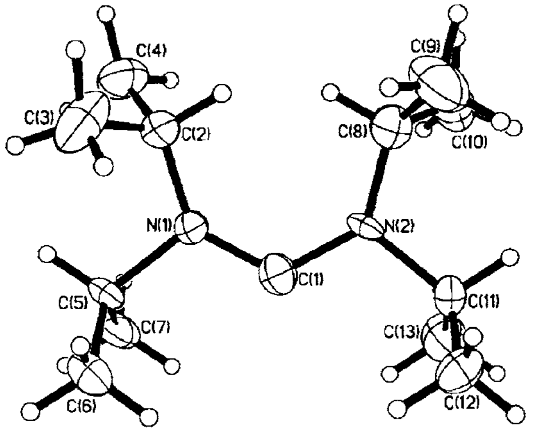


Figure 8. Molecular structure of carbene **IIIa**, as determined from X-ray diffraction analysis. Reprinted with permission from ref 24. Copyright 1996 Wiley.

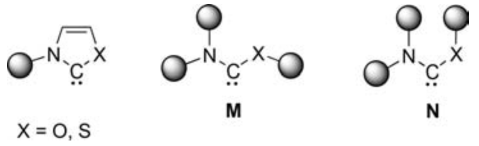
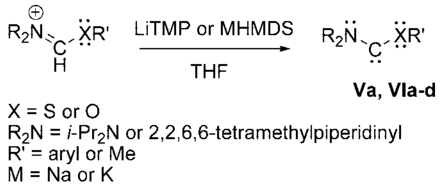
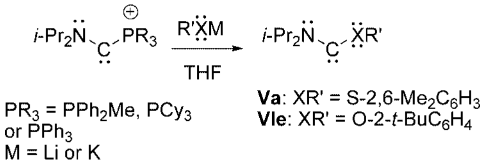


Figure 9. Comparison of the steric shielding in cyclic and acyclic aminothio- and aminooxycarbenes.

Scheme 11



Scheme 12



2.2.2. Aminothio- and Aminooxycarbenes

Besides nitrogen and phosphorus, sulfur and oxygen are good candidates to provide stabilization to carbenes via π donation to the vacant orbital. From a steric viewpoint, cyclic aminothio- or aminooxycarbenes are only protected by the nitrogen substituent, while both sides of the carbene center are encumbered in their acyclic counterparts **V** and **VI** (Table 5), with the *trans* conformation **M** being favored over the *cis* arrangement **N** (Figure 9).

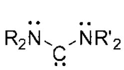
Two cyclic thiazol-2-ylidenes have been described to date: one is a stable crystalline solid while the other is only persistent in solution up to 0 °C and has been characterized by NMR spectroscopy.[42] Cyclic aminooxycarbenes remain transient species[43] that have only been isolated in complexed form.[44] To date, one acyclic aminothiocarbene **Va** and six aminooxycarbenes **VIa−f** have been isolated (Table 5). As early as 1998, Alder et al. prepared compounds **Va** and **VIa−d** by deprotonation of the corresponding amidinium salts with TMPLi or metalated hexamethyldisilazane MHMDS (M = Na or K) (Scheme 11).[45]

Nucleophilic substitution at the carbene center of aminophosphoniocarbenes (see section 3.4.4) also provided an efficient entry to aminothio- and aminooxycarbenes **V** and **VI**, as illustrated by the preparation of the known carbene **Va** and the new compound **VIe** (Scheme 12).[46]

Lastly, formal insertion of an *ortho*-quinone into the P−C bond of the aminophosphinocarbene **XIIIa** (see section 3.4.4) afforded the new aminooxycarbene **VIf** featuring a pendant phosphine moiety (Scheme 13).[46]

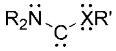
The ^{13}C NMR signals of aminooxycarbenes **VIa−f** appear at 260−280 ppm, at the upper limit of those of dinitrogen-

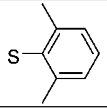
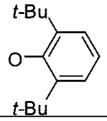
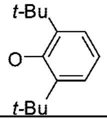
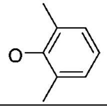
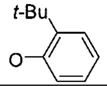
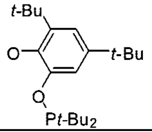
Table 4. Optimized Geometries for the Model Diaminocarbenes III* and IIIf[40b] **and Aminohydrazinocarbenes IV***[37,41] **(at the B3LYP/6-31G* Level of Theory**



	R_2N	NR'_2	spin state	$NC_{carbene}$ (Å)	ΣN_α (°)	$NC_{carbene}N$ (°)	ΔE_{ST} (kcal/mol)
III*	H_2N	NH_2	S	1.344	359.7	112.2	52.0
III*	H_2N	NH_2	T	1.393	337.3	122.2	
IIIf	Me_2N	NMe_2	S	1.354	360	119.7	41.3
IIIf	Me_2N	NMe_2	T	1.389	347.3	121.8	
IV*	H_2N	$NH(NMe_2)$	S	1.341/1.347	360.0	112.5	58.5
IV*	H_2N	$NH(NMe_2)$	T	1.401/1.374	335.8/338.7	121.0	

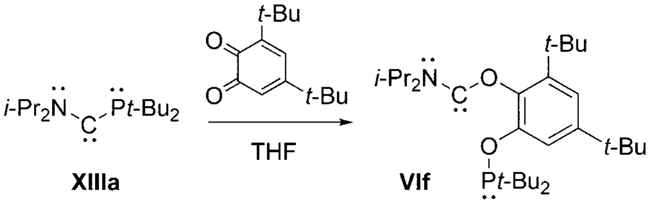
Table 5. Stable Aminothiocarbene Va and Aminooxycarbenes VIa−f



	R_2N	XR'	$\delta^{13}C_{carbene}$ (ppm)	Ref
Va	*i*-Pr_2N		296.6	45,46
VIa	tmp[a]	OMe	277.8	45
VIb	*i*-Pr_2N		267.3	45
VIc	Me_2N		263.8	45
VId	*i*-Pr_2N		262.8	45
VIe	*i*-Pr_2N		262.4	46
VIf	*i*-Pr_2N		268.1	46

[a] tmp = 2,2,6,6-tetramethylpiperidino.

Scheme 13



substituted carbenes **III**−**IV**. A further downfield shift is observed for the aminothiocarbene **Va** ($\delta^{13}C$ = 296 ppm), while its cyclic analogues resonate at much lower frequency (∼250 ppm). The acyclic carbenes **Va** and **VIa**−**f** are all stable at room temperature in solution, and no sign of decomposition was found upon heating toluene solutions of **VIb**−**d** at 100 °C.[45]

Only few data points are available concerning the stabilization mode and the role played by the substituents in carbenes **V** and **VI**. The X-ray diffraction study carried out on **VIb**[45] shows that the molecule adopts conformation **M** (Figure 9) with the OC_{aryl} bond positioned *trans* to the $C_{carbene}N$ bond (Figure 10). This minimizes the steric repulsion between the isopropyl groups at nitrogen and the *tert*-butyl group of the aryloxy substituent and thereby maximizes the steric protection of the carbenic center. The carbene bond angle in **VIb** [$NC_{carbene}O$ = 109.3(3)°] is significantly smaller than that of the acyclic diaminocarbene **IIIa** [$NC_{carbene}N$ = 121.0(5)°]. The presence of only one substituent on the oxygen side probably results in less repulsion between the substituents of the carbene. The $C_{carbene}O$ bond [1.379(5) Å)] is rather long, while the $NC_{carbene}$ bond [1.319(5) Å] is shorter than in **IIIa** (1.36−1.38 Å), suggesting that the π donation to the carbene vacant orbital is more important from the nitrogen than from the oxygen lone pair. This is consistent with the large rotation barrier around the $NC_{carbene}$ bond determined experimentally for the aminooxycarbene **VIc** (>21 kcal/mol versus 12.7 kcal/mol for the diaminocarbenes **IIIa**). Notably, the dissymmetry in π donation from the two substituents seems slightly more pronounced in **VIb** than in the thiazol-2-ylidene [$NC_{carbene}$ = 1.345(3) Å and $C_{carbene}S$ = 1.715(3) Å].[42] Further studies will clearly be needed to precisely estimate the contribution of the thio/oxy substituent. Overall, however, it seems rather clear that the introduction of a thio or oxy substituent at the carbene center enforces π donation from the remaining amino group so that aminooxy- and aminothiocarbenes **V** and **VI** are best described as unsymmetrical push−push carbenes.

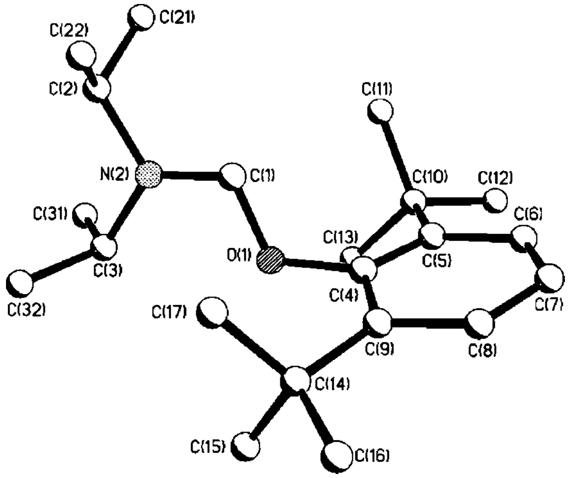
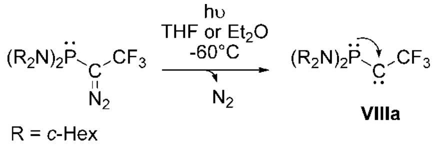


Figure 10. Molecular structure of carbene **IVb**, as determined from X-ray diffraction analysis. Reprinted with permission from ref 45. Copyright 1998 American Chemical Society.

2.3. Phosphinoaryl- and Phosphinoalkylcarbenes

As discussed in sections 2.1 and 2.2, the presence of two heteroatomic substituents may efficiently stabilize carbenes to such an extent that stable compounds can be obtained. Accordingly, the archetypal phosphinosilylcarbenes **I** and

Scheme 14



diaminocarbenes **III** have evidenced two different stabilization modes referred to as push−pull and push−push, respectively. Aiming at extending further the variety of stable carbenes, Bertrand and co-workers started in 2000 to investigate monoheteroatom-substituted carbenes. The phosphinotrifluoromethylcarbene **VIIIa** was generated by photolysis ($\lambda = 300$ nm) of the corresponding diazo precursor at −60 °C (Scheme 14).[47] This carbene is stable for days at −30 °C in donor solvents such as tetrahydrofuran or diethyl ether and was characterized by multinuclear NMR spectroscopy. In particular, the ^{13}C NMR signal for the carbene center ($\delta = 136$ ppm; $^1J_{CP} = 24$ Hz; $^2J_{CF} = 55$ Hz) appears in the same range as that for most phosphinosilylcarbenes. Remarkably, the reactivity of **VIIIa** exactly matches that of its transient congeners (see section 3), and even subtle effects, such as weak interaction with aromatics, could be reproduced.[47] DFT calculations were carried out on the model compound $(H_2N)_2P{-}\ddot{C}{-}CF_3$ to gain insight into the structure of **VIIIa**.[48] The phosphinotrifluoromethylcarbene was predicted to be significantly more bent that the related phosphinosilylcarbene $(H_2N)_2P{-}\ddot{C}{-}SiH_3$ ($PC_{carbene}C = 126.4°$ versus $PC_{carbene}Si = 151.1°$), while the $PC_{carbene}$ bond distance was similarly short (1.58 and 1.56 Å for $(H_2N)_2P{-}\ddot{C}{-}CF_3$ and $(H_2N)_2P{-}\ddot{C}{-}SiH_3$, respectively). The combination of the π-donating phosphino group and σ-withdrawing trifluoromethyl substituent thus brings enough stabilization for carbene **VIIIa** to be persistent in solution at low temperature.

To further increase the stability of the carbene, the trifluoromethyl group was replaced by the sterically demanding 2,6-bis(trifluoromethyl)phenyl substituent. The phosphinoarylcarbene **VIIa**, prepared once again by irradiation of the diazo-precursor, is stable for weeks in the solid state and even at 80 °C in toluene solution.[47,49] Carbene **VIIa** was the first monoheteroatom-substituted carbene to be isolated. X-ray diffraction analysis (Figure 11) unambiguously established its push−pull stabilization mode resulting from (i) π donation of the phosphorus to the carbene center [the phosphorus atom is in a planar environment and the $PC_{carbene}$ bond distance is short at 1.544(3) Å] and (ii) the interaction of the carbene lone pair with the withdrawing aryl ring [the carbene tends to linearity with a $PC_{carbene}C$ angle of 162.1(3)°, short $C_{carbene}C$ bond distance at 1.390(4) Å, and aromatic ring orientated perpendicularly to the $NNPC_{carbene}$ plane].

The π-acceptor 2,6-bis(trifluoromethyl)phenyl group was then replaced by an electron-rich aryl ring. The phosphinomesitylcarbene **VIIe** is stable up to ~40 °C in solution and exhibits very similar ^{31}P and ^{13}C NMR chemical shifts to those of **VIIa**, but a substantially smaller $^1J_{PC}$ coupling constant (65 versus 271 Hz).[50] The stabilization mode of carbene **VIIe** was assessed by X-ray diffraction (Figure 12). As expected, the carbene center is stabilized by π donation from the phosphorus atom, but the mesityl group merely acts as a spectator substituent: the $C_{carbene}C$ bond distance [1.438(3) Å] is in the range typical for $C(sp^2){-}C(sp^2)$ single bonds, and the $PC_{carbene}C$ angle [148.7(2)°] is significantly smaller than that observed for **VIIa** (162.1°).

Following this work, a variety of phosphinoarylcarbenes **VIIb**−**d** and **VIIf**−**h** (Table 6) were prepared in order to better understand the factors governing the role of the aryl substituent on the carbene stabilization mode.[51] The stability of the CF_3−aryl-substituted carbenes **VIIa**−**d** was found to depend essentially on the steric hindrance of the aromatic ring [o,o'-$(CF_3)_2 > o,p$-$(CF_3)_2 \approx o$-$(CF_3) > p$-(CF_3)]. In addition, DFT calculations substantiated the key role of the bulky diisopropylamino substituents at phosphorus in widening the $PC_{carbene}C$ bond angle and thereby increasing the interaction between the carbene lone pair and the aryl ring. Accordingly, the aryl group participates significantly in π delocalization only in carbene **VIIa**, while carbenes **VIIb**−**d** roughly adopt the push−spectator stabilization mode. Similarly, the pentafluorophenyl group was found to behave neither as a π-donor nor as a π-acceptor group in the related phosphinocarbenes **VII(′)f** (Table 6). The phosphinocarbene **VIIg** featuring a dimethylamino group in *para*-position was then investigated in order to enforce

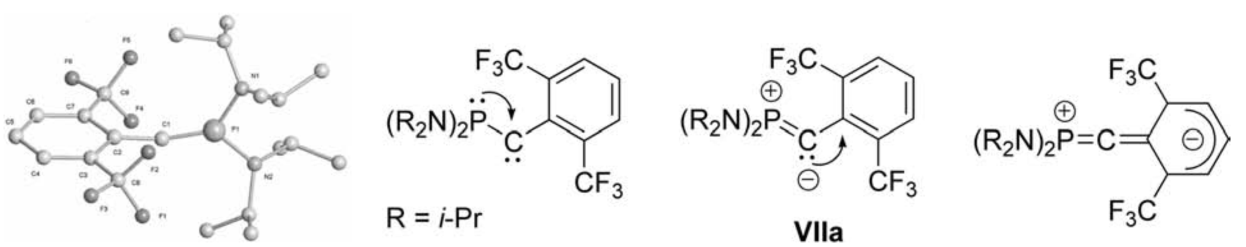


Figure 11. Molecular structure and schematic representation of the stabilization mode of the phosphinoarylcarbene **VIIa**. Reprinted with permission from ref 47. Copyright 2000 American Association for the Advancement of Science.

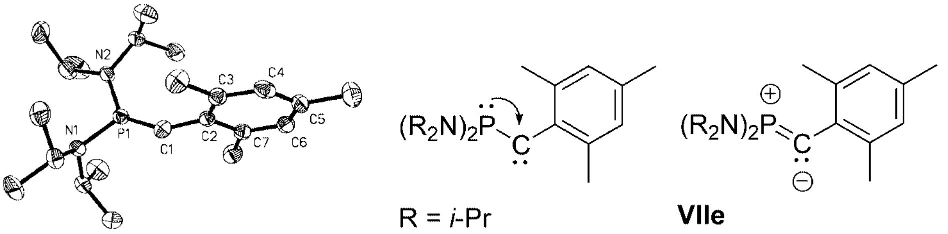
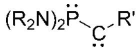
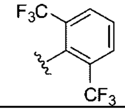
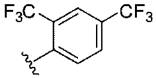
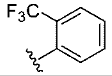
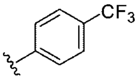
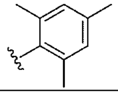
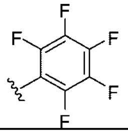
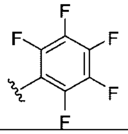
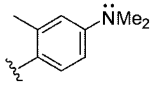
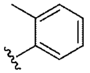


Figure 12. Molecular structure and schematic representation of the stabilization mode of the phosphinomesitylcarbene **VIIe**. Reprinted with permission from ref 50. Copyright 2002 Wiley.

Table 6. Phosphinoarylcarbenes VIIa−h and Phosphinoalkylcarbenes VIIIa−c



compound[a]	R'	$\delta^{13}C_{carbene}$ in ppm ($^1J_{CP}$ in Hz)	$\delta^{31}P$ in ppm	Stability[b]	Ref
VIIa		146.1 (271)	- 22.2	weeks at rt in solution and solid state (m.p.: 68-70°C)	47
VIIb		149.2 (193)	- 19.3	T_{dec} ~ 40°C	51
VIIc		148.6 (124)	- 20.1	T_{dec} ~ 40°C	51
VIId		159.7 (66)	- 12.9	T_{dec} ~ -20°C	51
VIIe		151.1 (65)	- 23.5	weeks at rt in solution and solid state (m.p.: 148°C)	50
VIIf		133.3 (55)	9.4	days at –30°C in solution T_{dec} ~ 20°C	51
VII′f			5.9	days at –30°C in solution T_{dec} ~ 20°C	51
VIIg			- 17.9	T_{dec} ~ -70°C	51
VIIh		156.1 (46)	- 19.8	T_{dec} ~ 0°C	51
VIIIa	CF_3	135.8 (24)	37.1	days at –30°C in THF or Et_2O	47
VIIIb	*t*-Bu	186.3 (32)	- 36.4	T_{dec} ~ -50°C Few minutes in solution at -10°C	50
VIIIc	CH_3	164.8 (44)	- 17.8	$t_{1/2}$ ~ 10 min at -50°C	50

[a] R = *i*-Pr excepted for **VII′f** and **VIIIa** (R = *c*-Hex). [b] T_{dec} corresponds to the temperature above which degradation occurs within a few hours in solution.

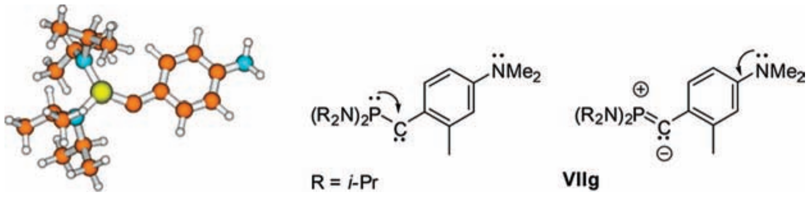
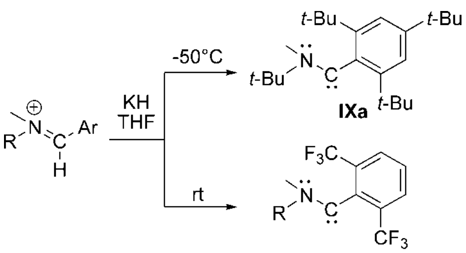


Figure 13. Optimized structure and schematic representation of the stabilization mode of the phosphinoarylcarbene **VIIg**. Reprinted with permission from ref 51. Copyright 2003 American Chemical Society.

the aryl group to behave as a π-donor substituent. Such a push−push stabilization mode was supported theoretically, with a coplanar rather than perpendicular arrangement of the aryl ring and $NNPC_{carbene}$ plane being predicted in this case (Figure 13). Experimentally, photolysis of the corresponding diazo-derivative allowed characterization of carbene **VIIg** by ^{31}P NMR spectroscopy, but decomposition occurred even at −70 °C, while the corresponding amino-free carbene **VIIh** proved stable up to 0 °C! Thus, phosphinoarylcarbenes can be characterized spectroscopically under standard laboratory conditions whatever the acceptor, spectator, or donor contribution of the aryl substituent. The most stable carbene along this series (**VIIa**) is stabilized by push−pull effect, while the combination of π-donor groups results overall in a destabilizing effect (**VIIg**).

The remarkable ability of the phosphino group to stabilize carbenes was also exploited to characterize alkylcarbenes

Scheme 15



IXb: R = *t*-Bu (X-ray)
IXc: R = 1-adamantyl
IXd: R = *i*-Pr

under standard conditions (direct observation of their transient analogues typically requires matrix-isolation conditions or ultrafast time-resolved techniques). The phosphino-*tert*-butylcarbene **VIIIb** (Table 6) was characterized by NMR spectroscopy at −50 °C and proved stable up to −10 °C in solution. Even the related phosphinomethylcarbene **VIIIc** could be observed spectroscopically at −85 °C. Despite the minimal steric protection and the potential to undergo 1,2-shifts (see section 3.1.4.1), carbene **VIIIc** survived up to −50 °C ($t_{1/2} \approx 10$ min).[50]

2.4. Aminoaryl- and Aminoalkylcarbenes

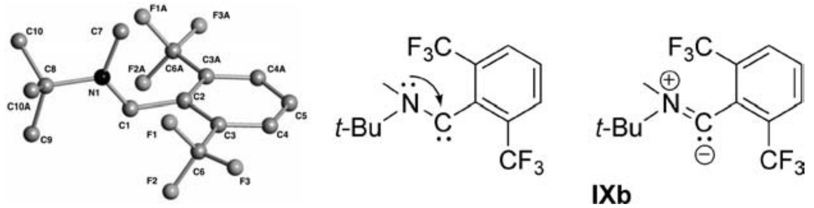
The quest for stable aminoarylcarbenes **IX** started in 2001 with the aim of reducing the degree of carbene perturbation compared to diaminocarbenes **III**. The deprotonation of iminium salts featuring sterically demanding aryl groups with KH in THF was monitored spectroscopically at low temperature.[52] Accordingly, the monoaminocarbene **IXa** proved stable for days at −50 °C but rearranged within a few hours at room temperature via intramolecular C−H insertion (see section 3.1.3.1). With trifluoromethyl instead of *tert*-butyl groups in the *ortho* positions of the aryl ring, this process is no longer possible (C−F bonds are less prone to insertion), and the related aminoarylcarbenes **IXb**−**d** were isolated at room temperature (Scheme 15). For all carbenes **IXa**−**d**, the ^{13}C NMR signal for the carbene center appears at 299−314 ppm, shifted to lower frequencies by ~50 ppm compared to that observed for acyclic diaminocarbenes **III** (228−260 ppm). The X-ray diffraction study carried out on the aminoarylcarbene **IXb** (Figure 14) allows comparison with both the bis(diisopropylamino)carbene **IIIa** and the phosphinoarylcarbene **VIIa**. The NC$_{carbene}$ bond distance in **IXb** [1.283(3) Å] is significantly shorter than those observed for the diaminocarbene **IIIa** (1.36−1.38 Å), which indicates a stronger π donation from the nitrogen to the carbene center. The C$_{carbene}$C bond distance in **IXb** [1.453(3) Å] is substantially longer than that of the cumulenic system **VIIa** (1.390 Å), and the carbene bond angle is much smaller in the amino- versus phosphinoarylcarbene [NC$_{carbene}$C = 121.0(2)° in **IXb** versus PC$_{carbene}$C = 162.1° in **VIIa**]. Thus, in marked contrast with its π-acceptor contribution in **VIIa**, the bis-*ortho*-(trifluoromethyl)phenyl substituent merely behaves as a spectator group in **IXb**. The push−spectator stabilization of **IXb** demonstrated for the first time that a single electron-active substituent is sufficient to isolate a carbene, opening the way to a broader variety of stable amino- and phosphinocarbenes. Compared with the phosphino group, the amino group is a better π donor and more strongly enforces bent geometry at the carbene. This most likely explains why aminoarylcarbenes **IX** are not prone to push−pull or push−push stabilization and, in this respect, are somewhat less flexible electronically than phosphinoarylcarbenes **VII**.

With the aim of reducing the steric protection around the carbene center, the bis-*ortho*-(trifluoromethyl)phenyl substituent was then replaced for a 9-anthryl group.[53] With a half-life time of about 12 h at 4 °C, the new aminoarylcarbene **IXe** (Table 7) could be efficiently trapped at low temperature. In particular, its reaction with metal precursors provided a direct unprecedented access to monoaminocarbene complexes (see section 3.5.1).

Recently, aminobiarylcarbenes **IXf** and **IXg** (Table 7) have also been prepared by deprotonation of the corresponding iminium salts.[54] Despite the presence of only one *ortho*-substituent on the aryl ring, the aminobiphenylcarbene **IXf** is indefinitely stable at room temperature in THF. The related aminobinaphthylcarbene **IXg** is only moderately stable under the same conditions with a half-life time of about 30 min. The aminobiarylcarbenes **IXf** and **IXg** are directly related to the phosphines SPhos and MeO−MOP,[55] (see section 3.5.1 for their coordination properties). Note also that the methoxy groups on the remote aryl ring play a major role in the stability of carbenes **IXf** and **IXg**, with the corresponding unsubstituted aminobiphenyl- and aminobinaphthylcarbenes being only transient species that spontaneously rearrange via intramolecular C−H insertion reactions (see section 3.1.3.1).[56]

Besides the classical deprotonation route, nucleophilic substitution at the carbene center of aminophosphoniocarbenes (see section 3.4.4) was elegantly exploited to prepare stable aminoarylcarbenes.[57] In particular, *ortho*-lithiation of the aminophosphoniocarbene **XIf** readily afforded the aminoarylcarbene **IXh** featuring a pendant phosphino group (Scheme 16).

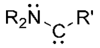
The amino group also proved very effective in stabilizing alkylcarbenes. The iminium precursor, prepared by *C*-methylation of the corresponding enamine, was readily deprotonated by the lithium salt of 2,2,6,6-tetramethylpiperidine (Figure 15). This deprotonation route is limited to carbenes featuring tertiary alkyl groups but de facto prevents 1,2-hydrogen shift, as observed for the phosphinomethylcarbene **VIIIc**. The amino-*tert*-butylcarbene **Xa** could be isolated as low-melting yellow crystals (mp < 20 °C) (in solution at room temperature, it undergoes β-fragmentation within days; see section 3.4.1).[58] The ^{13}C NMR chemical shift of the carbene center (326.3 ppm) is slightly deshielded



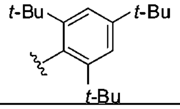
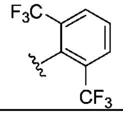
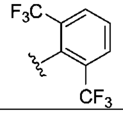
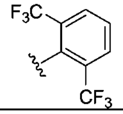
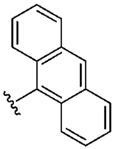
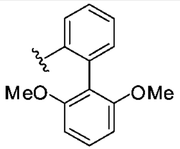
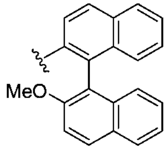
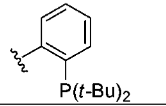
IXb

Figure 14. Molecular structure and schematic representation of the stabilization mode of the aminoarylcarbene **IXb**. Reprinted with permission from ref 52. Copyright 2001 American Association for the Advancement of Science.

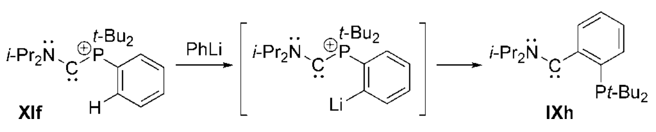
Table 7. Aminoarylcarbenes IXa−h and Aminoalkylcarbene Xa



$R_2\ddot{N}-\ddot{C}-R'$

	R_2N	R'	$\delta^{13}C_{carbene}$ (ppm)	Stability	Ref
IXa	Me(*t*-Bu)N		314.2	days at – 50°C in solution	52
IXb	Me(*t*-Bu)N		302.2	days at rt in solution m.p.: 16°C	52
IXc	Me(Ad)N		303.3	days at rt in solution	52
IXd	Me(*i*-Pr)N		299.2	days at rt in solution	52
IXe	Me(*t*-Bu)N		315.0	days at –30°C in solution $t_{1/2}$ = 12 h at 4°C	53
IXf	*i*-Pr_2N		304.6	indefinitely at rt in solution	54
IXg	*i*-Pr_2N		307.1	$t_{1/2}$ = 30 min at rt in solution	54
IXh	*i*-Pr_2N		314.9	days at rt in solution	56
Xa	*i*-Pr_2N	*t*-Bu	326.3	$t_{1/2}$ = 1.5 days at rt in solution Indefinitely in solid state m.p.: < 20°C	58

Scheme 16



compared to those observed for aminoarylcarbenes **IX** (299−315 ppm). The X-ray analysis revealed the strongly bent geometry of **Xa** with a $NC_{carbene}C$ bond angle of 120.5(1)° (121.0° in the aminoarylcarbene **IXb**). The $NC_{carbene}$ bond distance [1.298(2) Å] is very short, similar to that encountered in **IXb** (1.283 Å) and consistent with the strong interaction of the amino group with the vacant orbital of the carbene center. Interestingly, calculations at the (U)B3LYP/ 6-31g* level of theory predicted a significantly smaller singlet−triplet energy gap (26.7 kcal/mol) and a much higher

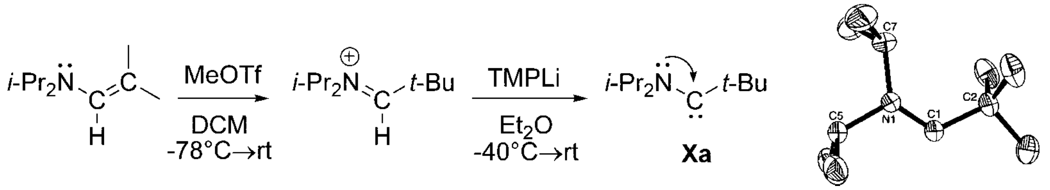


Figure 15. Synthesis and molecular structure of the aminoalkylcarbene **Xa**. Reprinted with permission from ref 58. Copyright 2004 American Chemical Society.

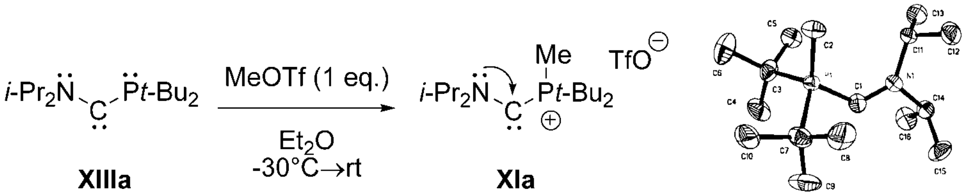
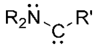


Figure 16. Synthesis and molecular structure of the aminophosphoniocarbene **XIa**. Reprinted with permission from ref 46. Copyright 2003 American Association for the Advancement of Science.

Table 8. Aminophosphoniocarbenes XIa−i and Aminosilylcarbenes XII(′)a



compound[a]	R′	$\delta^{13}C_{carbene}$ in ppm ($^1J_{CP}$ in Hz)	stability	ref
XIa	$^+PMe(t\text{-}Bu)_2$	302.0 (111)	months in solution at −10 °C and in the solid state at rt (mp = 58 °C)	46
XIb	$P(=S)(t\text{-}Bu)_2$	322.0 (108)	few days at rt	61
XIc	$P(\rightarrow BH_3)(t\text{-}Bu)_2$	325.0 (79)	indefinitely in solution and in the solid state (mp = 100−102 °C)	61
XId	$^+PCy_3$	304.5 (109)	indefinitely in solution and in the solid state (mp = 164 °C)	34
XIe	$^+PPh_3$	292.4 (111)	indefinitely in solution and in the solid state (mp = 178 °C)	34
XIf	$^+PPh(t\text{-}Bu)_2$	309.4 (121)	characterized in solution at rt	57, 62
XI′f	$^+PPh(t\text{-}Bu)_2$	310.2 (124)	characterized in solution at rt	62
XIg	$^+PAr(t\text{-}Bu)_2{}^b$	292.0 (114)	characterized in solution at −40 °C	57
XIh	$^+P(i\text{-}Pr)(t\text{-}Bu)_2$	307.5 (113)	characterized in solution at rt	57
XIi	$^+PAr'(Ph)_2{}^c$	291.4 (112)	characterized in solution at −40 °C	63
XIIa	$SiPh_2(t\text{-}Bu)$	377.3	$t_{1/2}$ = 12 h at 0 °C	62
XII′a	$SiPh_2(t\text{-}Bu)$	380.8	few days at 0 °C, $t_{1/2}$ = 1 h at rt	62

[a] R = *i*-Pr excepted for **XI′f** and **XII′a** (R = *c*-Hex). [b] Ar = *o*-(*i*-Pr)−C_6H_4. [c] Ar′ = *o*-(2-BrC_6H_4)−C_6H_4.

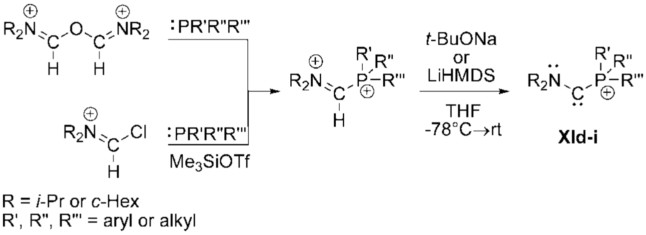
energy of the highest occupied molecular orbital (HOMO) (−4.3 eV) for **Xa**, relative to the acyclic diaminocarbenes **III** (58 kcal/mol and −5.2 eV, respectively). This suggests that carbene **Xa** should behave rather differently than diaminocarbenes **III** (with the aminoalkylcarbene being both more nucleophilic and more electrophilic), and indeed markedly different reactivity was evidenced experimentally (see section 3).

Very little is known for related cyclic aminoarylcarbenes,[59] but cyclic aminoalkylcarbenes (CAACs) have attracted increasing attention over the past few years, not only as ligands within highly active and robust complexes[60] but also as reaction partners toward small molecules such as H_2, NH_3, CO, and P_4.[7]

2.5. Aminophosphonio and Aminosilylcarbenes

The first isolated aminophosphoniocarbene **XIa** was prepared in 2003 by selective *P*-methylation of the corresponding aminophosphinocarbene **XIIIa** with 1 equiv of methyl trifluoromethylsulfonate (Figure 16).[46] Such reactivity at the periphery of the carbene center will be discussed in section 3.4.3. Carbene **XIa** is stable for months both in solution at −10 °C and in the solid state at room temperature. The ^{13}C NMR chemical shift of the carbene center (302 ppm, $^1J_{PC}$ = 111 Hz) is similar to those observed for aminoaryl- and aminoalkylcarbenes **IX** and **X** (299−326 ppm). This suggests negligible, if any, contribution of the phosphonio group in the stabilization of the carbene, and the X-ray diffraction analysis indeed confirmed the push−spectator stabilization mode of **XIa**. The $NC_{carbene}$ bond distance is very short [1.287(6) Å], the $C_{carbene}P$ bond distance is rather long [1.770(5) Å compared to ~1.70 Å in the phosphinophosphoniocarbene **IIa**], and the carbene is strongly bent (with a carbene bond angle of 127.3° compared to 164−165° in **IIa**). Note that the related neutral aminocarbenes **XIb** and **XIc** (Table 8) have also been prepared by selective derivatization of the phosphorus atom of **XIIIa** with S_8 and BH_3, respectively (see section 3.4.3).[61]

Scheme 17



Although the selective *P*-alkylation of aminophosphinocarbenes **XIII** is a very elegant route to aminophosphoniocarbenes **XI**, it is limited to the introduction of a methyl group. In order to increase the variety of accessible aminophosphoniocarbenes, and thereby extend their synthetic interest via nucleophilic substitution reactions (see section 3.4.4), a more general approach relying on the deprotonation of phosphonio iminium salts has recently been developed (Scheme 17).[34,57,62] The required dicationic precursors are readily prepared by addition of phosphines to Alder's dimers $[(R_2NCH)_2O]^{2+}$ or to *C*-chloro formamidinium salts. The deprotonation is performed with *t*-BuONa or LiHMDS as the base and was first illustrated by the preparation of the indefinitely stable crystalline carbenes **XId** and **XIe** featuring three cyclohexyl and phenyl groups at phosphorus, respectively.[34] Despite the different substitution pattern of the phosphonio group, the spectroscopic data and molecular structures of **XId** and **XIe** are very similar to those of **XIa**, which further confirms the propensity of aminophosphoniocarbenes **XI** to adopt the push−spectator, rather than push−pull, stabilization mode. The generality of the deprotonation was subsequently illustrated by the preparation of the aminophosphoniocarbenes **XIf−i** featuring different groups at phosphorus (Table 8).[57,62] The difference observed

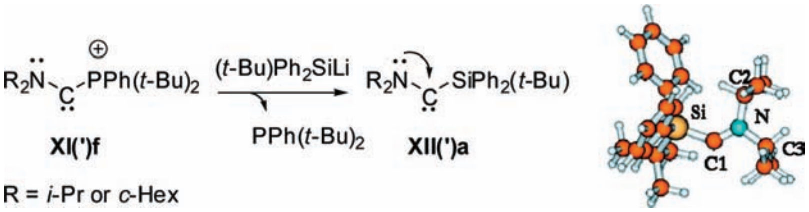
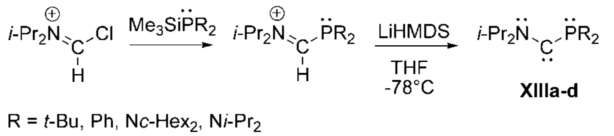


Figure 17. Synthesis and optimized structure of the aminosilylcarbene **XII(′)a**. Reprinted with permission from ref 62. Copyright 2005 American Chemical Society.

Scheme 18



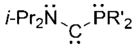
in terms of stability between carbenes **XIg**,**i** and **XIh** pointed out that subtle modifications may have major effects.[57]

Given the historical impact of phosphinosilylcarbenes **I** as the first carbenes to be isolated, aminosilylcarbenes **XII** have also been considered as interesting targets, although their preparation has long been limited by synthetic difficulties. In this respect, the reaction of the aminophosphoniocarbenes **XI(′)f** with the silyl lithium derivative (t-Bu)Ph_2SiLi nicely illustrates the synthetic interest of the nucleophilic substitution at the carbene center (Figure 17).[62] Indeed, the desired aminosilylcarbenes **XII(′)a** were readily obtained, and they feature extraordinarily downfield-shifted ^{13}C NMR signals (377−381 ppm). Once again, subtle steric effects were found to noticeably affect the carbene stability: **XIIa** is only stable at low temperature ($t_{1/2} = 12$ h at 0 °C), while **XII′a** is stable for a few days under these conditions and even survives for a while at room temperature ($t_{1/2} = 1$ h). In contrast with the push−pull stabilization of phosphinosilylcarbenes **I**, aminosilylcarbenes **XII** adopt the push−spectator stabilization mode, as substantiated by DFT calculations: (i) the carbene is strongly bent [with a carbene bond angle of 116.8° for $H_2N-\ddot{C}-SiH_3$ versus 151.1° for $(H_2N)_2P-\ddot{C}-SiH_3$], and (ii) the $C_{carbene}Si$ bond distance is slightly elongated in $H_2N-\ddot{C}-SiH_3$ (1.866 Å) versus $(H_2N)_2P-\ddot{C}-SiH_3$ (1.838 Å). The singlet−triplet energy gap calculated for $H_2N-\ddot{C}-SiH_3$ (20.9 kcal/mol) is significantly larger than that predicted for the related phosphinosilylcarbene $(H_2N)_2P-\ddot{C}-SiH_3$ (11.1 kcal/mol) but slightly smaller than that estimated for $H_2N-\ddot{C}-CH_3$ (33.3 kcal/mol), consistent with the stronger π-donor ability of the amino versus phosphino group and the more electropositive character of silicon versus carbon.

2.6. Aminophosphinocarbenes

As discussed in sections 2.3 and 2.4, a single amino or phosphino group is sufficient to obtain stable carbenes, providing that the other substituent brings enough steric protection. The preparation of mixed aminophosphinocarbenes **XIII** was then envisaged, with the hypothesis that strong π donation from the nitrogen to the carbene center would leave the phosphino group a spectator, potentially functionalizable, substituent. The most general entry to aminophosphinocarbenes relies on the deprotonation of the corresponding *C*-phosphino iminium salts that are readily accessible from *C*-chloro iminium salts and trimethylsilylphosphines (Scheme 18).[64] Accordingly, carbenes **XIIIa**−**d** were generated in tetrahydrofuran at −78 °C, using LiHMDS as the base (Table 9).[61] For all carbenes **XIIIa**−**d**, a diagnostic signal was observed in the ^{13}C NMR spectrum in the range of 320−350 ppm, typical for monoaminocarbenes.

Table 9. Aminophosphinocarbenes XIIIa−d


$i\text{-}Pr_2\ddot{N}-\ddot{C}-\ddot{P}R'_2$

compound	R′	$\delta^{13}C_{carbene}$ in ppm ($^1J_{CP}$ in Hz)	$\delta^{31}P$ in ppm	stability	ref
XIIIa	*t*-Bu	346.6 (57)	7.9	few days in solution at 0 °C $t_{1/2} \approx 12$ h at rt in solution	61
XIIIb	Ph	320.4 (102)	−19.4	days in solution below −20 °C $t_{1/2} \sim 5$ min at rt in solution	46, 61
XIIIc	N*c*-Hex$_2$	329.7 (23)	30.4	days in solution below −20 °C $t_{1/2} \approx 10$ min at rt in solution	61
XIIId	N*i*-Pr$_2$	329.2 (22)	23.8	days in solution below −20 °C $t_{1/2} \approx 5$ min at rt in solution	61, 65

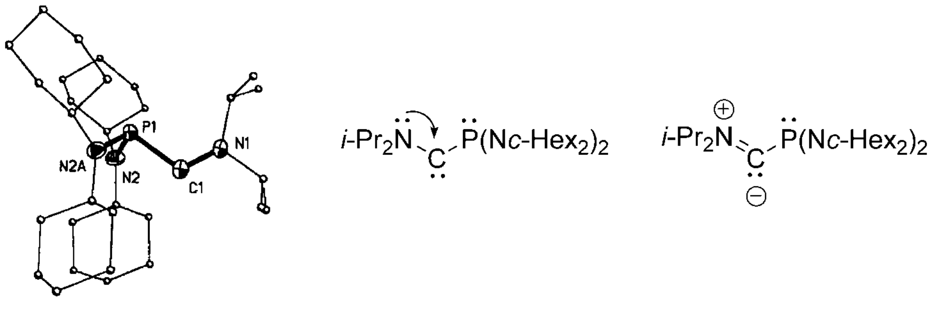
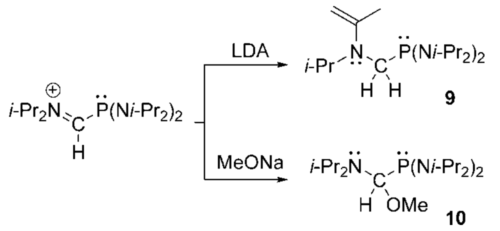
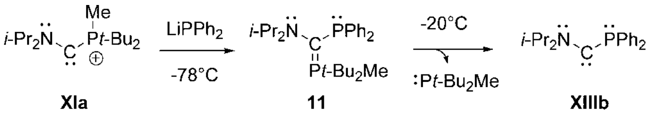


Figure 18. Molecular structure and schematic representation of the stabilization mode of the aminophosphinocarbene **XIIIc**. Reprinted with permission from ref 61. Copyright 2002 American Chemical Society.

Scheme 19



Scheme 20



The X-ray diffraction study carried out on **XIIIc**[61] confirmed the expected push−spectator stabilization mode (Figure 18): (i) the $NC_{carbene}$ bond distance is short [1.296(4) Å], (ii) the carbene bond angle is acute [$NC_{carbene}P$ = 116.5(2)°], (iii) the phosphorus atom is in a pyramidal environment (with a sum of bond angles of 304.5°), and (iv) the $C_{carbene}P$ bond distance is rather long [1.856(3) Å]. Chemical transformation of the spectator phosphino group at the periphery of the carbene center indeed proved feasible, and this will be discussed in section 3.4.3.

The nature of the substituents at phosphorus strongly influences the stability of aminophosphinocarbenes, but all compounds **XIIIa**−**d** are stable for days at −20 °C. Carbene **XIIIc** undergoes β-fragmentation at 40 °C (see section 3.4.1), while carbenes **XIIIc**,**d** rearrange by intramolecular C−H insertion at room temperature (see section 3.1.3.1).[61] The nature of the base also dramatically influences the outcome of the reaction. Deprotonation with LDA or MeONa did not afford the desired carbene **XIIId** but led to the enamine **9** and hemiaminal **10**, respectively (Scheme 19).[64]

Although less general than the deprotonation route, two other strategies have been shown to give access to aminophosphinocarbenes. The aforementioned propensity of aminophosphoniocarbenes to undergo nucleophilic substitution at the carbene center has been exploited to prepare carbene **XIIIb** by reaction of lithium diphenylphosphide with the aminophosphoniocarbene **XIa** (Scheme 20).[46] Monitoring the reaction by ^{31}P NMR at low temperature allowed characterization of the intermediate phosphorus ylide **11**.

Similarly, the *C*-aminophosphorus ylides **13** generated by [4 + 1]-cycloaddition between the phosphaalkenes **12** and 2,4-di-*tert*-butyl-*ortho*-quinone were found to spontaneously and cleanly fragment, affording the aminophosphinocarbene **XIIId** along with an equimolar amount of the corresponding benzodioxaphospholane (Scheme 21).[65] To date, no cyclic aminophosphinocarbene has been isolated, but a persistent version has been recently characterized by NMR spectroscopy.[66]

3. Reactivity

3.1. Typical Carbene Behavior

3.1.1. Coupling Reactions

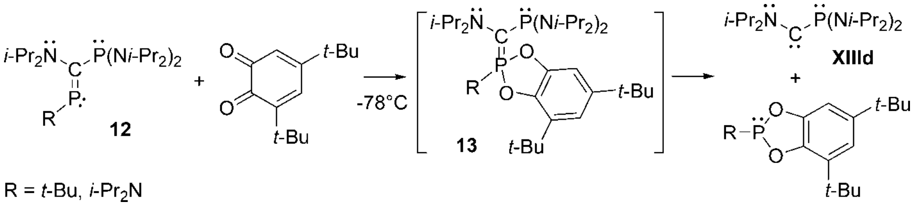
3.1.1.1. Carbene Dimerization. *From Phosphinocarbenes.* As discussed in section 2.1.1, the stability of phosphinosilylcarbenes **I** strongly depends on the steric demand of the phosphorus substituents. When moderately encumbering groups are employed, the photolysis of the diazo precursors does not allow the characterization of carbenes and leads directly to head-to-tail dimers, namely, 1,3-diphosphetes (Scheme 22).[13,16,67]

Upon heating to 40 °C, the persistent phosphinoarylcarbene **VIIc** was found to undergo a somewhat similar process, affording the nonsymmetrical head-to-tail dimer **14** with concomitant elimination of 1 equiv of the imine $Me_2C{=}N(i\text{-}Pr)$ (Scheme 23).[51] Mechanistically, it has been proposed that the nucleophilic carbene center of one molecule first attacks the electrophilic phosphorus center of another carbene molecule. At this stage, the formation of the symmetrical head-to-tail dimer would be sterically impeded, so that an elimination of imine would occur, and the 1,2-dihydro-1,3-phosphete **14** would be obtained by electrocyclization. In addition, the persistent phosphinotrifluoromethylcarbene **VIIIa** provided the first example of a carbene-to-alkene dimerization from a phosphinocarbene.[47] As mentioned in section 2.3, carbene **VIIIa** is stable for days in diethyl ether and tetrahydrofuran solution at −30 °C. However, evaporation of the solvent, even at −50 °C, results in the exclusive formation of the *trans*-dimer **15**, which can also be obtained directly from the diazo precursor via irradiation in a nondonor solvent such as pentane (Scheme 24).

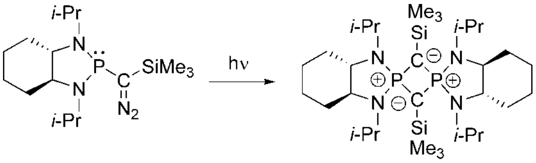
From Aminocarbenes. Since the pioneering contribution of Wanzlick and Lemal, the dimerization of diaminocarbenes has attracted considerable attention. Better understanding has been gained on the factors that control both the thermodynamic and kinetic issues, as comprehensively reviewed recently by Alder.[33] Thus, only the major features concerning acyclic diaminocarbenes **III** will be discussed here.

Most acyclic diaminocarbenes are prone to dimerization to the corresponding tetraamino ethylenes,[26,30,31] with the notable exception of the bis(diisopropylamino)carbene **IIIa**.[24] The ΔG values, obtained through computations, for the dimerization of representative diaminocarbenes are summarized in Table 10. In line with experimental observations, the dimerization was found to be thermodynamically favorable for the methyl- and ethyl-substituted compounds **IIIf** and **IIIg** but not for the isopropyl-substituted carbene **IIIa**. The dimerization of acyclic carbenes is ~25 kcal/mol more favorable than that of their five- and six-membered cyclic analogues **16** and **17** with similar steric demand. This noticeable difference predominantly results from the relatively smaller stabilization of acyclic versus medium-size cyclic diaminocarbenes as the result of the wider $NC_{carbene}N$

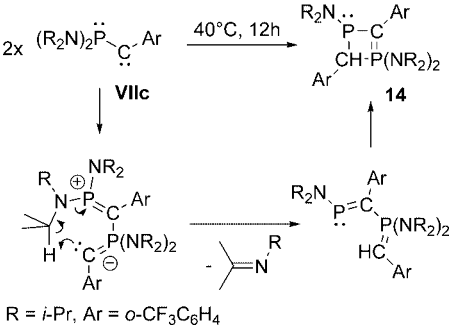
Scheme 21



Scheme 22



Scheme 23



Scheme 24

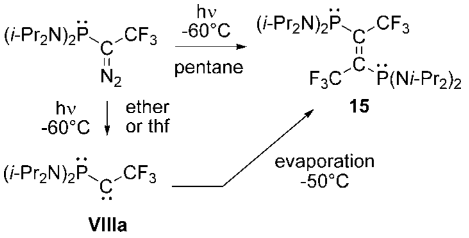
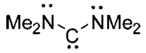
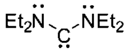
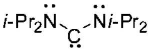
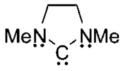
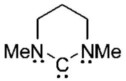


Table 10. Energetic Data for the Dimerization of Representative Diaminocarbenes III Computed at the B3LYP/6-31G* Level of Theory ($\Delta G^{\ddagger}$ Refers to the Uncatalyzed Pathway, ΔG and $\Delta G^{\ddagger}$ are Estimated at 298 K and Given in kcal/mol)

	carbene	ΔG	$\Delta G^{\neq}$
IIIf		–33.1	26.7
IIIg		–22.7	37.4
IIIa		9.8	-
16		–10.5	25.1
17		–8.7	32.8

bond angle and weaker π conjugation due to some twisting about the $NC_{carbene}$ bonds.[33,40]

Mechanistically, the "classic" pathway for the dimerization of singlet carbenes involves the interactions of the in-plane n_{σ} lone pair of each carbene with the formally vacant p_{π} orbital of the other carbene (Figure 19).[68] However, for diaminocarbenes, both acyclic and cyclic, the corresponding activation barriers[33,40] (computed values of $\Delta G^{\ddagger}$ are listed in Table 10) seem prohibitively high for the dimerization to occur via such a pathway. This is further supported experimentally by the reluctance of the free bis(diethylamino)carbene **IIIg** and even the bis(dimethylamino)carbene **IIIf**[32,33] to dimerize, although the corresponding dimers are favored thermodynamically.

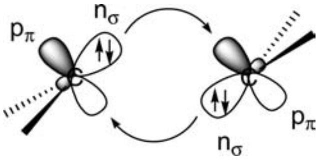
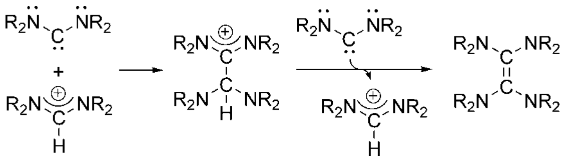
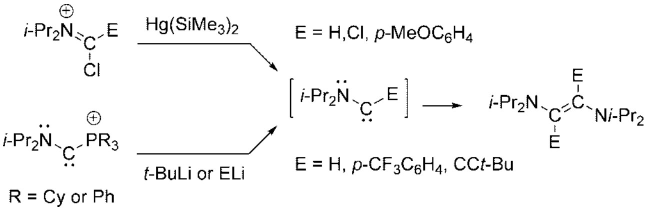


Figure 19. Schematic representation of the "classical" pathway for the dimerization of singlet carbenes.

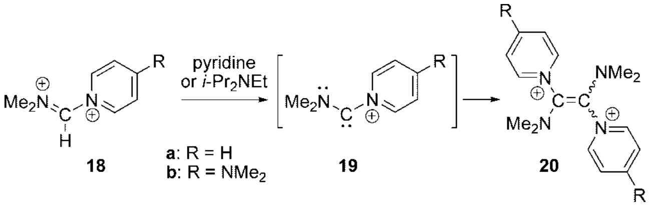
Scheme 25



Scheme 26



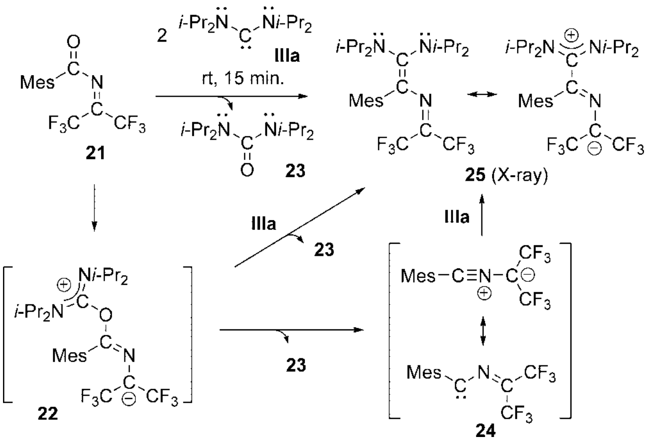
Scheme 27



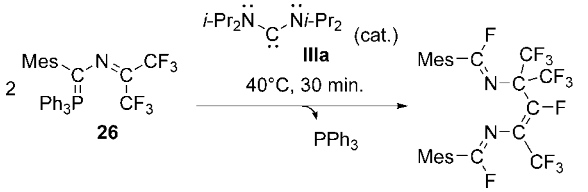
Instead of carbene–carbene coupling, the dimerization of diaminocarbenes **III** most likely proceeds by the nucleophilic addition of the carbene to its formamidinium precursor, followed by an intermolecular proton transfer presumably involving the carbene itself as a base (Scheme 25). This proton-catalyzed mechanism has been supported experimentally by the spectroscopic characterization of the protonated dimer intermediates derived from a thiazol-2-ylidene[69] and an imidazolidin-2-ylidene.[33] In addition, the order of addition of the tetraethylformamidinium salt and lithium diisopropylamide (LDA) was found to significantly affect the carbene/dimer ratio. Upon addition of the base to the formamidinium, the carbene is typically contaminated by ca. 30% of the corresponding dimer, while nearly pure carbene (<5% dimer) was obtained by reverse addition.[31] Similarly, complexation to lithium, while thermodynamically stabilizing the unhindered carbenes, likely promotes dimerization.[31,33]

Because of their less perturbed character (higher HOMO and smaller HOMO–LUMO (lowest unoccupied molecular orbital) separation), the dimerization of monoaminocarbenes can be anticipated to be more favorable, both thermodynamically and kinetically. Unfortunately, much less data is available. Indeed, no such dimerization has been evidenced to date for stable or persistent monoaminocarbenes, presumably due to their high steric protection. However, the transient aminocarbenes $i\text{-Pr}_2N-\ddot{C}-X$ (X = H, Cl, $p\text{-MeOC}_6H_4$, $o\text{-F}_3CC_6H_4$, CC*t*-Bu) were found to dimerize even when generated by $Hg(SiMe_3)_2$-mediated dechlorination of *C*-chloro iminium salts (see section 2.2.1)[32] or nucleophilic substitution from aminophosphoniocarbenes (see section

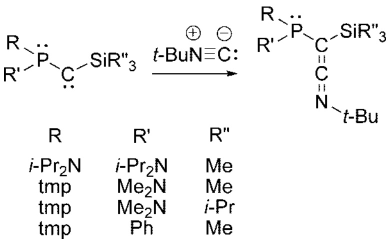
Scheme 28



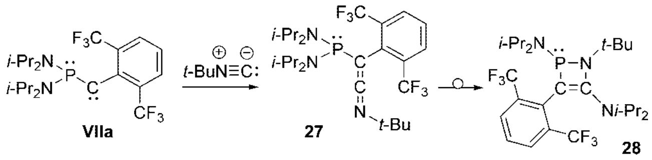
Scheme 29



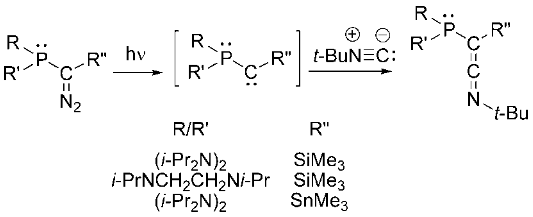
Scheme 30



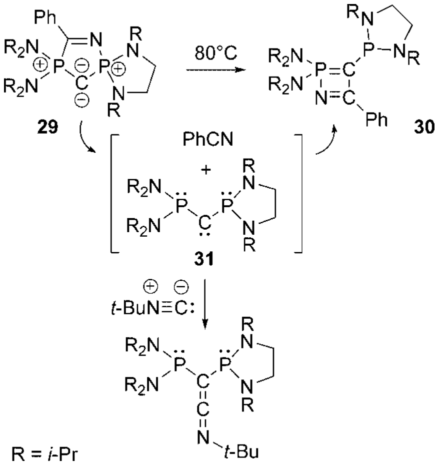
Scheme 31



Scheme 33



Scheme 34



3.4.4),[34] two methods that prevent proton-catalyzed coupling (Scheme 26). Recently, 1,2-bisonio-1,2-diaminoethenes **20a**,**b** were prepared by deprotonation of the pyridinio-substituted *N*,*N*-dimethyliminium salts **18a**,**b** (Scheme 27). In this case, the dimerization of the transient aminopyridiniocarbenes **19a**,**b** most likely proceeds via carbene−iminium coupling (proton-catalyzed mechanism).[70]

Recently, the reaction of the bis(diisopropylamino)carbene **IIIa** with the aroylimine **21** was shown to give alkene **25**, the formal coupling product between the stable nucleophilic carbene **IIIa** and the transient electrophilic imine-substituted carbene **24** (Scheme 28).[71] The reaction likely proceeds through nucleophilic addition of **IIIa** on the oxygen atom of **21**. The ensuing zwitterion **22** would then react with a second molecule of **IIIa** in a concerted or stepwise process to give urea **23** along with the hetero-coupling product **25**. As revealed from the X-ray structure, this azabutadiene is strongly stabilized by a push−pull effect and is best described by its zwitterionic mesomeric structure.

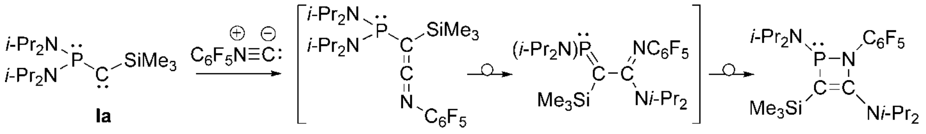
A similar hetero-coupling reaction was proposed to account for the nonsymmetrical dimerization of the nitrile ylide **24** when the corresponding phosphorus ylide **26** was treated with a catalytic amount of carbene **IIIa** (Scheme 29).[72,73]

3.1.1.2. Carbene−Isonitrile Coupling. The formation of ketenimines by coupling transient carbenes with isonitriles is well-documented.[74] Stable phosphinosilylcarbenes **I** readily react with *tert*-butyl isocyanide, usually at room temperature and even sometimes at −78 °C (Scheme 30). Since the reactive site of the isonitrile is rather unhindered, the reaction occurs even with the carbene featuring a sterically demanding tri(isopropyl)silyl substituent, although it requires, in that case, 2 days at rt.[75]

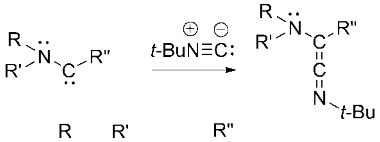
Tert-butyl isocyanide also reacts smoothly with the phosphinoarylcarbene **VIIa** at room temperature (Scheme 31). The resulting ketenimine **27** could be characterized spectroscopically, but it was found to slowly isomerize at room temperature into the 1,2-dehydro-1,2-azaphosphete **28**.[49]

Such a phosphino ketenimine to 1,2-dehydro-1,2-azaphosphete rearrangement had been previously proposed in the coupling reaction of the phosphinosilylcarbene **Ia** with pentafluorophenyl isocyanide (Scheme 32).[76] The reaction proceeds by P → C 1,3-shift of a diisopropylamino group followed by electrocyclization. All of the structural isomers

Scheme 32

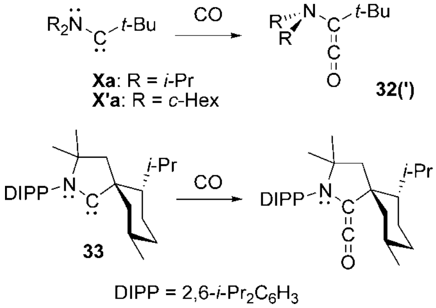


Scheme 35



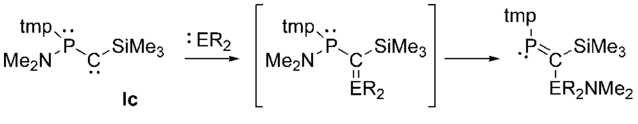
	R	R'	R''
IXc	Ad	Me	$2,6\text{-}(CF_3)_2C_6H_3$
IXd	*i*-Pr	Me	$2,6\text{-}(CF_3)_2C_6H_3$
XIIa	*i*-Pr	*i*-Pr	Si(*t*-Bu)Ph_2
XIIIa	*i*-Pr	*i*-Pr	P(*t*-Bu)$_2$

Scheme 36



DIPP = $2,6\text{-}i\text{-}Pr_2C_6H_3$

Scheme 37



E = Ge, R = N$(SiMe_3)_2$ or NHMes*
E = Sn, R = N$(SiMe_3)_2$ or CH$(SiMe_3)_2$
tmp = 2,2,6,6 tetramethylpiperidine
Mes* = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$

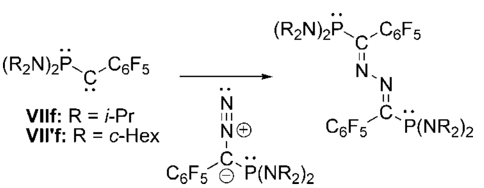
involved in this process have been isolated by using different substituents and various synthetic routes.[77]

Because of its high reactivity, *tert*-butyl isocyanide is a well-suited trapping agent for transient phosphinocarbenes, as illustrated by moderately encumbered phosphinosilylcarbenes[13,16] and phosphinostannylcarbenes (Scheme 33).[14]

Tert-butyl isocyanide may even be used as a mechanistic probe, as recently reported for the thermal conversion of the cyclic carbodiphosphorane **29** into the 1,2-azaphosphete **30**.[78] Computational studies supported a [3 + 2]-retrocycloaddition/[2 + 2]-cycloaddition sequence (see section 3.1.2.3), and the putative diphosphinocarbene intermediate **31** could be intercepted, albeit in low yield, by chemical trapping with *tert*-butyl isocyanide (Scheme 34).

The coupling reactions involving phosphinocarbenes and isocyanides are likely dominated by $\text{LUMO}_{\text{carbene}}$−$\text{HOMO}_{\text{isocyanide}}$ interactions. In this respect, it is not surprising that no reactions involving diaminocarbenes (acyclic as well as cyclic) and isocyanides have been reported to date. Only the less perturbed monoaminocarbenes **IXc**,**d**, **XIIa**, and **XIIIa**, which feature a more accessible LUMO, react with *tert*-butyl isocyanide to give the corresponding aminoketenimines (Scheme 35).[52,61,62]

Scheme 39



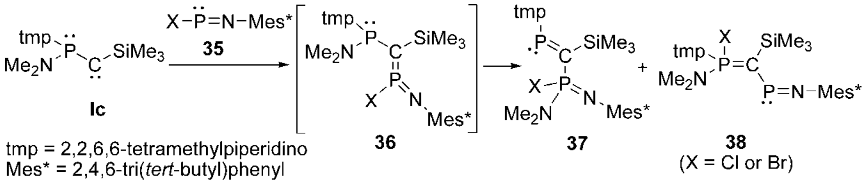
3.1.1.3. Carbene−Carbon Monoxide Coupling. Both triplet and singlet transient carbenes are known to react with CO to give the corresponding ketenes.[79] In 1994, the carbonylation of the stable 1,3-diadamantyl-imidazol-2-ylidene was claimed to give a diaminoketene.[80] However, Dixon and Arduengo later found no evidence for the formation of the putative ketene under the same conditions, and no stable structure associated with a diaminoketene could be located computationally for the parent imidazol-2-ylidene.[81]

By exploiting the less-perturbed character of monoamino- versus diaminocarbenes, Bertrand et al. reported in 2006 the first unambiguous example of ketene formation by carbonylation of stable carbenes (Scheme 36). Bubbling carbon monoxide into solutions of the aminoalkylcarbenes **X(′)a** cleanly afforded the corresponding aminoketenes **32(′)**.[7b] The X-ray diffraction study carried out on **32′** revealed the absence of an interaction between the nitrogen lone pair and the C=C=O moiety as deduced from their antiperiplanar arrangement, the long NC bond, and the strongly pyramidalized environment around the nitrogen atom. Notably, a similar carbonylation reaction was observed from the cyclic aminoalkylcarbene **33**. As anticipated, the incorporation of the nitrogen atom in a ring enforced its planarization. The electronic structure of the aminoketene strongly depends on the acyclic/cyclic nature of its aminocarbene fragment, and marked differences were found in the spectroscopic and optical properties of both variants. Apart from the phtalimido-*tert*-butylketene whose nitrogen lone pair is "deactivated" by the adjacent carbonyl groups,[82] no other aminoketene had been observed so far. The formation of **32(′)** by carbonylation of **X(′)a** thus represents a spectacular illustration of the synthetic interest of stable carbenes for the preparation of hitherto unknown derivatives.

3.1.1.4. Carbene−Carbenoid Coupling. The phosphinosilylcarbene **Ic** reacts with germylenes and stannylenes to afford the corresponding *C*-germyl and *C*-stannyl phosphaalkenes **34** (Scheme 37).[83] These reactions presumably proceed by carbene−carbenoid coupling, followed by chemoselective P → Ge or P → Sn 1,3-shift of the dimethylamino group, which is the least sterically demanding substituent at phosphorus.

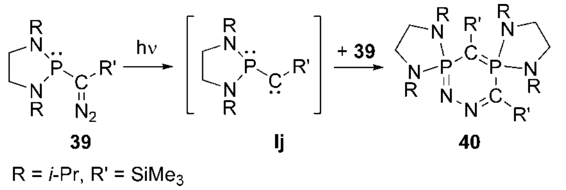
Similar transformations, leading to methylenephosphine−iminophosphoranes **37**, were observed with a variety of iminophosphines **35** (Scheme 38).[84] Given that iminophos-

Scheme 38

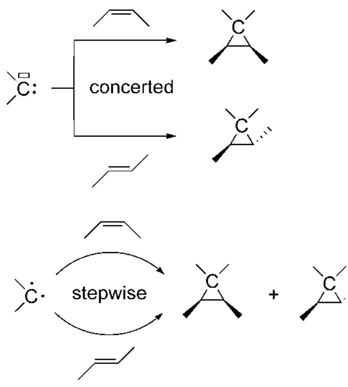


tmp = 2,2,6,6-tetramethylpiperidino
Mes* = 2,4,6-tri(*tert*-butyl)phenyl
X = *t*-Bu, OMe, F, Cl, Br

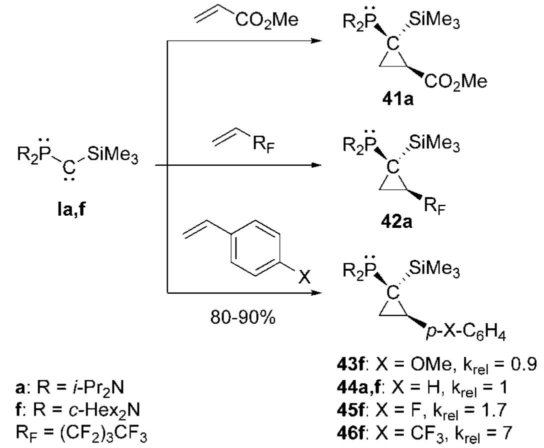
Scheme 40



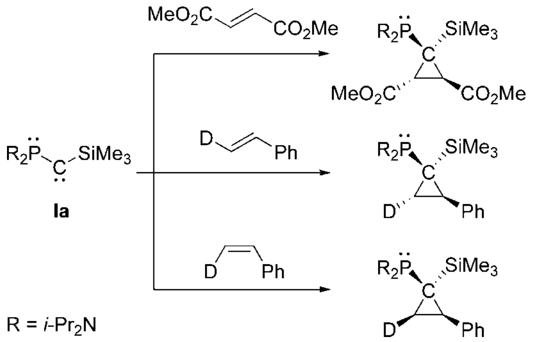
Scheme 41



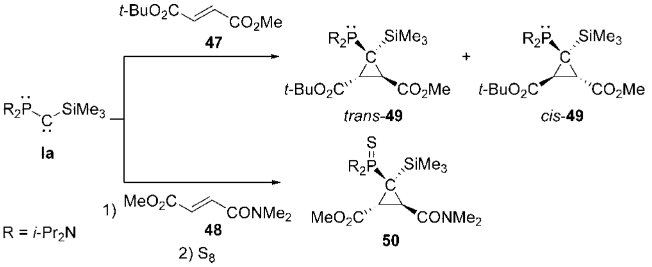
Scheme 42



Scheme 43



Scheme 44



phines are known to eventually behave as carbenoids,[85] it is likely that (methylene)(imino)phosphoranes **36** are first formed and then rapidly rearrange by λ^3-P → λ^5-P 1,3-migration of the dimethylamino group. Starting from *P*-chloro or *P*-bromo iminophosphines, intermediates like **36** may also undergo λ^5-P → λ^3-P 1,3-shift of the halogen, leading to minor amounts of the isomeric methylenephosphorane-iminophosphine **38** (see section 3.2.4).

3.1.1.5. Carbene−Diazo Coupling. The formation of azines from carbene−diazo coupling is a reaction typical of transient carbenes[86] that has also been observed for a stable *N*-heterocyclic carbene[87] and the phosphinopentafluorophenylcarbenes **VII(′)f**. Carbenes **VII(′)f** can be generated in good yield by photolysis of their diazo precursors at −50 °C. When the irradiation is stopped at half-conversion, and the reaction mixture is warmed up to room temperature, the symmetrical azines were obtained in 63−72% yield (Scheme 39).[51] Notably, the carbene−diazo coupling occurs with complete selectivity, and no trace of the conceivable phosphine−diazo coupling (Staudinger−Meyer reaction)[88] is detected.

Carbene−diazo coupling was also observed with the transient phosphinosilylcarbene **Ij**, affording in that case an unsymmetrical heterocyclic structure **40** as the result of phosphine−carbene and phosphine−diazo cross-couplings (Scheme 40).[16]

3.1.2. Cycloaddition Reactions

3.1.2.1. Cyclopropanation Reactions. The reaction of alkenes with carbenes, carbenoids, and carbene−metal complexes provides straightforward and efficient access to cyclopropanes. In addition to its synthetic interest, the so-called cyclopropanation reaction has been frequently used to determine the ground-state spin multiplicity of transient carbenes (stepwise versus concerted reaction of triplet versus singlet carbenes, Scheme 41) and to estimate their nucleophilic, electrophilic, or amphiphilic character (Moss classification).[89] As far as stable carbenes are concerned, cyclopropanation reactions have long been observed only with phosphinocarbenes, but a monoaminocarbene was recently found to also undergo [1 + 2]-cycloaddition. Starting from stable nucleophilic carbenes and electron-deficient alkenes, highly functionalized cyclopropanes could be prepared in very good yield and high stereoselectivity.

Soon after its preparation, the phosphinosilylcarbene **Ia** was reacted with alkenes in order to assess its carbenic character. No reaction was observed with electron-rich alkenes, but **Ia** readily added to methyl acrylate to give the corresponding cyclopropane **41a** (Scheme 42).[75] Later on, nonafluorohex-1-ene and styrene were also found to be suitable partners, and competitive cyclopropanation reactions between **If** and *para*-substituted styrenes unambiguously confirmed the nucleophilic behavior of phosphinosilylcarbenes **I**.[90]

The stereochemical outcome of these cyclopropanation reactions has been of particular interest. The reaction of **Ia**

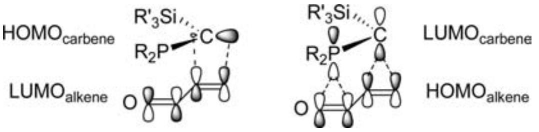
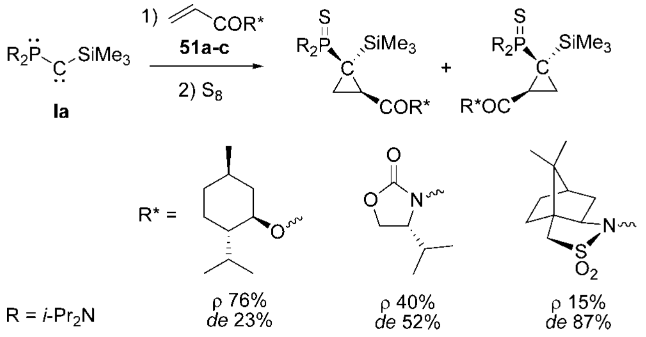
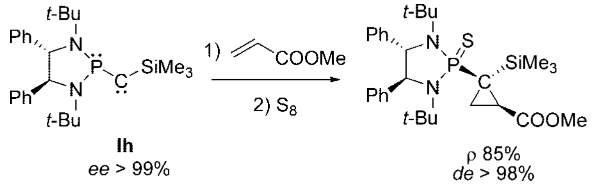


Figure 20. Schematic representation of the orbital interactions in the reaction of phosphinosilylcarbenes with acroleine.

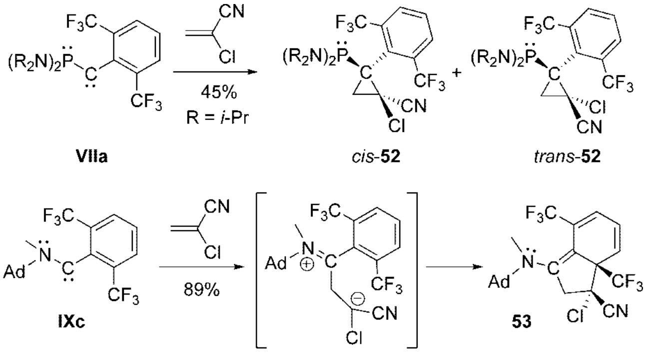
Scheme 45



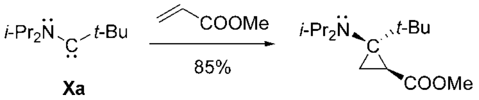
Scheme 46



Scheme 47



Scheme 48



with dimethyl fumarate was found to occur with retention of the *trans*-arrangement between the two ester groups (Scheme 43).[75] Similar results were obtained with 2-deuterio styrenes, supporting a concerted process.[90]

In addition, all cyclopropanation reactions from **Ia** and **If** proved to be highly diastereoselective, with monosubstituted alkenes leading exclusively to *cis*-cyclopropanes (with respect to the phosphorus atom). The reaction of **Ia** with the nonsymmetrical alkenes **47** and **48** provided more insight into the origin of the stereocontrol (Scheme 44).[90] The sterically dissymmetrized fumarate **47** led to a 9:1 mixture of *trans*/*cis*-cyclopropanes **49**, suggesting that the phosphino group is more sterically demanding than the silyl substituent. The electronically dissymmetrized alkene **48** led exclusively to cyclopropane **50**, with *cis*-arrangement of the phosphorus atom and amido group. Therefore, electronic rather than steric effects were supposed to be responsible for the complete *syn*-selectivity. Secondary orbital interactions between the phosphorus atom of the carbene and the alkene substituent were thus invoked (Figure 20), analogous to that proposed for the *endo*-selectivity in Diels−Alder reactions.

Valuable mechanistic insights were recently gained by Cossio, Branchadell, et al. from a detailed computational study carried out with model phosphinosilylcarbenes.[19b] The cyclopropanation reactions were first confirmed to proceed in a concerted asynchronous fashion, involving early transition states with significant charge transfer from the carbene to the alkene. Calculations of the *cis*- and *trans*-cyclopropanation of the model carbene $(Me_2N)_2P-\ddot{C}-SiMe_3$ with methyl acrylate supported kinetic control for the diastereoselectivity (the *trans*-cyclopropane is favored thermodynamically by 1.5 kcal/mol, but the activation barrier for the *cis*-cyclopropanation is lower by 2 kcal/mol). Careful examination of the corresponding transition states suggested that electrostatic effects rather than secondary orbital interactions are responsible for the *syn*-selectivity. Indeed, large distances leading to negligible overlaps were found between the two groups, but a noticeable attractive Coulombic interaction was found between the phosphorus atom ($q_P = +1.63$) and the oxygen atom of the carbonyl group of methyl acrylate ($q_O = -0.66$).

The asymmetric version of these cyclopropanation reactions has also been recently studied using first the enantiopure acrylate **51a** and acrylamides **51b**,**c** (Scheme 45).[91] The corresponding cyclopropanes were obtained with diastereomeric excesses *de* ranging from 23 to 87% depending on the chiral auxiliary, but the rise in *de* was accompanied by a detrimental decrease in chemical yield (from 76 to 15%).

Better results were obtained with the enantiopure phosphinosilylcarbene **Ih** (Scheme 46). With methyl acrylate, the corresponding cyclopropane was obtained in 85% yield as a single diastereomer (*de* > 98%).[16]

Cyclopropanation has also been used to trap persistent or even transient phosphinocarbenes. Accordingly, the trifluoromethylcarbene **VIIIa**[47] and *tert*-butylcarbene **VIIIb**[50] (Table 6) were found to exhibit typical behavior of nucleophilic carbenes, reacting readily with methyl acrylate at low temperature to give the corresponding cyclopropanes with complete *syn*-selectivity. A similar reaction was also reported from the transient phosphinostannylcarbene $(i\text{-}Pr_2N)_2P-\ddot{C}-Sn(c\text{-}Hex)_3$, generated by irradiation of the corresponding diazo precursor.[14]

The phosphinoarylcarbene **VIIa** proved less reactive in cyclopropanation reactions. At room temperature, no reaction occurred with methyl acrylate, but carbene **VIIa** reacted with the more electron-deficient 2-chloroacrylonitrile within a few minutes (Scheme 47).[49] The corresponding cyclopropane **52** was obtained as a 3:1 mixture of *anti*/*cis*-diastereomers. The absence of stereoselectivity in that case may reflect the possibility of both the chlorine atom and the cyano group interacting with the phosphorus atom at the transition state. Remarkably, a completely different outcome was observed with the corresponding aminoarylcarbene **IXc**.[92] Instead of the expected cyclopropane, the reaction afforded the original dearomatized bicyclic adduct **53**, likely via Michael addition of the carbene to the alkene, followed by nucleophilic attack at one of the *ortho* positions of the aryl ring. The formation of the aminocyclopropane by nucleophilic attack at the *C*-iminium center is presumably impeded by steric congestion.

Because of larger HOMO−LUMO gaps, aminocarbenes are clearly less prone to cyclopropanation than phosphinocarbenes, and to date, only the amino-*tert*-butylcarbene **Xa** was shown to exhibit such reactivity. Carbene **Xa** reacts instantaneously with methyl acrylate at −40 °C, affording the corresponding aminocyclopropane in 85% yield and with complete *syn*-selectivity (Scheme 48).[58] The less-perturbed character of monoamino- versus diaminocarbenes probably explains why such cyclopropanation reactions have not been

Scheme 49

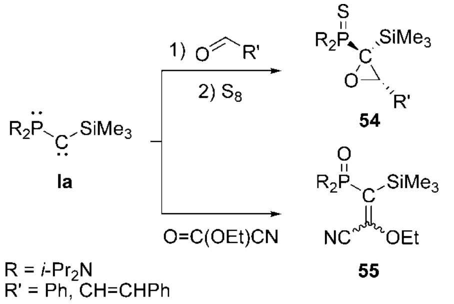
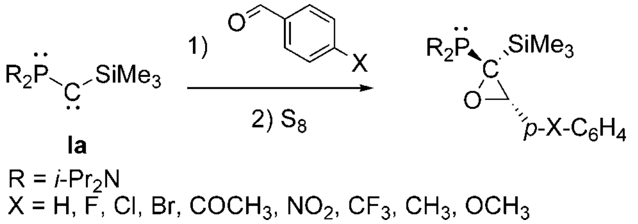


Table 11. Reaction of the Phosphinosilylcarbene Ia with *para*-Substituted Benzadehydes



X[a]	E_{LUMO} (in au)	$\Delta G^{\ddagger\,b}$ (in kcal/mol)
NO_2	−0.1146	21.0
Br	−0.0733	23.2
H	−0.0629	24.1
OMe	−0.0511	26.2
NMe_2	−0.0391	28.8

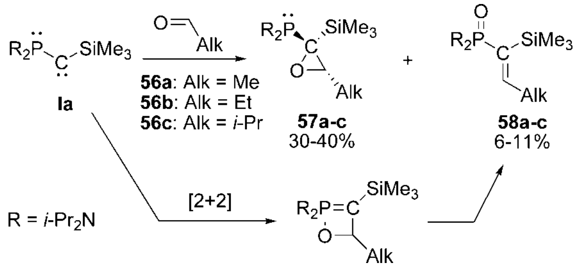
[a] Calculations carried out on the model carbene **X** at the B3LYP/6-31G(d) level of theory. [b] Gibbs activation energy estimated for the *trans*-epoxidation in THF at 1 atm and 25 °C.

observed with diaminocarbenes, regardless of their acyclic or cyclic nature. Even with transient species, cyclopropanation reactions of aminocarbenes are so far limited to the 3,5,7-trimethyl-1-azatricyclo-[3.3.1.1$^{3.7}$]decan-2-ylidene, whose adamantane core prevents efficient N → $C_{carbene}$ π donation.[93]

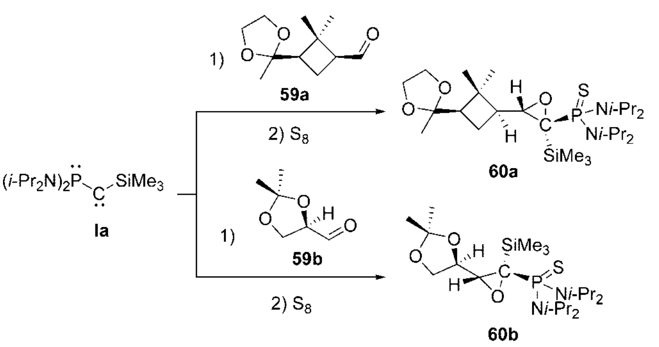
3.1.2.2. Epoxidation Reactions. The [1 + 2]-cycloaddition of carbenes with carbonyl compounds is a very attractive route to oxiranes. To date, it is limited to phosphinosilylcarbenes **I** and aldehydes, but it provides very efficient and stereoselective access to highly functionalized epoxides. Carbene **Ia** was first reported to rapidly react with benzaldehyde and *trans*-cinnamaldehyde at room temperature (Scheme 49).[75] The corresponding oxiranes **54** were isolated in high yields after thiolation with elemental sulfur. The complete diastereoselectivity in favor of the *trans*-oxiranes (with respect to the phosphorus atom) was established later on by X-ray diffraction analyses.[94] In a marked contrast with this Corey–Chaykovski-type behavior, the phosphinosilylcarbene **Ia** reacts with ethyl cyanoformate via a Wittig-type reaction, affording an equimolar mixture of *Z*- and *E*-phosphorylalkenes **55**.[75]

In order to assess the influence of electronic effects on the epoxidation reaction, carbene **Ia** was then reacted with various *para*-substituted benzaldehydes. With electron-withdrawing and moderate electron-donating groups, the *trans*-epoxides are formed within a few minutes at room temperature, but under the same conditions, no reaction was observed after 20 h for aldehydes bearing stronger electron-donating groups (such as dimethylamino and acetamido).[94a] A detailed theoretical investigation performed on the model carbene $(Me_2N)_2P{-}\ddot{C}{-}SiH_3$ revealed the formation of the *trans*-oxiranes being favored kinetically by 2.6 kcal/mol (the Gibbs activation energies $\Delta G^{\ddagger}$ for the *trans*- and *cis*-epoxidation of benzaldehyde in THF at 25 °C are 24.1 and 26.7 kcal/mol, respectively). The reaction is concerted but asynchronous and involves electronic charge transfer from the nucleophilic carbene to the aldehyde. The predominant orbital interaction arises between the n_σ orbital of the carbene and the π^*_{CO} of the aldehyde. Consistent with the experimental observations, a good correlation was observed between the computed values of $\Delta G^{\ddagger}$ and the electrophilicity of the *para*-substituted aldehydes, as estimated from the LUMO energy E_{LUMO} (Table 11).

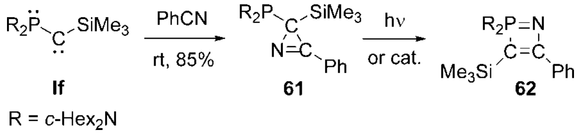
Scheme 50



Scheme 51



Scheme 52

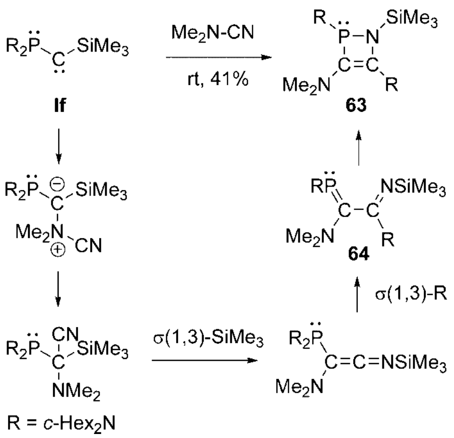


Aliphatic aldehydes **56a–c**, but not pivaldehyde *t*-BuCHO, could also be epoxidized with the phosphinosilylcarbene **Ia**. The corresponding *trans*-oxiranes **57a–c** were isolated in 30–40% yields but were accompanied by small amounts of the phosphorylalkenes **58a–c** as a result of competitive Wittig-type reactions (Scheme 50).[94b] Calculations on the reaction of the model carbene $(Me_2N)_2P{-}\ddot{C}{-}SiH_3$ with acetaldehyde substantiated the kinetic preference for the *trans*-epoxidation ($\Delta G^{\ddagger}$ of 25.6 kcal/mol in heptane at 25 °C versus 28.2 kcal/mol for the *cis*-epoxidation). The [2 + 2]-Wittig-type cycloaddition requires only a slightly higher Gibbs activation barrier (26.0 kcal/mol), consistent with the concomitant formation of phosphinooxiranes **57** and phosphorylalkenes **58**.

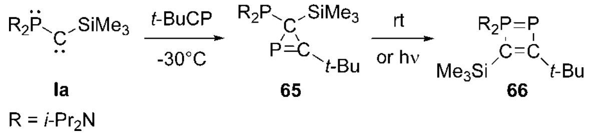
The asymmetric version of these epoxidation reactions, involving the enantiopure aldehydes **59a**,**b**, has recently been studied (Scheme 51).[95] Excellent π-facial diastereoselection of the aldehydes, combined with the complete diastereoselectivity in favor of the *trans*-epoxidation, afforded the oxiranes **60a**,**b** as single diastereomers.

To date, no epoxidation reaction between acyclic aminocarbenes and carbonyl compounds has been described,

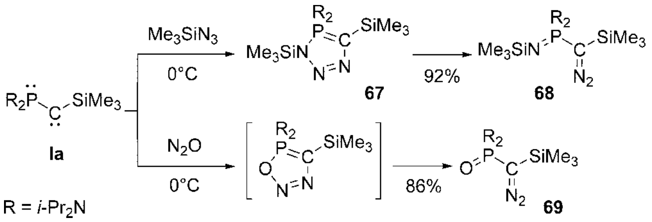
Scheme 53



Scheme 54



Scheme 55



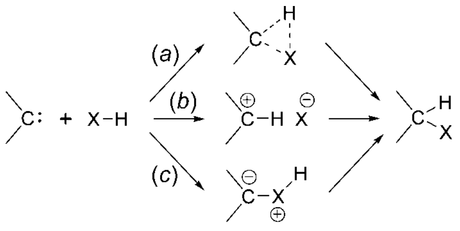
although *N*-heterocyclic carbenes proved to be very efficient catalysts for the benzoin condensation and related reactions.[6]

3.1.2.3. [1 + 2]- and [2 + 2]-Cycloaddition Reactions with Nitriles and Phosphaalkynes. The propensity of phosphinosilylcarbenes **I** to participate in cycloaddition reactions has been further extended to nitriles[96] and phosphaalkynes. The phosphinosilylcarbene **If** reacts with benzonitrile at room temperature to give the phosphino 2*H*-azirine **61** (Scheme 52). This is the first and so far only example of azirine formation by [1 + 2]-cycloaddition. The presence of a phosphino group on the 2*H*-azirine skeleton induced a rich chemical reactivity, including ring expansion into the 1,2-λ^5-azaphosphete **62** upon irradiation or addition of a catalytic amount of a transition metal complex.[97]

Notably, carbene **If** behaves very differently toward the electron-rich dimethyl cyanamide, leading to the novel 1,2-dihydro-1,2-azaphosphete **63** (Scheme 53).[77] This reaction likely proceeds by a nucleophilic attack of the amino group at the carbene center (see section 3.3 for the electrophilic behavior of phosphinocarbenes). The ensuing nitrogen ylide would then undergo a Stevens rearrangement with migration of the cyano group, followed by 1,3-shifts of the $SiMe_3$ (C → N) and N*c*-Hex$_2$ (P → C) groups. Electrocyclization of the heterobutadiene **64** would finally afford the 1,2-dihydro-1,2-azaphosphete **63**.

In addition, the thermal conversion of the cyclic carbodiphosphorane **29** into the 1,2-azaphosphete **30** was proposed to result from a [3 + 2]-retrocycloaddition/[2 + 2]-cycloaddition sequence (see Scheme 34, section 3.1.1.2.[78] The putative diphosphinocarbene intermediate **31** was trapped chemically, and DFT calculations supported the ability of a model carbene **31*** (featuring Me instead of *i*-Pr groups at the phosphorus atoms) to undergo [3 + 2]- as well as direct [2 + 2]-cycloaddition with benzonitrile. The [3 + 2]-cycloaddition leading to the carbodiphosphorane is favored kinetically ($\Delta E^{\ddagger} = 9.6$ versus 30.4 kcal/mol), but the [2 + 2] cycloaddition leading to the 1,2-azaphosphete is favored thermodynamically ($\Delta E = -38.7$ versus -15.5 kcal/mol).

Scheme 56



The phosphinosilylcarbene **Ia** also reacts readily with *tert*-butyl phosphaalkyne at −30 °C, affording the phosphino 2*H*-phosphirene **65**,[98] which then cleanly rearranges into the $1\lambda^5,2\lambda^3$-diphosphete **66** upon warming or irradiation (Scheme 54).[99]

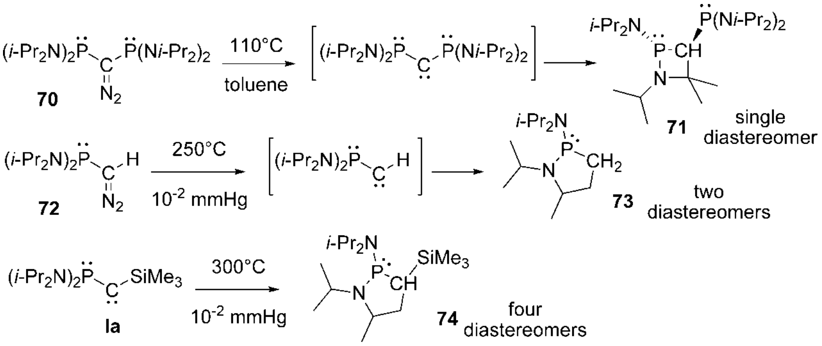
3.1.2.4. [3 + 2]-Cycloaddition Reactions. [3 + 2]-Cycloaddition reactions across the PC bond of the phosphinosilylcarbene **Ia** have been observed with trimethylsilyl azide and nitrous oxide (Scheme 55). The diazo compounds **68** and **69** were isolated in high yields, and the initially formed [3 + 2]-cycloadduct **67** was detected spectroscopically at 4 °C.[2,75b,100]

3.1.3. Insertion Reactions

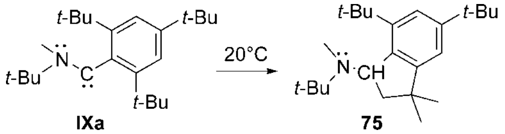
In addition to cyclopropanation, insertion into X−H bonds (X = C as well as heteroelements) are the most characteristic reactions of carbenes. Concerted as well as stepwise mechanisms are conceivable with singlet carbenes:[101] (a) direct, three-center insertion, (b) carbene protonation followed by rapid collapse of the resulting ion pair, and (c) ylide formation upon nucleophilic addition to the carbene (X = O, S, N) followed by X → C proton shift (Scheme 56). The favored route strongly depends on both the polarity of the X−H bond and the philicity of the carbene. To date, no detailed mechanistic investigation has been performed experimentally with stabilized acyclic singlet carbenes, but DFT calculations have supported concerted, asynchronous processes at the borderline between mechanisms (a) and (b) for the insertions of monoaminocarbenes into C−H, H−H, and N−H bonds.

3.1.3.1. C−H Insertion Reactions. *Carbenes Stabilized by a Phosphino Group.* Intramolecular C−H insertion reactions were observed from transient diphosphino- and phosphinohydrogenocarbenes generated by thermolysis of the corresponding α-(phosphino)diazo derivatives at high temperatures (Scheme 57). After two days in refluxing toluene, the bisphosphino derivative **70** undergoes selective C−H insertion into the methine group of the diisopropylamino substituent at phosphorus. The azaphosphetane **71** is obtained as a single diastereomer in 92% yield.[102] In contrast, the monophosphino compound **72** regioselectively inserts at 250 °C under vacuum into one C−H bond of the methyl groups, affording the azaphospholidine **73** (60% yield) as a 70/30 mixture of two diastereomers.[2] A similar reaction was observed for the stable phosphinosilylcarbene **Ia**. Upon

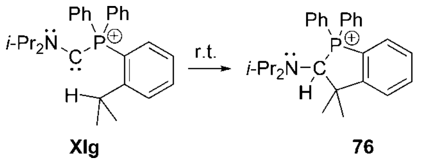
Scheme 57



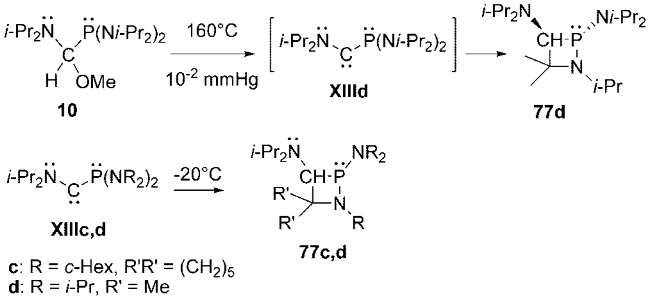
Scheme 58



Scheme 59



Scheme 60



pyrolysis at 300 °C under vacuum, the five-membered heterocycle **74** was obtained in 90% yield as a mixture of four diastereomers.[2,100] The total and different regioselectivity observed in these C−H insertion reactions is surprising and may result from subtle stereoelectronic effects and/or alternative mechanistic pathways. In this respect, the possible participation of excited states of the phosphinocarbenes has been recognized, especially when forcing experimental conditions are used.[100]

Carbenes Stabilized by an Amino Group. Because of their high-lying vacant orbital, diaminocarbenes **III** are not prone to undergo C−H insertion reactions. With *N*-heterocyclic carbenes, no intramolecular reaction has been observed so far, but a few intermolecular examples involving C_{sp^3}−H as well as C_{sp}−H bonds have been reported.[103] In contrast, persistent and transient monoaminocarbenes have been shown over the past few years to readily rearrange via intramolecular insertion into C_{sp^3}−H or C_{sp^2}−H bonds.

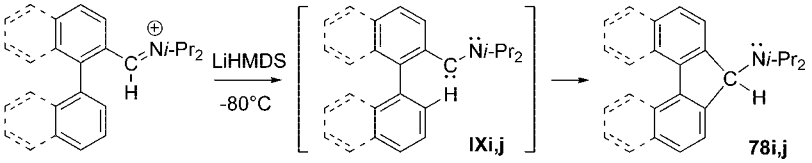
The aminoarylcarbene **IXa**, stable for days in solution at −50 °C, isomerizes within a few hours at room temperature via insertion of the carbene center into one C−H bond of the *ortho*-*tert*-butyl groups (see section 2.4).[52] The formation of the aminoindane **75** in mild conditions substantiates the less-perturbed character of aminoarylcarbenes **IX** versus diaminocarbenes **III** (Scheme 58).

The aminophosphoniocarbene **XIg** exhibits a similar behavior. Deprotonation of the corresponding phosphonio-substituted aldiminium salt with sodium *tert*-butoxide with in situ monitoring allowed the characterization of **XIg** by NMR spectroscopy at −40 °C. Upon warming, the cyclic phosphonium salt **76** was isolated in 82% yield after insertion of the carbene center into the methine group of the *ortho*-*i*-Pr substituent (Scheme 59).[57]

Intramolecular C−H insertion reactions have also been reported for aminophosphinocarbenes. Pyrolysis of the aminal **10** at 160 °C under vacuum induced α-elimination of methanol and afforded the azaphosphetane **77d** in 85% yield (Scheme 60).[64] The complete regio- and stereoselectivities of this reaction are reminiscent to that observed for the formation of **71** upon thermolysis of the α-bis(phosphino)diazo derivative **70**. Notably, the aminophosphinocarbenes **XIIIc**,**d** could be characterized spectroscopically at low temperature when generated by deprotonation of the corresponding iminium salts (see section 2.6). Upon warming, both carbenes undergo clean C−H insertion reactions into the methine group of the *i*-Pr and *c*-Hex substituents at phosphorus, leading to the corresponding azaphosphetanes **77c**,**d**.[61]

Recently, the first examples of C_{sp^2}-H insertion reactions were reported from the biphenyl and binaphthyl aminocarbenes **IXi**,**j**. In a marked contrast with their methoxylated analogues **IXf**,**g** (see Table 7, section 2.4), carbenes **IXi**,**j** were found to exist as transient species, which spontaneously and quantitatively isomerize into the corresponding aminofluorenes **78i**,**j** (Scheme 61).[56] According to DFT calculations,

Scheme 61



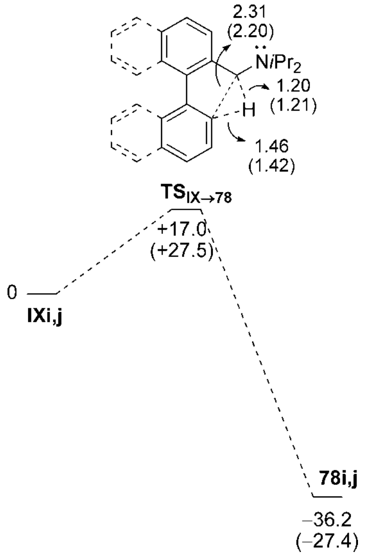
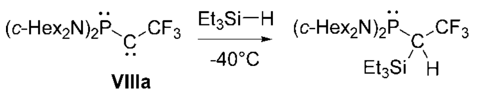
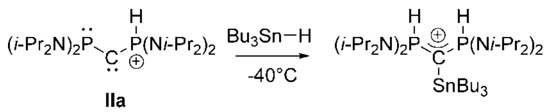


Figure 21. Energy profiles computed at the BP3LYP/6-31G** level (free enthalpies *G* at 25 °C and 1 atm including ZPE correction in kcal/mol, distances in Å) for the rearrangement **IX** → **78** (values in parentheses are associated with **IXj** → **78j**).

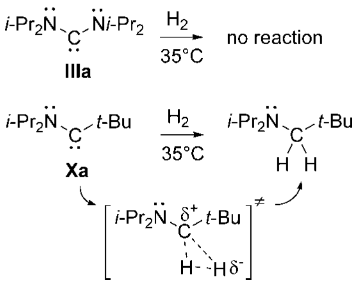
Scheme 62



Scheme 63



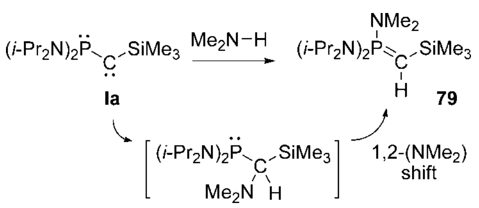
Scheme 64



the insertion of the carbene center into the proximal aromatic C−H bond results from a low-energy concerted but strongly asynchronous process, which is dominated by $C_{arom} \rightarrow C_{carbene}$ proton transfer (Figure 21). With *N*-heterocyclic carbenes, only the reverse reaction, namely, α-elimination of $H-C_6F_5$, has been evidenced upon thermolysis of bisaminals.[104]

3.1.3.2. Si−H and Sn−H Insertion Reactions. The phosphinotrifluoromethylcarbene **VIIIa**, persistent in solution up to −30 °C, does not undergo intramolecular C−H insertion reactions upon warming. Instead, it dimerizes or rearranges via 1,3-F shift (see sections 3.1.1.1 and 3.1.4.2). However, it readily reacts with triethylsilane at −40 °C (Scheme 62).[47] This intermolecular Si−H insertion reaction parallels those known for related transient trifluoromethylcarbenes.[105]

Scheme 65



Similarly, the phosphinophosphoniocarbene **IIa** reacts at −40 °C with tributyltin hydride.[23] The spectroscopic data support a 1,2- rather than a 1,1-insertion of the carbene center into the Sn−H bond (Scheme 63).

3.1.3.3. H−H Insertion Reactions. The insertion of aminoalkylcarbenes (both acyclic and cyclic) into dihydrogen, as recently reported by the Bertrand group, represents a major breakthrough in this field.[7a] It is a very rare example of metal-free activation of dihydrogen[106] and points out some similarities between transition metals and singlet carbenes. Experimentally, bubbling dihydrogen into a solution of the amino-*tert*-butyl-aminocarbene **Xa** cleanly afforded the corresponding amine (Scheme 64). A similar reaction was observed with cyclic aminoalkylcarbenes, but the bis(diisopropylamino)carbene **IIIa** as well as *N*-heterocyclic carbenes remain inert under these conditions. This striking difference is likely a result of the higher-energy HOMO and smaller singlet−triplet energy gap in mono- versus diaminocarbenes. Calculations on model systems suggest that the fixation of H_2 is thermodynamically and kinetically favored for monoamino versus diaminocarbenes ($\Delta E = -51$ and $\Delta E^{\ddagger} = 22$ kcal/mol for $H_2N-\ddot{C}-CH_3$ versus $\Delta E = -29$ and $\Delta E^{\ddagger} = 35$ kcal/mol for $H_2N-\ddot{C}-NH_2$). Moreover, the formal oxidative addition of H_2 to the carbene center was predicted to occur via a concerted but strongly asynchronous process. Accordingly, the carbene would primarily act as a base toward H_2, creating a pseudohydride that would attack back the partially positive charged carbene center.

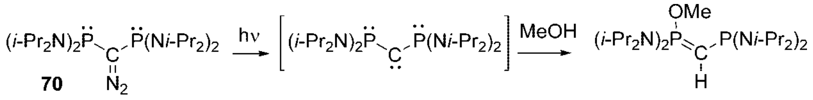
3.1.3.4. O−H and N−H Insertion Reactions. Besides weakly polarized C−H, Si−H, and Sn−H bonds and nonpolarized H−H bond, a few insertion reactions of acyclic carbenes into strongly polarized O−H and N−H bonds have been reported.

Carbenes Stabilized by a Phosphino Group. Accordingly, the phosphinosilylcarbene **Ia** readily reacts with dimethylamine to afford phosphorus ylide **79** (Scheme 65).[2] From a mechanistic viewpoint, the formation of **79** may result from (i) carbene protonation followed by recombination of the ensuing ion pair (pathway b in Scheme 56), (ii) direct 1,2-addition of the N−H bond across the PC bond of **Ia**, or (iii) insertion of the carbene into the N−H bond followed by a classical C → P 1,2-shift of the dimethylamino group.[107]

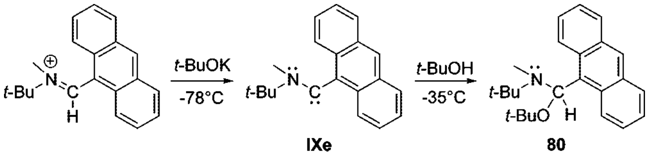
A similar process has been observed for methanol and a transient diphosphinocarbene (Scheme 66).[108]

Carbenes Stabilized by an Amino Group. The aminoanthrylcarbene **IXe**, which can be generated by deprotonation of the corresponding aldiminium salt with potassium *tert*-butoxide at −78 °C, inserts into the O−H bond of the liberated *tert*-butyl alcohol within a few minutes at −35 °C, leading quantitatively to the aminal **80** (Scheme 67).[53] This O−H insertion reaction substantiates the lower steric protection provided by the anthryl group compared to the 2,4,6-tri-*tert*-butylphenyl and 2,6-bis(trifluoromethyl)phenyl substituents, while the corresponding aminoarylcarbenes **IXa−d** (Table 7) are inert toward *tert*-butyl alcohol.[52]

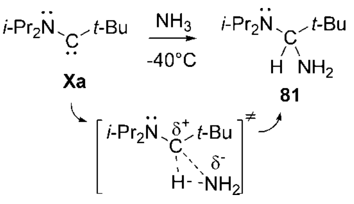
Scheme 66



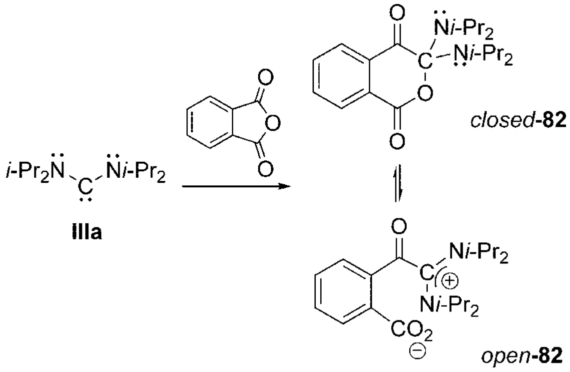
Scheme 67



Scheme 68



Scheme 69

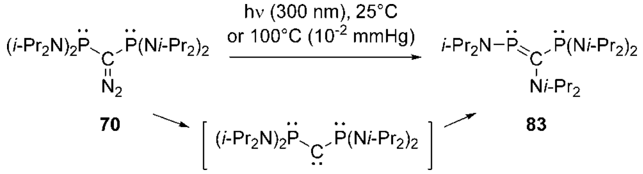


Stimulated by the results observed for dihydrogen, Bertrand et al. investigated the propensity of aminoalkylcarbenes to activate ammonia, a particularly difficult task for transition metals, which tend to form Werner-type amine-complexes instead. Accordingly, the amino-*tert*-butylcarbene **Xa** (as well as its cyclic analogue) was found to rapidly react with liquid NH_3 at −40 °C, cleanly affording the insertion product **81** (Scheme 68).[7a] DFT calculations predicted a slightly less exothermic reaction with NH_3 compared to H_2 ($\Delta E = -39$ kcal/mol for $H_2N{-}\ddot{C}{-}CH_3$) but a similar activation barrier ($\Delta E^{\ddagger} = 21$ kcal/mol for $H_2N{-}\ddot{C}{-}CH_3$). Similar to H_2, the reaction of the aminoalkylcarbene **Xa** with NH_3 is proposed to proceed via a concerted, strongly asynchronous process dominated by nucleophilic activation.[7a]

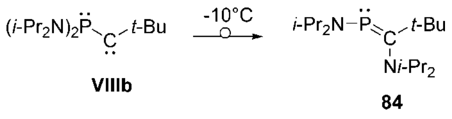
3.1.3.5. Miscellaneous Insertion Reactions. Phosphinosilylcarbenes **I** readily react with group 14 and 15 electrophiles to yield 1,2-addition products. These transformations may involve an insertion reaction followed by a C → P 1,2-shift, but they are likely governed by the nucleophilic character of the carbene and will, therefore, be discussed in sections 3.2.2 and 3.2.4.[2,84,109]

Formal insertion into a C−O bond has recently been evidenced by a reaction involving the bis(diisopropylamino)carbene **IIIa** and phthalic anhydride. Strikingly, the resulting isochromane derivative **82** was obtained in both closed neutral and opened zwitterionic forms (Scheme 69). These two structural isomers coexist in the solid state and rapidly equilibrate in solution.[110] The formation of the isochromane derivative clearly results from the nucleophilic attack of the carbene at one of the C=O groups of the anhydride. This process is related to the nucleophilic activation of lactones with *N*-heterocyclic carbenes, for which an analogous product of C−O insertion into *β*-butyrolactone product has recently been isolated.[112]

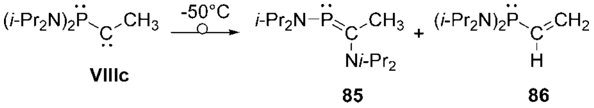
Scheme 70



Scheme 71



Scheme 72



3.1.4. Migration Reactions

Migration reactions, and especially 1,2-shifts leading to alkenes, are well-established reactions for transient singlet carbenes.[113] Both 1,2- and 1,3-migration reactions have been observed with stable/persistent noncyclic carbenes, and unusual mechanistic pathways have been evidenced, including an excited-state reaction and a radical process.

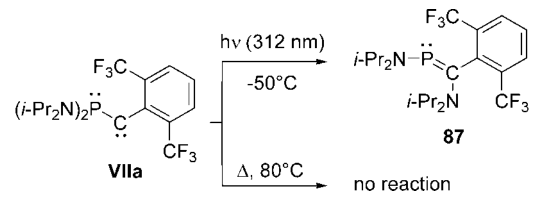
3.1.4.1. 1,2-Shifts. Irradiation (300 nm) or thermolysis (100 °C, 10^{-2} mmHg) of the α-bis(phosphino)diazo derivative **70** directly affords the *C*-phosphino phosphaalkene **83** (Scheme 70). Since the putative diphosphinocarbene could not be detected spectroscopically, it is not clear if the P → C 1,2-shift of the diisopropylamino group occurs concomitantly or after the dinitrogen extrusion.[108]

The first unambiguous evidence for such a 1,2-migration was observed with the phosphino-*tert*-butylcarbene **VIIIb**.[50] Indeed, this alkylcarbene was found to rearrange within a few minutes above −10 °C into the corresponding phosphaalkene **84** (Scheme 71).

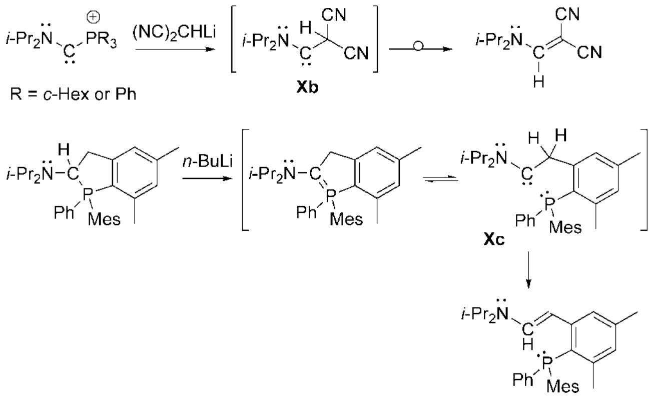
The related phosphinomethylcarbene **VIIIc** is even more fleeting and rapidly isomerizes at −50 °C to a 1:1.6 mixture of the phosphaalkene **85** and phosphinoalkene **86** as the result of competitive 1,2-migration of an amino group (P → C) and a hydrogen atom (C → C), respectively (Scheme 72).

In contrast to these thermal isomerizations, an excited-state 1,2-shift has been observed. The phosphinoarylcarbene **VIIa** is stable after prolonged heating at 80 °C in solution but readily rearranges into the corresponding phosphaalkene **87** from photolysis at 312 nm at −50 °C (Scheme 73).[49] This P → C 1,2-migration is the first, and so far unique, example of an excited-state reaction from a stable carbene.[114]

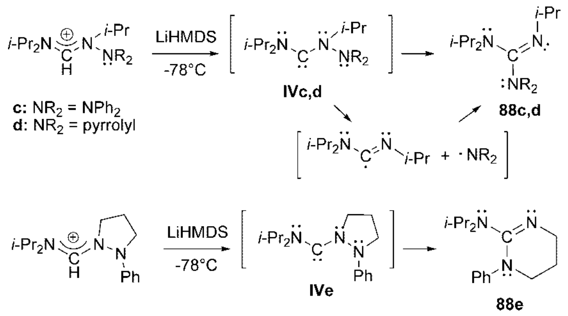
Scheme 73



Scheme 74



Scheme 75

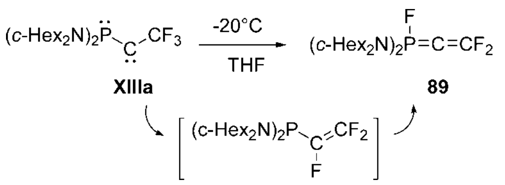


Note that C → C 1,2-hydrogen shifts leading to enamines have also been reported from the transient aminoalkylcarbenes **Xb**[34] and **Xc**,[57] which are generated by nucleophilic substitution at the carbene center (see section 3.4.4) and dissociation of *C*-amino phosphorus ylide, respectively (Scheme 74).

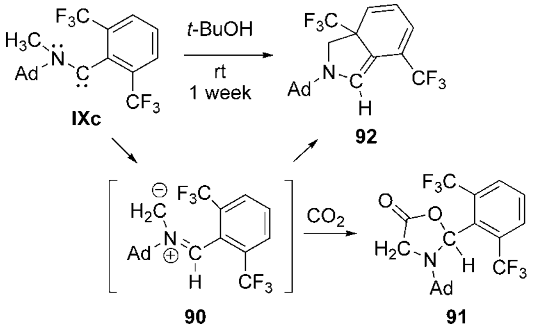
In addition, the transient aminohydrazinocarbenes **IVc**−**e** were found to readily rearrange into the corresponding guanidines **88c**−**e** via N → C 1,2-migration of an amino group (Scheme 75).[38] The intramolecular nature of the rearrangement is supported by the selective formation of guanidine **88e** upon deprotonation of the corresponding formamidinium salt.[115] According to DFT calculations, these reactions likely proceed via a dissociative radical pathway involving homolytic cleavage of the weak N−N bond (see section 3.4.1). Note also that the isomerization of aminohydrazinocarbenes into guanidines parallels to some extent that of the bis(amino)phosphinocarbenes $(R_2N)_2P{-}\ddot{C}{-}R'$ into *C*-amino phosphaalkenes $R_2NP{=}C(NR_2)R'$.

3.1.4.2. 1,3-Shifts. The thermal rearrangement of the persistent phosphinotrifluoromethylcarbene **VIIIa** in tetrahydrofuran at −20 °C cleanly yields cumulene **89** after C → P migration of a fluorine atom (Scheme 76). This formal 1,3-F shift presumably results from a sequence of two successive C → C and C → P 1,2-F migrations.[47]

Scheme 76



Scheme 77



Finally, a 1,3-hydrogen shift was observed from the aminoarylcarbene **IXc**. In the presence of protic reagents such as *tert*-butanol, carbene **IXc** was found to slowly rearrange into the indenyl derivative **92**, formally resulting from the isomerization of **IXc** into the corresponding azomethine ylide **90**, followed by electrocyclization (Scheme 77).[116] The transient azomethine ylide **90** could be trapped with CO_2, affording the adduct **91** with complete regioselectivity. On the basis of labeling experiments and DFT calculations, the overall 1,3-H shift from **IXc** to **90** was proposed to occur by protonation of the carbene followed by deprotonation of the *N*-methyl group of the ensuing iminium salt.

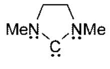
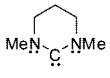
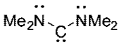
3.2. Basic/Nucleophilic Behavior

3.2.1. Protonation of Carbenes

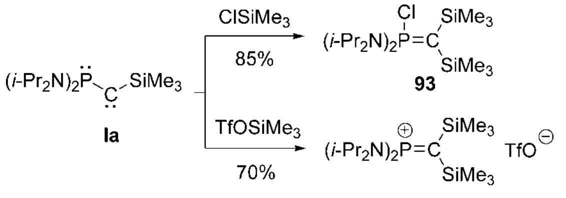
The acid−base chemistry of phosphino- and aminocarbenes has been the subject of continued interest. The pK_a values for the protonation of a few stable diaminocarbenes have been determined experimentally,[117] although not for acyclic compounds. For phosphinosilylcarbenes **I**, such experiments can hardly be carried out since the conjugate acids, namely, methylene phosphonium salts,[118] are extremely electrophilic compounds that readily react with the counteranion of the proton source.[119] Theoretical methods were thus preferred, and the precise influence of the carbene structure was examined. Such calculations typically concern proton affinities (PAs) in the gas phase and pK_a in dimethyl sulfoxide (DMSO) or MeCN, where high-level methods are required to get reliable predictions.

The first estimation of the proton affinity for the parent systems $H_2P{-}\ddot{C}{-}SiH_3$ and imidazol-2-ylidene (243.1 and 257.3 kcal/mol, respectively, at 300 K, at the MP-4 level of theory) was reported by Dixon et al. in 1991.[120] More recent calculations at the B3LYP/6-31G* level of theory estimated a PA of 256.9 kcal/mol at 298 K for the acyclic diaminocarbene $H_2N{-}\ddot{C}{-}NH_2$ **III***. The introduction of methyl groups at the nitrogen atoms led to an increase of the PA (274.9 kcal/mol at 298 K), as expected from stronger inductive and polarizability effects.[40b] Recently, high-level calculations, using the CBS-QB3 model in conjunction with the CPCM solvation methodology, have allowed more accurate estima-

Table 12. Gas-Phase Proton Affinity (PA) and pK_a in DMSO or MeCN Computed for Model Acyclic and Cyclic Diaminocarbenes

carbene	NCN (°)	gas-phase PA (kcal/mol)	pK_a in DMSO	pK_a in MeCN
 **16**	105.9	259.0	22.3	33.6
 **17**	115.9	267.3	27.1	38.4
 **IIIf**	120.0	268.2	27.9	39.1

Scheme 78



94 (X-ray)

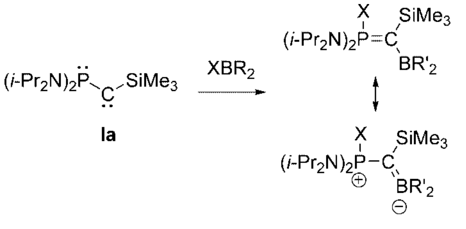
tion of the basicity of acyclic and cyclic diaminocarbenes. The values computed for the gas-phase PAs and pK_a in MeCN and DMSO (Table 12) indicate that the acyclic diaminocarbene $Me_2N-\ddot{C}-NMe_2$ **IIIf** is the most basic carbene. Interestingly, the basicity of diaminocarbenes was found to correlate with the carbene bond angle. Accordingly, the widening of the NCN bond angle from the five-membered ring carbene **16** (105.9°) to the acyclic carbene **IIIf** (120.0°) is accompanied by a noticeable increase in basicity of the carbene. An intermediate basicity was predicted for the six-membered ring carbene **17** (NCN bond angle = 115.9°).[121]

High-level calculations have also been performed recently on phosphinosilylcarbenes **I**.[119] Although CBS-QB3 calculations could only be carried out on model systems, a careful estimation of the "method error" allowed one to reliably conclude that the actual carbene $(i\text{-}Pr_2N)_2P-\ddot{C}-SiMe_3$ **Ia** is slightly more basic than the di-*tert*-butyl-imidazol-2-ylidene both in the gas phase (PA = 273.9 versus 270.4 kcal/mol at 298 K at the B3LYP/6-31G* level) and in DMSO solution (pK_a = 23.0−23.4 versus 22.8). Although the Brönsted basicity of acyclic phosphino- and aminocarbenes remains experimentally unexplored, their Lewis basicity has been demonstrated toward a variety of electrophiles.

3.2.2. Reactions with Group 14 Electrophiles

The nucleophilic character of the phosphinosilylcarbene Ia was evidenced early on upon reaction with silicon electrophiles. With chlorotrimethylsilane, the corresponding *C*-(bis)silylated *P*-chlorophosphonium ylide **93** was obtained in 85% yield (Scheme 78).[2] From a mechanistic viewpoint, the formation of **93** can be explained by (i) direct 1,2-addition of the chlorosilane across the PC bond of **Ia**, (ii) nucleophilic substitution at silicon, followed by the attack of the liberated chloride anion on the electrophilic phosphorus of the methylene phosphonium, or (iii) insertion of the carbene into the Si−Cl bond followed by a classical C → P 1,2-shift of the chlorine atom.

Scheme 79



95: R = Mes, X = F (X-ray)
96: R = X = OMe

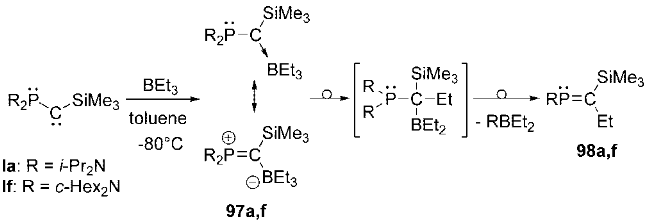
Treatment of **Ia** with trimethylsilyl trifluoromethanesulfonate at room temperature cleanly afforded the expected methylene phosphonium **94**.[122] This compound was the first heavier analogue of the well-known iminium salts,[118] and its preparation nicely illustrates the synthetic interest of stable carbenes for accessing virtually unknown compounds. The ^{31}P and ^{13}C NMR signals for the $(P=C)^+$ fragment of **94** (^{31}P: δ = 131 ppm; ^{13}C: δ = 76 ppm, $^1J_{PC}$ = 88 Hz) are significantly deshielded compared to those associated with the P=C core of the related phosphonium ylide **93** (^{31}P: δ = 72 ppm; ^{13}C: δ = 12 ppm, $^1J_{PC}$ = 151 Hz). In the solid state, no interaction with the trifluoromethane sulfonate was observed, demonstrating the ionic character of **94**. The PC distance [1.620(3) Å] is shorter than in phosphaalkenes (1.64−1.69 Å), although the dihedral angle between the coordination planes of phosphorus and carbon atoms corresponds to a twist of the double bond by as much as 60°! These unusual structural features have been rationalized in terms of the superposition of Coulombic attraction and steric hindrance.[21,123]

3.2.3. Reactions with Group 13 Lewis Acids

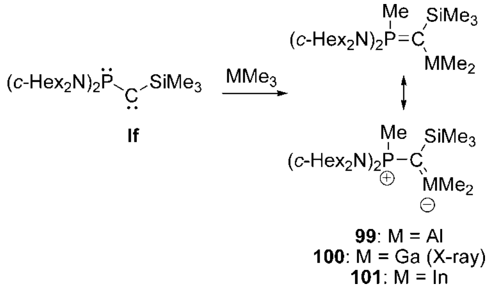
The reactivity of the phosphinosilylcarbenes **Ia**,**f** has been examined toward a variety of group 13 Lewis acids, and different outcomes have been observed depending on the nature of the main group element and of its substitution pattern. With dimesitylfluoroborane or trimethoxyborane, the 1:1 adducts **95** and **96** were obtained via formal 1,2-addition of B−F and B-OMe bonds (Scheme 79).[124] Compound **95** was the first phosphonium ylide stabilized by a group 13 susbtituent to be structurally characterized. Both the carbon and boron atoms are in trigonal planar environments with a dihedral angle of 31.5°. In addition, the CB bond length [1.525(4) Å] is intermediate between those of single (1.58−1.62 Å) and double (mean value of 1.44 Å for $CH_2=BMes_2^-$) bonds. These results suggest that the *C*-borylated phosphonium ylide **95** has a substantial character of *C*-phosphonio borataalkene in the solid state.

From a mechanistic viewpoint, the formation of **95** and **96** may once again result either from direct 1,2-addition across the PC bond of **Ia**, or alternatively from an insertion/1,2-shift sequence. The latter hypothesis is supported by the results obtained with triethylborane (Scheme 80).[15] Starting from **Ia**,**f**, the transient adducts **97a**,**f** could be detected spectroscopically (**97a**: δ ^{31}P = 116 ppm; **97f**: δ ^{31}P = 121 ppm and δ ^{13}C = 54 ppm, $^1J_{CP}$ = 63 Hz). These data are very similar to those observed for the trimethylsilyl adduct **94**, suggesting that these carbene−borane adducts are best described as *C*-borata methylene phosphoniums. The adduct **97a** is stable for only a few minutes at −80 °C, while **97f** is stable for several weeks at −20 °C and for 24 h at rt. They both decompose into the corresponding phosphaalkenes **98a**,**f** via 1,2-migration of an ethyl group from the borate to the

Scheme 80



Scheme 81



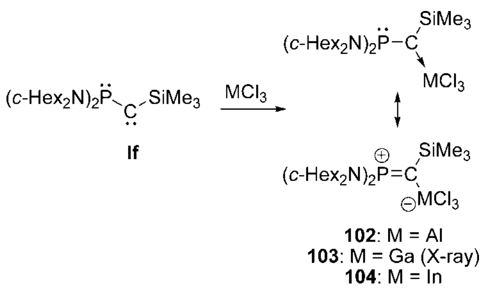
very electrophilic carbon center followed by 1,2-elimination of the aminoborane RBEt$_2$ (R = *i*-Pr$_2$N or *c*-Hex$_2$N).

The phosphinosilylcarbene **If** also readily reacts with AlMe$_3$, GaMe$_3$, and InMe$_3$ in diethyl ether at −78 °C to afford the corresponding 1:1 adducts **99**, **100**, and **101**, respectively (Scheme 81).[125] No intermediates were detected spectroscopically, but the ^{1}H and ^{13}C NMR data suggested that, in each case, formal addition of a Me−M bond across the PC bond of **If** had taken place. This was confirmed crystallographically for the gallium derivative **100**. As for its boron analogue **95**, both the carbon and gallium atoms of **100** are in trigonal planar environments, with a dihedral angle of 36.7°. Along with the relatively short CGa bond [1.935(6) Å], these data suggest noticeable contribution of the zwitterionic canonical form. But the PC bond length [1.658(7) Å] is slightly shorter than in **95** [1.696(2) Å], suggesting a higher contribution of the neutral phosphonium ylide form with gallium than with boron.

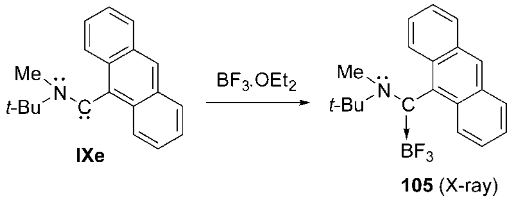
Reactions of **If** with the related trichlorides MCl$_3$ (M = Al, Ga, In) revealed the dramatic influence of the substituent on the reaction outcome. Instead of the 1,2-addition products, the simple carbene−Lewis acid adducts **102**, **103**, and **104** were obtained (Scheme 82). This was deduced from the ^{31}P NMR data. Compounds **102**−**104** display a signal at $\delta \approx 129$ ppm, in the range of **94**, while derivatives **99**−**101** exhibit a signal at $\delta \approx 57$ ppm. The structure of **103** was further confirmed by an X-ray diffraction study, revealing strong similarities with **94**. Both the phosphorus and carbon centers adopt trigonal planar geometries, and the PC bond length is short [1.610(15) Å] despite significant twisting (torsion angle = 34.1°). This suggests that compounds **102**−**104** are best described as zwitterionic methylene phosphoniums.

In contrast with the rich reactivity of phosphinosilylcarbenes **I** toward electrophiles, few data points are available concerning the Lewis basicity of acyclic aminocarbenes. Frenking et al. investigated theoretically the formation of adducts between the parent acyclic diaminocarbene $H_2N{-}\ddot{C}{-}NH_2$ **III*** and EF$_3$/ECl$_3$ (*E* = B, Al, Ga, In).[126] Carbene **III*** was shown to be a much stronger Lewis base than NH$_3$, irrespective of the Lewis acid (the bonding energies computed for $H_2N{-}\ddot{C}{-}NH_2$ exceed those predicted for NH$_3$ by 14−27 kcal/mol). The donor−acceptor bond between the carbene center and the group 13 element has a high degree of ionic character, and the covalent contribution decreases on going from boron to indium.

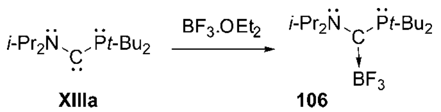
Scheme 82



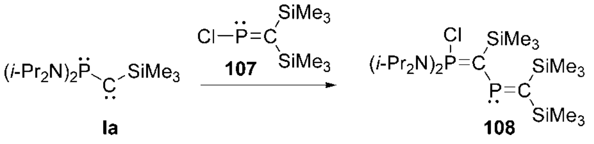
Scheme 83



Scheme 84



Scheme 85



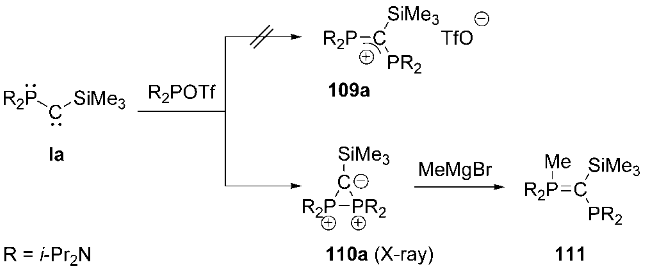
Experimentally, the coordination to BF$_3$ has been used to trap the persistent aminoanthrylcarbene **IXe** (Scheme 83). The corresponding adduct **105** was isolated in 67% yield (mp = 160 °C) and fully characterized including by an X-ray diffraction study. As expected from the presence of a single π-donating amino group, the NC bond of **105** [1.301(2) Å] is slightly shorter than those of the related NHC $\rightarrow$ BF$_3$ adducts (1.34−1.36 Å),[127] while the CB bond distance is slightly longer [1.688(3) Å compared to 1.63−1.67 Å].[53]

Remarkably, treatment of the aminophosphinocarbene **XIIIa** with an equimolar amount of BF$_3$·Et$_2$O in tetrahydrofuran led quantitatively to the carbene adduct **106** (Scheme 84) without any coordination to the adjacent phosphorus center (see section 3.4.3). The selective coordination of the hard carbene center was deduced from the quartet signals ($^1J_{BF}$ = 43 Hz) observed in the ^{11}B (δ = −14.6 ppm) and ^{19}F (δ = −62 ppm) NMR spectra.[61]

3.2.4. Reactions with Group 15 Electrophiles

In an early report,[109] the phosphinosilylcarbene **Ia** was shown to readily react with the *P*-chlorophosphaalkene **107** to give in nearly quantitative yield the *C*-phosphaalkene substituted phosphonium ylide **108** (Scheme 85). As for chlorotrimethylsilane, this reaction may proceed either by direct 1,2 addition of the P−Cl bond across the PC bond of

Scheme 86



Ia or alternatively by insertion of the carbene center in the P−Cl bond followed by C → P 1,2-shift of the chlorine atom.

Notably, the related adducts **38** were also formed, albeit only in small amounts, by reacting the phosphinosilylcarbene **Ic** with the *P*-halogeno iminophosphines **35** (Scheme 38, section 3.1.1.4).[84]

By analogy with that observed for trimethylsilyl trifluoromethanesulfonate, it was envisioned that the reaction of the phosphinosilylcarbene **Ia** with a phosphenium salt would give access to a diphosphinocarbocation **109**, a heavier congener of the well-known formamidinium salts. However, treatment of **Ia** with an equimolar amount of bis(diisopropylamino)phosphenium trifluoromethanesulfonate at 0 °C led, upon warming to room temperature, to the unexpected three-membered ring **110a** (Scheme 86), as deduced from the triplet ^{29}Si NMR signal ($\delta = -10.7$ ppm, $J_{\mathrm{PSi}} = 10$ Hz) and the high-field ^{31}P NMR signal ($\delta = 7.3$ ppm).[128]

The three-membered ring structure of **110a** was definitively proven by X-ray diffraction analysis. The carbon center is planar (sum of the bond angles is 359.8°) and the PP [2.120(2) Å] and PC [1.731(3) and 1.710(3) Å] bond lengths are slightly shorter than would be expected for single bonds. To gain insight into the electronic structure of **110a**, calculations were performed on the model compound **110b**, featuring a SiH_3 group on the carbon center and NH_2 groups on the phosphorus atoms (Figure 22). The optimized geometry of **110b** nicely reproduced the experimental parameters determined for **110a**. Interestingly, the carbon center bears a charge of −1.1 while each phosphorus atom bears a +1.05 charge, which explains the reactivity of MeMgBr at the phosphorus center to afford the phosphonium ylide **111**. Interestingly, calculations showed that the diphosphinocarbocation **109b** (C_{2v} symmetry) is not a minimum on the potential energy surface, while, surprisingly, the diphosphinocarbocation **109′b** with one pyramidalized phosphorus is lower in energy by 5.7 kcal/mol than the cyclic structure **110b**. The apparent discrepancy with the experimental observation of **110a** can be understood by considering that the cyclic structure **110** better accommodates the bulky diisopropylamino substituents than the linear form. The formation of **110b** from **109′b** can be explained by an intramolecular nucleophilic attack of the nucleophilic pyramidalized phosphorus atom of **109′b** on the highly electrophilic planar phosphorus center, which transforms the carbocationic center into a carbanionic center. This result illustrates the great interest of stable carbenes, which allows the synthesis of new structural moieties that are difficult or even impossible to access in the corresponding carbon or nitrogen family. For example, in the nitrogen series, the corresponding cyclic isomer was predicted to be 123.9 kcal/mol (at the B3LYP/6-31 g*) higher in energy than the linear formamidinium salt.

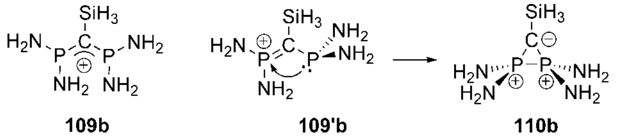
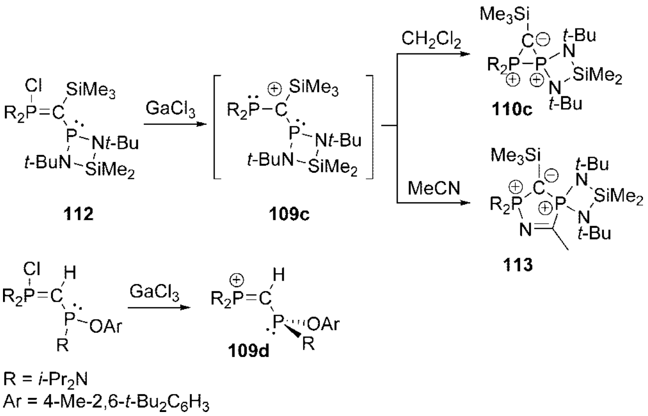


Figure 22. Possible structures of the model diphosphinocarbocation **109(′)b**, including the cyclic form **110b**.

Scheme 87



Such three-membered heterocycles were also found to be accessible by chloride abstraction from *C*-phosphino *P*-chlorophosphonium ylides.[129] Reaction of **112** with $GaCl_3$ directly provided the spiro bicyclic derivative **110c** in dichloromethane, but in acetonitrile, the transient diphosphinocarbocation **109c** was trapped and the [3 + 2]-cycloadduct **113** was obtained regioselectively (Scheme 87). The diphosphinocarbocation **109d** is the only phosphorus analogue of formamidinium salt that has been characterized so far. Although only persistent (stable for weeks at −20 °C in dichloromethane, but rapidly decomposing above 0 °C), the ^{31}P NMR data unambiguously established that it adopts a highly unsymmetrical structure featuring a localized double PC bond (involving the diamino-substituted phosphorus atom) and a single PC bond.

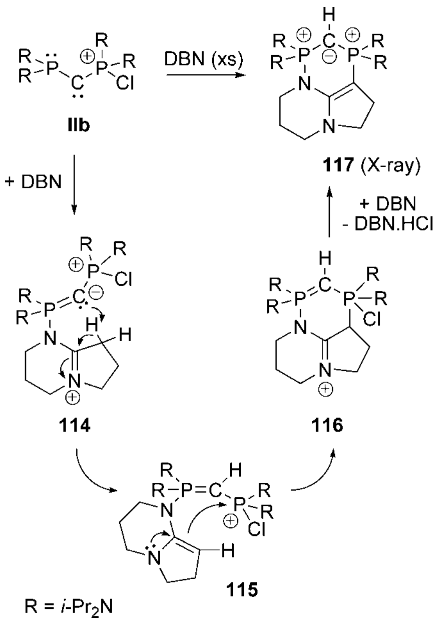
3.3. Electrophilic Behavior

As discussed in section 2, the weaker π-donating ability of phosphino versus amino substituents makes the LUMO of phosphinocarbenes much more accessible in energy than that of diamino- and even monoaminocarbenes. In line with these considerations, electrophilically governed reactivity has only been observed so far with phosphinosilylcarbenes **I** and phosphinophosphoniocarbenes **II**. This includes not only reactions typical of transient carbenes (such as the reaction with phosphines leading to phosphonium ylides)[130] but also original transformations [such as the 1,2-addition of *n*-butyllithium leading to a stable α-(lithiomethylene)phosphorane].

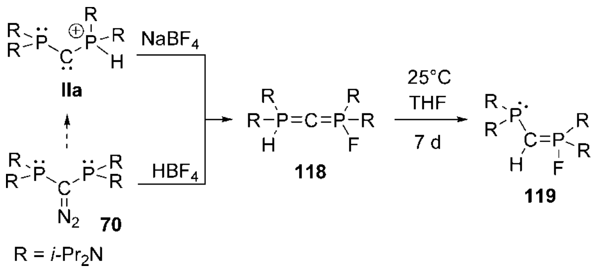
3.3.1. Reaction with 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN)

DBN (1,5-diazabicyclo[4.3.0]non-5-ene), a strong nonionic base frequently used in synthesis,[131] has been shown to also possess nucleophilic character toward main group electrophiles.[132] Its reaction with the phosphinophosphoniocarbene **IIb** provided the first evidence for the electrophilic character of phosphinocarbenes (Scheme 88).[133] The resulting tricyclic compound **117** has been unambiguously characterized by X-ray crystallography. The reaction likely proceeds by

Scheme 88



Scheme 89

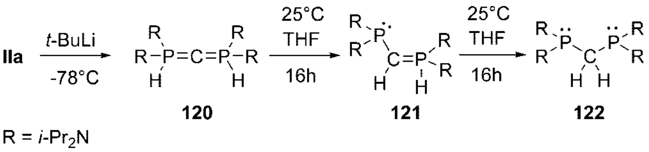


nucleophilic attack of the nitrogen atom of DBN at the σ^3 phosphorus center of **IIb**. The ensuing carbodiphosphorane **114** would then undergo an intramolecular proton transfer leading to the *P*-chlorophosphonium ylide **115**. Nucleophilic attack of the enamine fragment at the σ^4 phosphorus atom would give the tricyclic intermediate **116**, with compound **117** finally being obtained upon elimination of HCl.

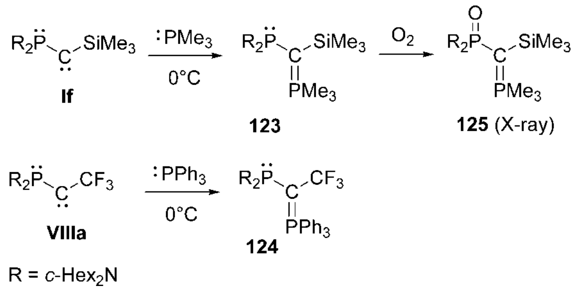
3.3.2. Reaction with Fluorides and Hydrides

Anionic nucleophiles (such as $NaBF_4$ and *t*-BuLi as sources of fluorides and hydrides, respectively) also react with the phosphinophosphoniocarbene **IIa** via addition at the σ^3-phosphorus center.[23] Treatment of **IIa** with an equimolar amount of $NaBF_4$ cleanly afforded the carbodiphosphorane **118**, which can also be directly obtained by reacting the carbene precursor, namely, the α-(bisphosphino)diazomethane **70**, with HBF_4 (Scheme 89). The presence of both P−H and P−F bonds in **118** was unambiguously established from the two diagnostic signals observed in the ^{31}P NMR spectrum (as the result of PP, PF, and PH couplings). Simple phosphonium ylides with a P−H bond are rare, and compound **118** is the first carbodiphosphorane featuring a P−H bond. Although compound **118** is a thermally stable solid (mp = 116 °C), it slowly rearranges in solution via P → C 1,2-H migration, leading to the phosphonium ylide **119**.

Scheme 90



Scheme 91



Using *t*-BuLi instead of $NaBF_4$, the phosphinophosphoniocarbene **IIa** could be converted into the carbodiphosphorane **120** featuring two P−H bonds (Scheme 90).[134] This compound was characterized in solution, and the definitive proof of its structure was given by the peculiar $AA'XX'M_4M'_4$ system observed at $\delta = -8.0$ ppm in the proton-coupled ^{31}P NMR spectrum ($^1J_{PH} = 465$ Hz, $^3J_{PH} = 1$ Hz, $^2J_{PP} = 158$ Hz, and $^3J_{PH(CH)} = 15$ Hz). As observed for **118**, compound **120** slowly rearranges in solution at room temperature via P → C 1,2-H migration reactions, successively affording the *C*-phosphino phosphorus ylide **121** and the diphosphinomethane **122**.

The surprising stability of the phosphorus ylide **121** and carbodiphosphoranes **118**/**120**, featuring respectively one and two P−H bonds, stimulated computational investigations on model compounds (with NH_2 instead of N*i*-Pr₂ groups) at the SCF and MP2 levels of theory.[21] Local minima were indeed found on the potential energy surfaces for both the (H,F) and (H,H) carbodiphosphoranes **118*** and **120***, which were predicted to be about 27 kcal/mol higher in energy than the corresponding phosphorus ylides **119*** and **121***, respectively.

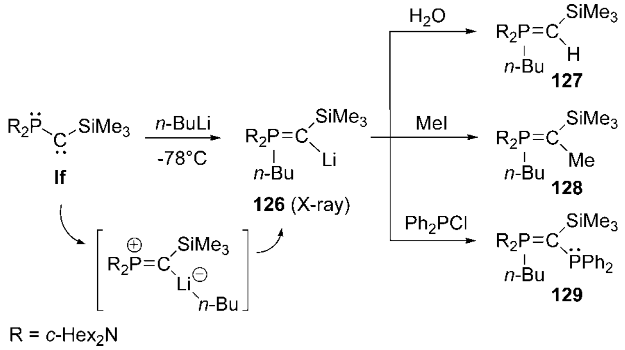
3.3.3. Reactions with Phosphines

Both the phosphinosilylcarbene **If**[135] and the phosphinotrifluoromethylcarbene **VIIIa**[47] react with phosphines, quantitatively affording the corresponding *C*-phosphinophosphonium ylides **123** and **124** (Scheme 91). Because of their extreme sensitivity to oxygen (ylide **123** readily transforms into the phosphine oxide **125**), compounds **123** and **124** have only been characterized spectroscopically. These reactions are the first examples of nucleophilic addition at the carbene center (and not at the σ^3-P) and provide, thereby, a striking evidence for the presence of an available empty orbital at the carbene center of **If** and **VIIIa**.

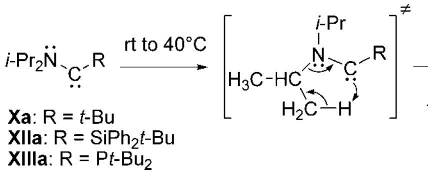
3.3.4. Reactions with n-Butyllithium

The phosphinosilylcarbene **If** reacts with *n*-BuLi at the positively charged phosphorus center to give the α-(lithiomethylene)phosphorane **126** (Scheme 92).[136] Compound **126** is the first stable α-(lithiomethylene)phosphorane.[137] Persistent α-(lithiomethylene)phosphoranes have been classically generated at low temperature by deprotonation of the corresponding phosphonium ylides.[138] The formal 1,2-addition of *n*-BuLi across the PC bond of **If** probably involves first coordination to the lithium atom, enhancing both the electrophilicity of the σ^3-phosphorus center and the

Scheme 92



Scheme 93



nucleophilicity of the *n*-butyl fragment. In the solid state, the structure of **126** is monomeric with two molecules of THF coordinated to the lithium. The geometry around the ylidic carbon is trigonal planar, and both the PC [1.636(11) Å] and CSi [1.775(10) Å compared to 1.87−1.91 Å for $SiCH_3$] bond lengths are very short. Compound **126** is extremely moisture-sensitive and readily hydrolyzes to the corresponding phosphonium ylide **127**. It also easily reacts with electrophiles such as MeI or Ph_2PCl at low temperature to yield the respective phosphonium ylides **128** and **129**, respectively, in near quantitative yields.

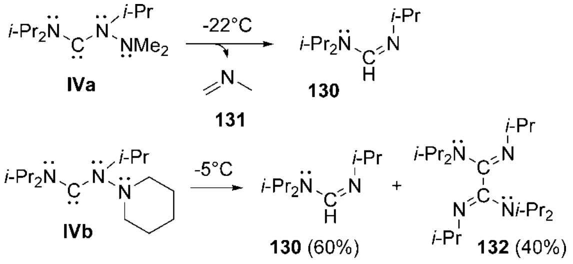
3.4. Unusual Reactivity

Besides typical carbene reactivity and reactions governed by nucleophilic or electrophilic character, stable and persistent carbenes have also been found to undergo unusual reactions, including radical fragmentation reactions, reactions at the periphery of the carbene, and nucleophilic substitution at the carbene center. The increasing variety of available carbenes plays a central role in these recent developments and allows one to further extend the reactivity pattern of carbenes to transformations without equivalent for transient species.

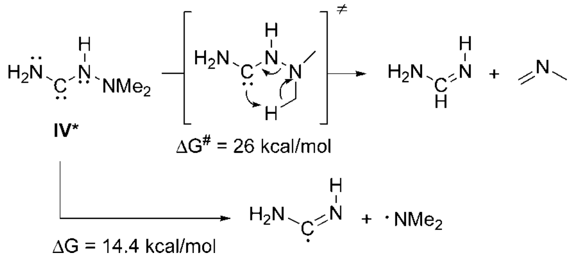
3.4.1. Fragmentation Reactions

The rearrangement of transient carbenes via fragmentation has been much less investigated than their isomerization or dimerization, but both heterolytic and homolytic β-scissions have been documented.[139] As far as stable/persistent carbenes are concerned, fragmentation reactions were first observed with diisopropylaminocarbenes featuring a spectator substituent (*tert*-butyl in **Xa**,[58] *tert*-butyldiphenylsilyl in **XIIa**,[62] and di-*tert*-butylphosphino in **XIIIa**[61]) (Scheme 93). These reactions occur at room temperature (with **Xa** and **XIIa**) or 40 °C (with **XIIIa**), thereby showing the limited stability of the carbenes in solution. The elimination of propene from one of the *i*-Pr substituent at nitrogen with formation of the corresponding imines may arise from a concerted process related to some extent with an intramolecular Hoffmann degradation.

Scheme 94



Scheme 95

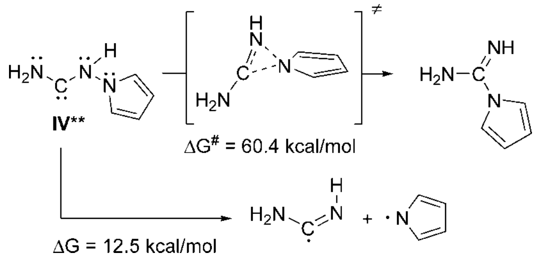


The persistent aminohydrazinocarbenes **IVa**,**b** (see section 2.2.1) were also found to undergo β-fragmentation reactions (Scheme 94).[37] These rearrangements proceed via selective cleavage of the weak NN bond of the hydrazino substituent, without affecting the *i*-Pr_2N group. Whereas the bis(diisopropylamino)carbene **IIIa** is indefinitely stable at room temperature, its related aminohydrazinocarbene **IVa** rapidly fragments at −22 °C, affording triisopropylformamidine **130** along with methylenemethylamine **131** (first-order kinetics, $t_{1/2} \approx 20$ min). Replacement of the dimethylamino group for a piperidinyl moiety significantly increased the stability of the carbene (**IVb**: $t_{1/2} \approx 2.5$ h at −5 °C), with the fragmentation leading, in this case, to a 6:4 mixture of formamidine **130** and oxamidine **132**.

DFT calculations performed on the model aminohydrazinocarbene **IV*** gave more insight into the mechanism of these β-fragmentation reactions.[37] The rearrangement was found to be exothermic by ~33.6 kcal/mol, and a transition state associated with a concerted asynchronous pathway was located 26 kcal/mol higher in energy than the reactive conformer of **IV*** (Scheme 95). However, the formation of the formamidine **130** and oxamidine **132** from **IVb** most likely results from a NN homolytic scission followed by competitive H-abstraction/σ(CC)-coupling of the resulting aminoimidoyl radicals. This alternative pathway was also investigated computationally, and the radical fragmentation of **IV*** was indeed found to be more favorable, requiring only 14.4 kcal/mol.

Notably, the homolytic β-scission of aminohydrazinocarbenes was also found to be responsible for the rearrangement of the transient species **IVc**−**e** via 1,2-migrations (see Scheme 75, section 3.1.4.1).[38] 1,2-Migration reactions have only been scarcely observed with stable or persistent carbenes, and especially for aminocarbenes for which activation barriers of ~40 kcal/mol have been predicted theoretically. Calculations carried out on the model aminohydrazinocarbene **IV**** rule out the concerted pathway that requires as much as 60.4 kcal/mol but strongly support the dissociative radical mechanism (the NN homolytic cleavage requiring only 12.5 kcal/mol in this case) (Scheme 96). The intramolecular nature of the rearrangement supported experimentally most probably results from fast recombination of the aminoimidoyl and aminyl radicals in the solvent cage.

Scheme 96



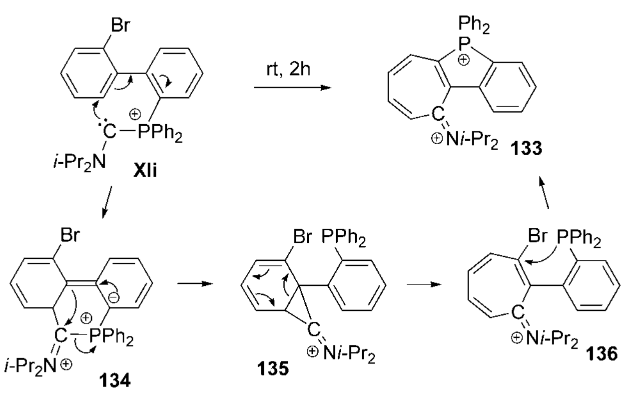
3.4.2. Cyclization Reaction

The aminophosphoniocarbene **XIi** featuring a bromobiphenyl group at phosphorus, prepared by deprotonation of the corresponding dication and spectroscopically characterized at −40 °C (see section 2.4), was found to cleanly rearrange upon warming to room temperature, affording the original tricyclic phospholium derivative **133**.[63] This process involves (i) enlargement of one phenyl ring of the biphenyl backbone, (ii) cleavage of the $C_{carbene}$−P bond, and (iii) creation of a new P−C bond with the phenyl ring not initially bonded to P. From a mechanistic viewpoint, the formation of **133** clearly results from a cascade sequence, probably initiated by the intramolecular nucleophilic attack of the aminocarbene on the biphenyl backbone. Then, the ensuing ylide **134** would react at the highly deficient carbon center to give the norcaradiene-type iminium **135**. Ring enlargement would then afford the aminotropylium salt **136**, and the phospholium derivative **133** would finally be obtained by nucleophilic attack of the phosphine at the brominated *ortho*-position (Scheme 97).

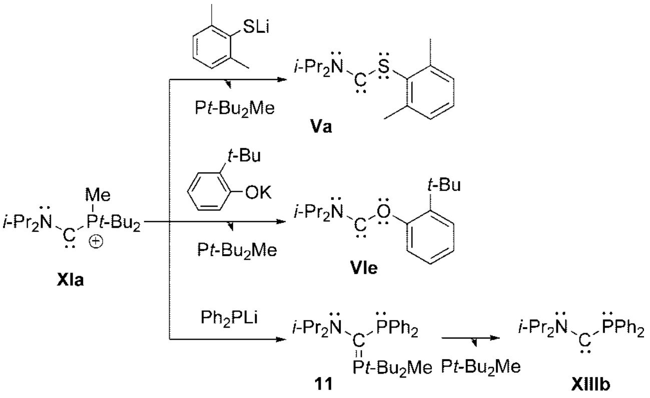
3.4.3. Reactions at the Periphery of the Carbene Center

As discussed in section 2.6, the aminophosphinocarbene **XIIIa** is stabilized by strong π donation from the amino substituent, while the phosphino group remains merely a spectator group. Thus, carbene **XIIIa** combines a hard (aminocarbene) and a soft (phosphine) center, and this hybrid difunctional character is nicely illustrated by the selective formation of the carbene adduct **106** (see Scheme 84, section 3.2.3) and phosphine adduct **XIc** (see Table 8, section 2.5) upon reaction with BF_3 and BH_3, respectively.[61] Treatment of **XIIIa** with elemental sulfur, which is known to react with both aminocarbenes and phosphines, selectively affords the new aminothiophosphoranylcarbene **XIb** (see Table 8, section 2.5). A further example of chemical transformation at the periphery of the carbene center is observed upon alkylation of **XIIIa** with methyl trifluoromethane sulfonate. The aminophosphoniocarbene **XIa** was obtained as the sole product and considered as a promising substrate for nucleophilic substitution at the carbene center (see Figure 16, section 2.5).

Scheme 97



Scheme 98



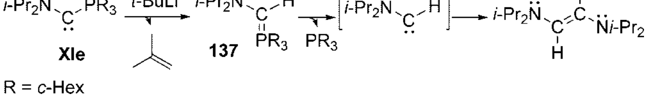
3.4.4. Nucleophilic Substitutions at the Carbene Center

The feasibility of substitution reactions at the carbene center of **XIa** was first demonstrated with lithium 2,6-dimethylthiophenolate and potassium 2-*tert*-butylphenolate, with the corresponding aminothio- and aminooxycarbenes **Va** and **VIe** being obtained quantitatively after displacement of the di-*tert*-butyl(methyl)phosphine (Scheme 98).[46] Upon reaction with lithium diphenylphosphide, the aminophosphoniocarbene **XIa** was converted back to an aminophosphinocarbene, namely, **XIIIb**. Monitoring this reaction by ^{31}P NMR allowed the mechanism of the nucleophilic substitution to be probed. The phosphorus ylide **11** resulting from the addition of the phosphide at the carbene center was characterized at −78 °C, and elimination of the di-*tert*-butyl(methyl)phosphine occurred upon warming up to −20 °C.

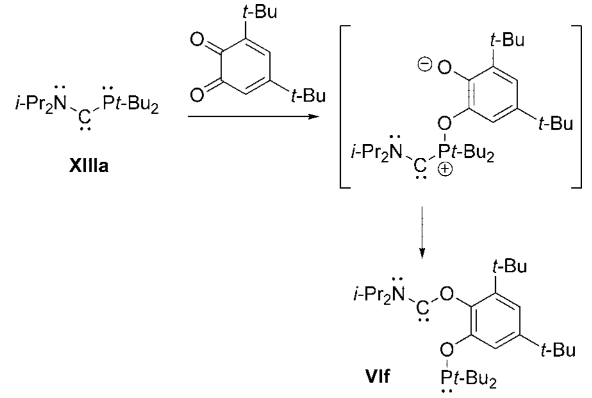
With more basic nucleophiles, carbene **XIa** does not afford the desired carbenes, but only undesirable products resulting from the deprotonation of the methyl group at phosphorus.[140] To circumvent this side reaction, the new carbenes **XId**, **XIe**, and **XI(′)f** featuring the triphenyl-, tricyclohexyl-, and di-*tert*-butyl(phenyl)phosphonio leaving groups, respectively, were prepared (see Table 8, section 2.5).[34] With these aminophosphoniocarbenes, the substitution reaction could be performed with lithium diphenylamide as well as diphenyl-*tert*-butylsilyl lithium. Accordingly, the new stable unsymmetrical diaminocarbene **IIIh**[34] (see Scheme 8, section 2.2.1) and the first persistent aminosilylcarbenes **XII(′)a**[62] (see Figure 17, section 2.5) could be readily obtained.

To further extend the scope of the reaction, the aminophosphoniocarbenes were then reacted with various carbanions.[34] In all cases, the substitution reaction occurred, but the ensuing carbenes were only transient species. With *tert*-butyl lithium (Scheme 99), the primary formed phosphonium ylide **137** was characterized at low temperature and found to rapidly dissociate at −20 °C, affording the corresponding aminohydrogenocarbene that spontaneously dimerized. Similarly, reactions of aryl and alkynyl lithium salts led to the corresponding diaminoalkenes (see Scheme 26, section

Scheme 99



Scheme 100



3.1.1.1). In contrast, with the lithium salt of malononitrile, an enamine was readily obtained, as the result of the substitution reaction at the carbene center followed by 1,2-hydrogen shift (see Scheme 75, section 3.1.4.1).

Starting from the aminophosphinocarbene **XIIIa**, a nucleophilic substitution could also be achieved with the 3,5-di-*tert*-butyl-*ortho*-quinone.[46] This formal insertion of the quinone into the $C_{carbene}P$ bond of **XIIIa** leads to a new aminooxycarbene **VIf** (see section 2.2.2) and most likely proceeds via quaternarization of the phosphorus atom to give a 1,5-zwitterionic adduct, followed by an intramolecular substitution reaction (Scheme 100). The position of the aromatic *tert*-butyl groups in carbene **VIf** has been unambiguously ascertained by an X-ray diffraction study after thiolation of the phosphine and carbene center with elemental sulfur.

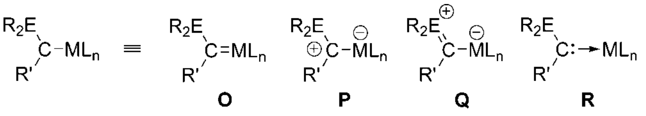
An intramolecular nucleophilic substitution reaction was also observed upon deprotonation of the aminophosphoniocarbene **XIf** (see Scheme 16, section 2.4).[57] Orthometalation of the phenyl group with phenyllithium affords the four-membered phosphorus ylide that spontaneously undergoes ring-opening, leading to the aminoarylcarbene **IXh**. The latter compound combines aminocarbene and phosphine moieties and is related to the well-known 1,2-bis(phosphino)benzene ligands.

3.5. Carbene−Transition Metal Adducts

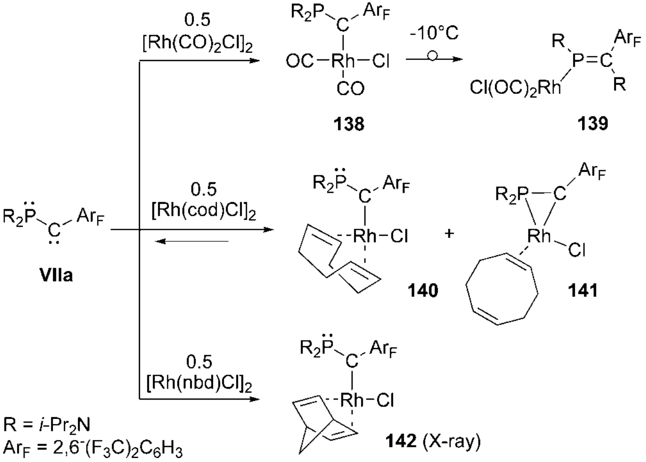
In this section, the preparation and coordination modes of transition metal complexes featuring acyclic phosphino- and aminocarbenes are discussed first. For sake of comparison, not only the direct coordination of stable or persistent carbenes is presented but also the main routes for generating such carbenes within the coordination sphere of metals are presented. The nature and strength of the metal−carbene bond are then discussed on the basis of experimental and computational data. The last part is dedicated to the applications of these carbene complexes in homogeneous catalysis.

For simplicity, the metal−carbene bond will be represented throughout this review as a single line. This formulation does not indicate the nature of the carbene−metal bond and may refer to any structure **O**−**R** or combination thereof (Scheme 101).

Scheme 101



Scheme 102

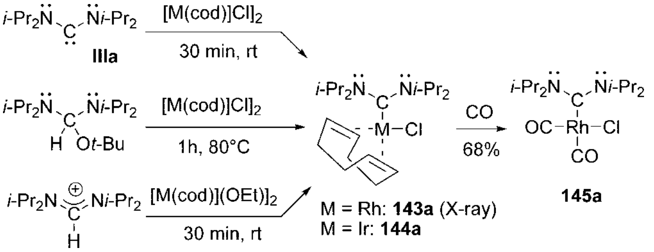


3.5.1. Synthesis and Coordination Modes of Carbene Complexes

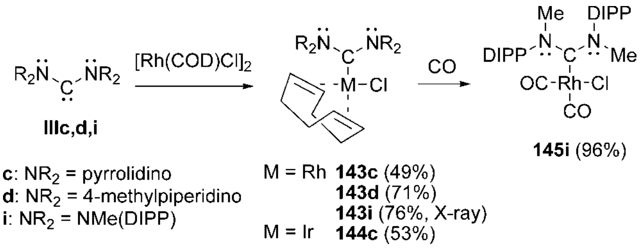
3.5.1.1. Synthesis by Direct Complexation of Stable/Persistent Carbenes. *From Phosphinocarbenes.* Direct complexation of phosphinosilylcarbenes **I** has so far been reported only to main group Lewis acids (see sections 3.2.2−3.2.4), but the related push−pull phosphinoarylcarbene **VIIa** was recently found to form transition metal complexes. Using various rhodium precursors, both η^1 (two-electron donor) and η^2 (four-electron donor) coordination modes have been evidenced (Scheme 102).[141] Treatment of **VIIa** with $[Rh(CO)_2Cl]_2$ at −50 °C quantitatively afforded the corresponding carbene complex **138**, as deduced from the dramatic low-field shift observed by ^{31}P NMR spectroscopy (from $\delta = -22$ ppm for the free carbene to $\delta = 109$ ppm in the complex). Moreover, the ^{13}C NMR chemical shift of the carbene center is shielded by ~35 ppm upon coordination (from $\delta = 146$ ppm in **VIIa** to $\delta = 114$ ppm, $^1J_{CRh} = 29$ Hz, $^1J_{CP} = 112$ Hz in **138**), something that is also typically observed with NHCs. Upon warm up, the phosphinocarbene complex **138** was found to quickly isomerize into the phosphaalkene complex **139** via 1,2-P → C migration of one amino group and 1,2-C → P migration of the metallic fragment (see section 3.1.4.1). Reaction of carbene **VIIa** with the more sterically demanding $[Rh(cod)Cl]_2$ (cod = 1,4-*cyclo*-octadiene) fragment led to a 16:1:2 equilibrium mixture of **VIIa**, **140**, and **141**. The η^1 coordination of the phosphinocarbene in **140** is supported by the similarity of its ^{31}P NMR chemical shift ($\delta = 110$ ppm) with that of **138**. In contrast, the high-field ^{31}P NMR signal ($\delta = -29$ ppm, $J_{PRh} = 138$ Hz) and low-field ^{13}C NMR signal ($\delta = 212$ ppm, $J_{CP} = 31$, $J_{CRh} = 36$ Hz) observed for **141** indicated η^2 coordination. With the somewhat less sterically demanding and less flexible nbd (nbd = 2,5-norbornadiene) coligand, coordination of the carbene **VIIa** proceeds quantitatively and selectively via η^1 coordination, as established from an X-ray diffraction study.

From Diaminocarbenes. Concomitantly to the work of Bertrand and co-workers on phosphinoarylcarbenes, Herrmann et al. reported the first examples of direct complexation of an acyclic diaminocarbene, namely, **IIIa**, using $[Rh(cod)Cl]_2$ and $[Ir(cod)Cl]_2$ as metallic precursors (Scheme 103).[142] The ensuing complexes **143a** and **144a** both adopt η^1 coordination. Thermolysis of the *tert*-butanol adduct of **Ia** in the presence of $[M(cod)Cl]_2$ as well as in situ deprotonation of the formamidinium salt with $[M(cod)(OEt)]_2$

Scheme 103



Scheme 104

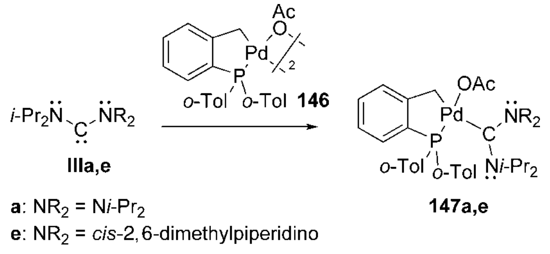


are efficient alternative routes to complexes **143a** and **144a**. The ^{13}C NMR signal for the carbene center is shifted upfield by ~30 ppm upon coordination (δ = 234 ppm, $^1J_{\mathrm{CRh}}$ = 68 Hz for **143a**, δ = 226 ppm for **144a** versus δ = 255 ppm for **IIIa**). Remarkably, although the free acyclic carbenes are significantly more sensitive than their cyclic analogues, complexes **143a** and **144a** are as robust to air and moisture as related NHC complexes. Complex **143a** was characterized structurally, and the related carbonyl complex **145a** was readily prepared by bubbling CO in solution.

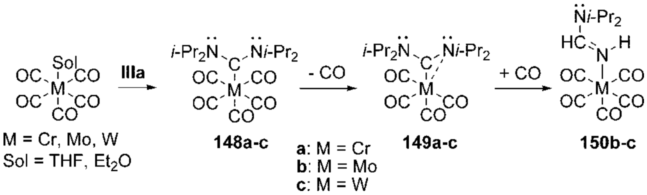
The direct coordination route has also been applied to the stable acyclic diaminocarbenes **IIIc**,**d**,**i** featuring 4-methylpiperidino, pyrrolidino, and NMe(DIPP) (DIPP = 2,6-diisopropylphenyl) substituents, respectively (Scheme 104).[27,28,35] The corresponding Rh(I) and Ir(I) η^1-complexes **143c**,**d**,**i** and **144c**, isolated in moderate-to-good yields (49−76%), all exhibit a characteristic low-field ^{13}C NMR signal for the carbene center (δ = 212−233 ppm). The solid-state structure of **143i** reveals that the *N*-DIPP substituents adopt a pseudo-*trans*-orientation about the diaminocarbene linkage, in agreement with the observation of two different NMe groups by ^{1}H NMR spectroscopy. Treatment of a chloroform solution of **143i** with CO at room temperature afforded the corresponding complex **145i** in near quantitative yield.

The coordination of acyclic diaminocarbenes to palladium has also been investigated using the dimeric acetate-bridged precursor **146** (Scheme 105).[29] The palladacycle **147a** (δ ^{13}C = 226 ppm) derived from the bis(diisopropylamino)carbene **IIIa** was isolated in 77% yield. Subtle steric variations were found to dramatically affect the stability of such complexes. Indeed, **147a** rapidly decomposed into [Pd(P(o-Tol)$_3$)$_2$] and palladium black upon addition of diethyl ether, while the related palladacycle **147e** (δ ^{13}C = 226 ppm) featuring the unsymmetrical (diisopropylamino)(*cis*-2,6-dimethylpiperidino)carbene **IIIe** was found to be perfectly stable under the same conditions.

Scheme 105



Scheme 106

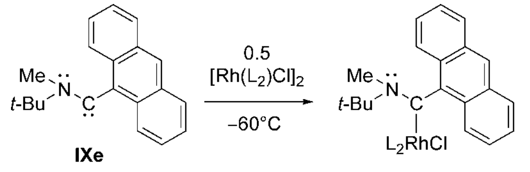


The coordination of the bis(diisopropylamino)carbene **IIIa** to group 6 metals has also been investigated using the photolytically generated [M(CO)$_5$(Sol)] precursors (M = Cr, Mo, W, and Sol = THF, Et$_2$O).[25,143] With molybdenum and tungsten, the pentacarbonyl η^1-complexes **148b** and **148c** could be characterized but proved highly unstable to CO elimination at room temperature, affording the corresponding tetracarbonyl η^2-complexes **149b** and **149c** (Scheme 106). With chromium, the η^2-complex **149a** was directly observed, something consistent with the weakness of the Cr−CO bond computed for the related pentacarbonyl η^1-complex **148a** (21.2 kcal/mol).[144] Under CO atmosphere, the η^2-complexes **149b**,**c** eliminate 2 equiv of propene, leading to complexes **150b**,**c**, whereas the chromium η^2-complex **149a** equilibrates with the corresponding η^1-complex **148a**. This suggests the presence of rather weak NM interactions in the η^2-complexes, something that is further supported by the X-ray diffraction studies carried out on both **149a** and **149c** [NCr = 2.207(1) Å and NW = 2.363(3) Å]. Note also that the η^2-complex **149a** exhibits single broad ^{1}H NMR signals at room temperature for the CH and CH$_3$ groups, while three signals are observed for each group at low temperature, consistent with a frozen structure featuring nonequivalent diisopropylamino groups and hindered rotation about the exocyclic CN bond. The ^{13}C NMR signal observed at 221 ppm for **149c** is not diagnostically different from those reported for related η^1-complexes. Noteworthy, such η^2 coordination was unprecedented for diaminocarbenes and can only be accommodated with flexible acyclic carbenes. This markedly contrasts with *N*-heterocyclic carbenes, whose rigid framework prevents geometrically the simultaneous coordination of the carbene center and adjacent nitrogen atom. In this respect, acyclic diaminocarbenes **III** possess quite unique coordination properties that may open interesting perspectives in catalysis via the hemilabile character of the NM interaction.

From Monoaminocarbenes. The availability of stable monoaminocarbenes such as the aminoarylcarbene **IXe**, aminoalkylcarbene **Xa**, and aminosilylcarbene **XIIa**, featuring a spectator substituent at the carbene center, has enabled the access of a variety of complexes, difficult or impossible to make by other methods. All of them exhibit η^1 coordination, and secondary interactions were eventually found when biaryl groups where used as the spectator substituent.

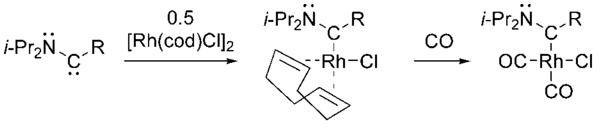
Direct coordination of a monoaminocarbene was first illustrated by the reaction of the persistent aminoanthrylcarbene **IXe** with [Rh(nbd)Cl]$_2$ and [Rh(cod)Cl]$_2$ (Scheme 107).[53] The ensuing complexes **151** and **152** were isolated as thermally stable but moisture-sensitive solids. The ^{13}C NMR signal for the carbene center is shifted upfield by about 50 ppm upon coordination (δ = 264 ppm, $^1J_{\mathrm{CRh}}$ = 45 Hz for **151** versus δ = 315 ppm for **IXe**).

Scheme 107



151: L$_2$ = nbd (56%, X-ray)
152: L$_2$ = cod (23%, X-ray)

Scheme 108



Xa: R = *t*-Bu
XIIa: R = SiPh$_2$*t*-Bu

153 (73%, X-ray)
154 (56%, X-ray)

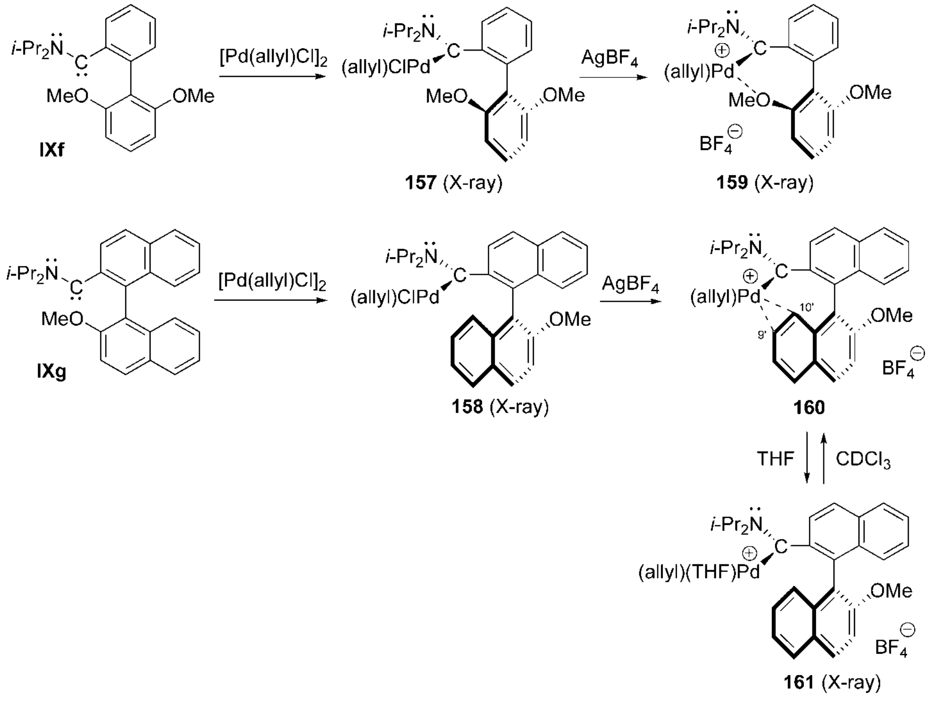
155 (67%)
156 (89%)

Similarly, the stable aminoalkylcarbene **Xa** readily reacts with [Rh(cod)Cl]$_2$ to afford the corresponding complex **153** (δ $^{13}C_{\mathrm{carbene}}$ = 279 ppm, $^{1}J_{\mathrm{CRh}}$ = 40 Hz) (Scheme 108).[58] In marked contrast with the reluctance of the push−pull phosphinosilylcarbenes **I** to give complexes with transition metals, the related push−spectator aminosilylcarbene **XIIa** afforded the air-stable complex **154** (δ = 306 ppm, $^{1}J_{\mathrm{CRh}}$ = 33 Hz) upon reaction with [Rh(cod)Cl]$_2$.[62] The cod ligand of complexes **153** and **154** was easily displaced by CO, leading to the corresponding carbonyl complexes **155** and **156**, respectively.

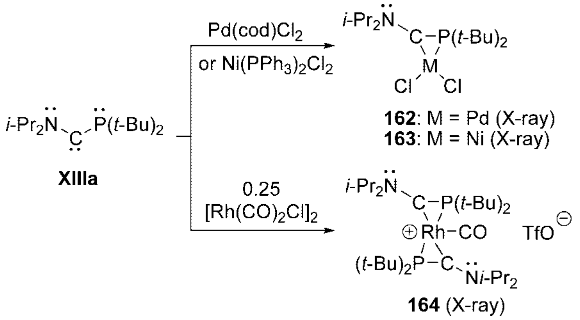
Modulation of the spectator substituent of monoaminocarbenes offered the opportunity to compare the coordination properties of aminobiarylcarbenes with those of the related biarylphosphines, where the remote aryl ring possibly forms secondary interactions with the metal.[145] With this aim, the stable aminobiarylcarbenes **IXf** and **IXg**, related to SPhos and MeO−MOP, respectively,[55] were reacted with [Pd(allyl)Cl]$_2$ to yield the air-stable complexes **157** and **158**, respectively (Scheme 109).[54] The cationization of **157** with AgBF$_4$ afforded complex **159** featuring a strong OPd interaction, in marked contrast with the Pd−arene interactions encountered in related SPhos and MeO−MOP complexes.[145a,b,146] The *anti*-orientation of the methoxy group and Pd center in the aminobinaphthylcarbene complex **158** precludes a similar Pd−O interaction, and cationization resulted here in an unprecedented η^2 coordination of the remote phenyl ring (involving $C_{9'}$ and $C_{10'}$), as shown by NMR spectroscopy. This weak interaction was easily displaced by a molecule of THF, affording the corresponding adduct **161**. Interestingly, dissolution of **161** in chloroform gave back **160** along with a molecule of THF, which further illustrates the hemilabile character of the aminobinaphthylcarbene ligand. As observed for biarylphosphines, the coordination of aminobiarylcarbenes to the [Pd(allyl)$^+$] fragment is thus accompanied by secondary interactions, albeit of different nature as the result of the different geometries of the carbene and phosphorus centers (planar versus pyramidal).

From Aminophosphinocarbenes. As mentioned in sections 3.2.3 and 3.4.3, aminophosphinocarbenes **XIII** are difunctional molecules combining aminocarbene and phosphine moieties that can both participate in the coordination of transition metals. Indeed, the aminophosphinocarbene **XIIIa** was found to behave as a bidentate four-electron donor in all the ensuing Pd(II), Ni(II), and Rh(I) complexes prepared so far.[147] Displacement of the cod and PPh$_3$ ligands from [Pd(cod)Cl$_2$] and [Ni(PPh$_3$)$_2$Cl$_2$] occurs at room temperature, affording the corresponding complexes **162** (60% yield) and **163** (80% yield), respectively (Scheme 110).[147b] The three-membered metallacyclic structure of **162** and **163** was supported spectroscopically by high-field ^{31}P NMR chemical shifts (δ = −44 ppm for **162** and −82 ppm for **163**) and unambiguously confirmed by X-ray diffraction analyses. Carbene **XIIIa** also reacts very cleanly with [Rh(CO)$_2$Cl]$_2$ to yield complex **164** (79% yield).[147a] The presence of two carbene ligands on the rhodium center was indicated by the multiplicity of the ^{13}C NMR signals for the CO group (δ = 201 ppm, dt, $^{1}J_{\mathrm{RhC}}$ = 86, J_{PC} = 16 Hz). The high-field ^{31}P NMR signal (δ = −59 ppm, J_{PRh} = 102 Hz) once again

Scheme 109



Scheme 110

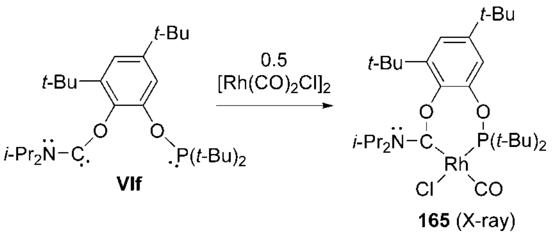


suggested η^2-CP coordination of the carbene, something that was further confirmed crystallographically. In all complexes **162**−**164**, the η^2 coordination proceeds exclusively through the phosphorus atom and not via the nitrogen center, as observed in the η^2-complexes **149a**−**c** deriving from the bis(diisopropylamino)carbene **IIIa**. This likely results from (i) the higher ability of phosphorus to accommodate three-membered ring structures and (ii) the stronger π-donating ability of nitrogen that both favor the η^2-CP over the η^2-CN form.

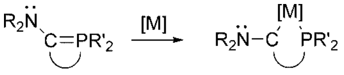
The aminooxycarbene **VIf** featuring a pendant phosphine group was also reacted with [Rh(CO)$_2$Cl]$_2$, affording the corresponding complex **165**, with both the carbene and phosphorus centers coordinated to the metal according to ^{31}P ($\delta = 202$ ppm, $^1J_{\mathrm{PRh}} = 199$ Hz) and ^{13}C ($\delta = 226$ ppm, $^1J_{\mathrm{RhC}} = 47$ Hz) NMR spectroscopy (Scheme 111).[147a] Notably, complex **165** is obtained as a single isomer, with *trans*-orientation of the carbene and CO ligands according to X-ray diffraction analysis.

From C-Amino Phosphonium Ylides. Transition metal complexes featuring heteroditopic bidentate aminocarbene/phosphine ligands have been prepared by coordination of *C*-amino phosphonium ylides.[148] Because of the destabilizing four-electron CN interaction, these ylides are prone to dissociate into aminocarbene and phosphine, which makes them valuable carbene transfer agents via formal insertion of metal fragments into the ylidic CP bond (Scheme 112). Accordingly, treatment of the in situ-generated cyclic ylide **166** with [Pd(cod)Cl$_2$] afforded the corresponding complex **167** (60% yield), with both the aminocarbene and the phosphine coordinated to the metal center (Scheme 113).[148] Similarly, the biphenyl-bridged ylide **168** reacts with [Pd(allyl)Cl]$_2$ and [Rh(cod)Cl]$_2$ to give the corresponding cationic complexes **169** (78% yield) and **170** (86% yield), respectively. This synthetic strategy has also been applied to the acyclic *C*-amino phosphonium ylide **171**, which readily afforded the heteroleptic complex **172** (81% yield) by displacement of the cod ligand around palladium (Scheme 114).[148] As mentioned in section 3.1.1.1, the aminohydrogenocarbene involved in this reaction is only a transient species that spontaneously dimerizes. In that respect, the clean formation of **172** clearly indicates that the PdCl$_2$ fragment inserts into the PC bond of **171** without formation of the free carbene.

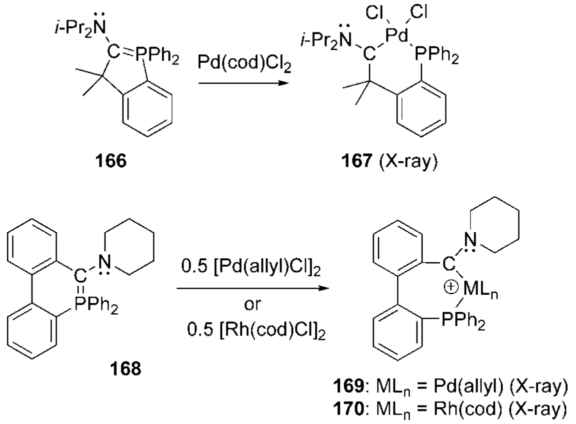
Scheme 111



Scheme 112



Scheme 113

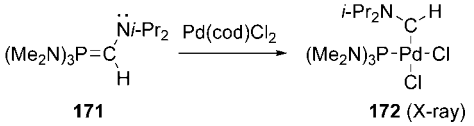


3.5.1.2. Synthesis in the Coordination Sphere of the Metal. Since the generation of phosphinocarbenes in the coordination sphere of transition metals has been recently reviewed comprehensively,[9] only aminocarbenes will be considered in this section. The main routes to aminocarbene complexes including transformation of *C*-bonded ligands and de novo formation of the metal−carbene bond will be summarized.

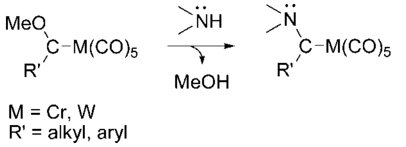
From Nucleophilic Substitution of Alkoxycarbene Complexes. Aminocarbene complexes are typically prepared from alkoxycarbene pentacarbonyl tungsten and chromium complexes by nucleophilic substitution of the alkoxy group with amines (Scheme 115).[149] The reaction proceeds most efficiently with primary and nonhindered secondary amines. The resulting complexes have been extensively used in organic synthesis. Notably, related hydrazinocarbene chromium and tungsten complexes are also accessible using 1,1- and 1,2-disubstituted hydrazines in the presence of LiCl.[150]

From the Coupling of Metallates with Amides, C-Chloro Iminium and Formamidinium Salts. Apart from the nucleophilic exchange of alkoxy groups from alkoxycarbene complexes with amines, aminocarbene chromium complexes are also accessible directly by reaction of Na$_2$Cr(CO)$_5$ or K$_2$Cr(CO)$_5$ with tertiary amides in the presence of an excess

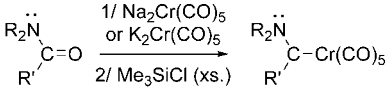
Scheme 114



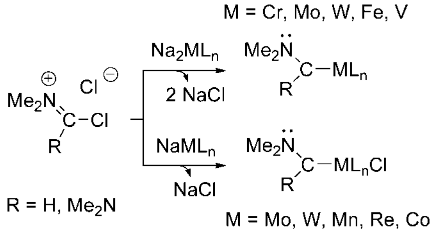
Scheme 115



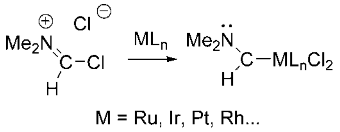
Scheme 116



Scheme 117



Scheme 118



of chlorotrimethylsilane (Scheme 116).[151] This efficient one-pot procedure provides access to a wide range of aminocarbene complexes, starting from alkyl, aryl, and ferrocenyl[152] amides and formamides. Related hydrazinocarbene complexes have also been prepared from hydrazides.[153]

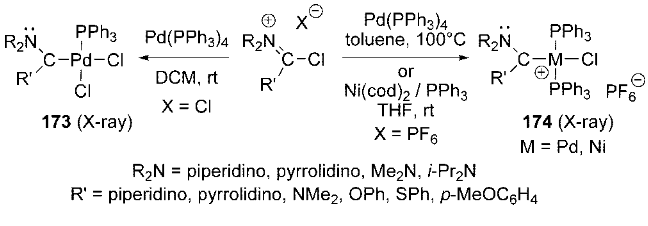
C-Chloro iminium and formamidinium salts also proved efficient sources of amino- and diaminocarbenes upon reaction with di- and monoanionic metallates (Scheme 117).[154] This synthetic route is somewhat limited by the sensitivity of the *C*-chloro iminium salts and usually leads only to modest yields, but it is applicable to a broad range of metals.

From Oxidative Insertion of Metals Into C-Chloro Iminium and Formamidinium Salts. This strategy was first evidenced by Lappert in the 1970s starting from the Vilsmeier's salt [Me_2NCHCl]Cl and various neutral electron-rich metal precursors (Scheme 118).[154,155]

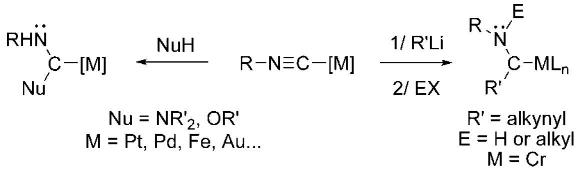
Recently, Fürstner et al. extended the scope of this route to Pd(0) and Ni(0) precursors. By varying the nature of the counteranion (Cl or PF_6), neutral as well as cationic complexes **173** and **174** were obtained (Scheme 119).[156] The catalytic properties of the ensuing Pd(II) and Ni(II) complexes were evaluated in various CC and CN coupling reactions (see section 3.5.3). Besides *N*-heterocyclic carbenes, this reaction was successfully applied to acyclic diaminocarbenes as well as various monoaminocarbenes featuring oxy, thio, or aryl substituents. Given that the involved carbenes are persistent at best as free species, the oxidative insertion of the readily available *C*-chloro formamidinium and iminium precursors is very attractive.

From Nucleophilic Addition to Isocyanide Complexes. Nucleophilic addition to coordinated isocyanides is a general and efficient route to aminocarbene complexes.[157] With protic nucleophiles such as amines and alcohols, diamino- and aminooxycarbene ligands have been readily obtained within the coordination sphere of various metals including Pt,[158] Pd,[159] Fe,[160] and Au[161] (Scheme 120). This synthetic strategy has also been applied to carbon-based nucleophiles, as nicely exemplified by the nucleophilic addition of lithiated alkynes to isocyanide pentacarbonyl chromium complexes, followed by electrophilic trapping via protonation or alkylation.[162]

Scheme 119



Scheme 120



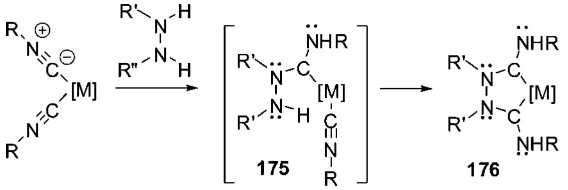
Remarkably, hydrazine derivatives were found to react with *cis*-coordinated Pd and Pt complexes to give bis(acyclic diaminocarbene) complexes **176**, so-called Chugaev-type complexes (Scheme 121).[163] The double addition of the hydrazine is typically promoted by the template effect of the metal, so that the intermediate aminohydrazinocarbene complexes **175** are only rarely observed.[163e,g]

This methodology is not limited to hydrazines and also gives access to related complexes featuring spacers between the two diaminocarbene moieties. In particular, Slaughter et al. recently prepared the chiral Pd complexes **177** in racemic as well as enantiopure forms from C_2 symmetric diamines (Scheme 122).[164]

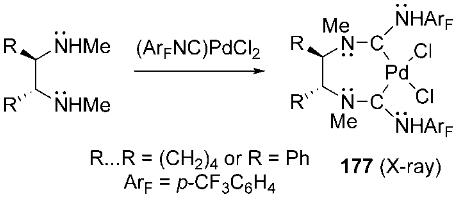
From Double Protonation of Isocyanide Complexes. Kubiak et al. reported recently an original approach to monoaminocarbene Ni(II) complexes. The electron rich Ni(0)−isocyanide complex **178** was first reacted with HBF_4 to give the dicationic complex **179** by protonation of both the carbon and nitrogen atoms of the isocyanide (Scheme 123).[165] Remarkably, this complex was shown to react with alkenes to yield the corresponding *anti*-Markovnikov hydrocarbation products **180**, resulting formally from the 1,2-addition of the $C_{carbene}$−H bond across the C=C double bond of the alkene.[166] This unusual hydrocarbation reaction proceeds with complete regioselectivity and gives access to a variety of new aminoalkylcarbene complexes.

From the Rearrangement of Enamides and Aldimines. The isomerization of unsaturated nitrogen compounds via 1,2-hydrogen shift represents an original route to generate the aminocarbene moiety in the coordination sphere of metals.

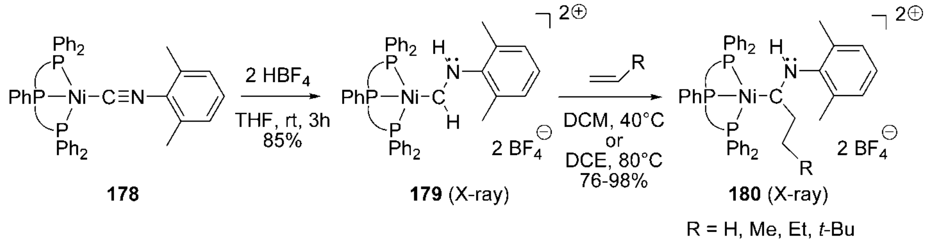
Scheme 121



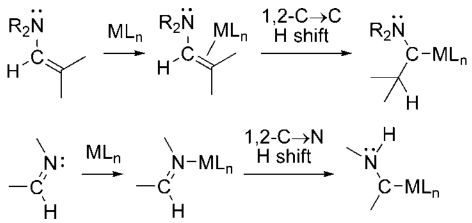
Scheme 122



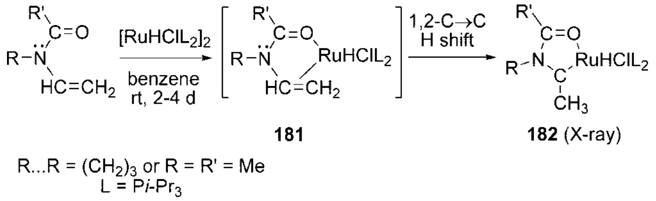
Scheme 123



Scheme 124



Scheme 125



The two conceivable processes, namely, C → C and C → N shifts starting from enamines and aldimines, respectively, have been evidenced recently (Scheme 124). But the thermodynamic balance of these rearrangements strongly depends on the substitutents at nitrogen and on the metal fragments, somewhat limiting the scope of this approach.

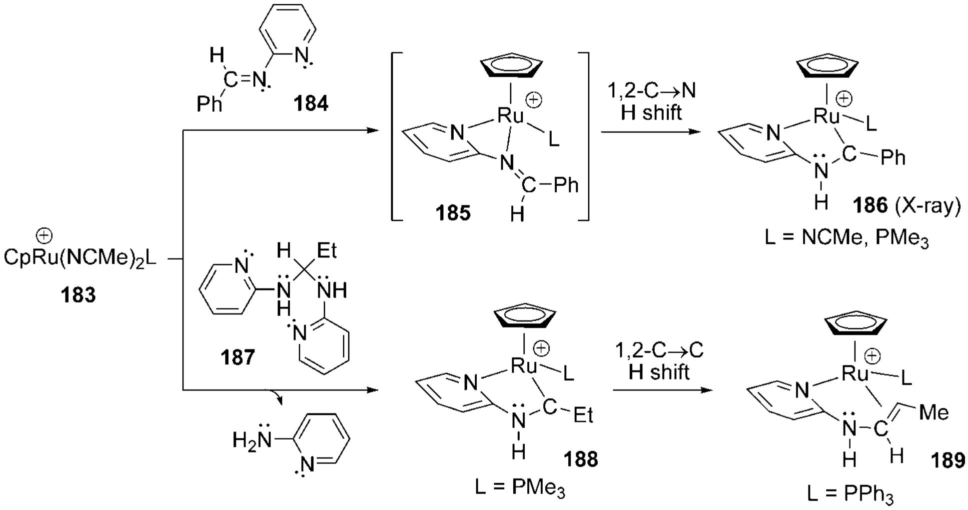
The highly unsaturated [RuHCl(P*i*-Pr$_3$)$_2$] fragment reacts slowly with cyclic and acyclic enamides to give the corresponding aminocarbene complexes **182** after 1,2-C → C hydrogen-shift (Scheme 125).[167] The reaction strongly depends on the π-donating ability of the nitrogen atom, with only the alkene complexes **181** being obtained with *N*-vinyl phthalimide and carbazole.

In 2002, Kirchner and co-workers reported the first preparation of aminocarbene complexes by rearrangement of aldimines in the coordination sphere of a metal. Starting from the aldimine **184** featuring a pyridine anchor and ruthenium(II) precursors **183**, a formal 1,2-C → N hydrogen-shift was found to readily occur, affording the corresponding aminocarbene Ru(II) complexes **186** (Scheme 126).[168] The reaction strongly depends on the coligand at ruthenium and stops at the stage of the pyridine/imine complex **185** with PPh$_3$ or CO. According to DFT calculations, the transformation of **185** into **186** does not proceed via direct hydrogen transfer from the carbon to the nitrogen atom but rather via a multistep process involving a C−H activation/deprotonation/reprotonation sequence. Interestingly, a similar reaction leading to complex **188** is observed with aminal **187** as an aldimine equivalent. Replacement of the PMe$_3$ coligand for PPh$_3$ resulted in further rearrangement of the aminocarbene complex **188** via 1,2-C → C hydrogen-shift, leading to the enamine complex **189**.

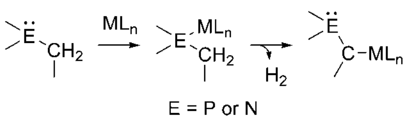
From Double C−H Activation of NCH$_2$R Moieties. By analogy with the formation of phosphinocarbene tantalum complexes from trimethylphosphine and dimethylphosphine,[169] the activation of two geminal C−H bonds in α position to a nitrogen atom has rarely been observed (Scheme 127). This synthetic route to aminocarbene complexes is very interesting conceptually (as a formal dehydrogenation) but remains practically limited to a few rather sophisticated examples.

Slugovc and Carmona reported the first example of such a process in 2000.[170] Treatment of the hydridotris(pyrazolyl)borate iridium complex **190** with *N*,*N*-dimethylaniline afforded a 2:1 mixture of the aminocarbene complexes

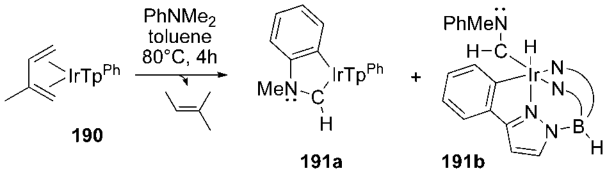
Scheme 126



Scheme 127

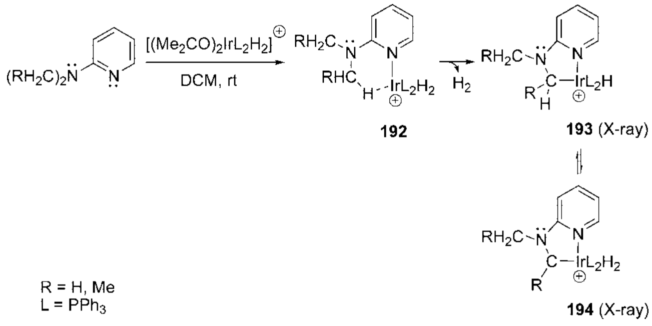


Scheme 128



Tp^{Ph} = hydridotris(3-phenylpyrazol-1-yl)borate

Scheme 129



191a,**b** resulting from *ortho*-metalation of one phenyl ring and double C−H activation of one methyl group at nitrogen (Scheme 128).

Similarly, treatment of [(Ph$_3$P)$_2$H$_2$Ir(OCMe$_2$)]$^+$ with 2-aminopyridines was found to give the corresponding aminocarbene complexes **194** under mild conditions (Scheme 129).[171] The reaction proceeds with both NMe and NEt moieties. Remarkably, the presence of an agostic C−H···M interaction in the initially formed pyridine complex **192** was deduced from low-temperature ^{1}H NMR monitoring, and the reversible character of the final α-elimination reaction from the alkyl complex **193** was substantiated both spectroscopically and structurally.

The chiral aminocarbene ruthenium complexes **195**[172] and **198**[173] have also been prepared following this strategy (Scheme 130). For the ferrocenyl-based aminophosphine, the double C−H activation of the NMe group only proceeds for the rigid ligand **196** and requires heating of the κ^2-P,N complex **197** at 130 °C for 12 h.[173]

In addition, Stradiotto et al. have reported the double geminal C−H activation of an aminophosphinoindenide ligand in the coordination sphere of ruthenium (scheme 131).[174] Treatment of **199a** or **199b** with NaHMDS in toluene at room temperature provided the aminohydrogenocarbene **200a** that subsequently rearranged into its allylic isomer **200b**.

Very recently, Grubbs et al. demonstrated the ability of the PNP-supported iridium dihydride complex (PNP)IrH$_2$ (PNP = [N(2-P^{i}Pr$_2$-4-Me-C$_6$H$_3$)$_2$]$^-$) to mediate the double C−H activation of *N*-methyl amines (such as tetramethylethylenediamine (TMEDA) and *N*-methylmorpholine). Norbornene was necessary to trap the generated dihydrogen and to ensure thereby quantitative formation of the aminocarbenes complexes **201a** and **201b** (scheme 132).[175]

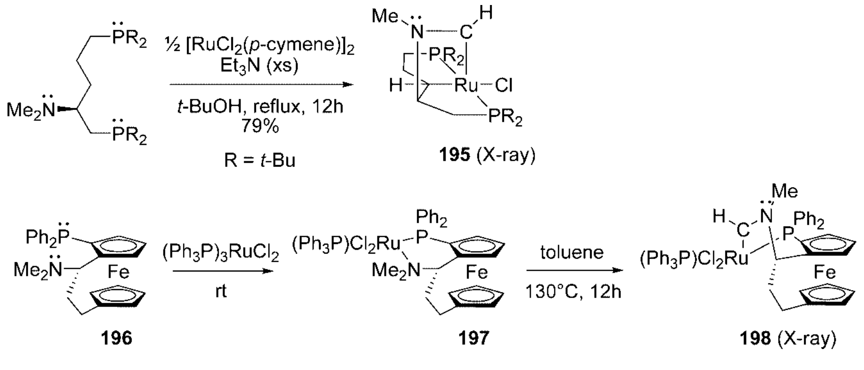
It is noteworthy that the (PNP)IrH$_2$ complex is also able to promote the double C−H activation of the O−Me group of *tert*-butyl methyl ether (TBME) to yield the corresponding oxycarbene complex **202** (Scheme 133).[176] This complex displays a unique reactivity toward a variety of heterocumulenic electrophiles, such as CO$_2$, SCO, and PhNCO, leading to the formal group transfer of O, S, and PhN, respectively, from the cumulene to the carbene fragment. While these reactions involve the concomitent formation of a stoichiometric amount of (PNP)Ir(CO), a catalytic version has been achieved using an azide as the reaction partner.[177]

From Carbene Transfer. Carbene transmetalation is a well-established process for cyclic diaminocarbenes that has been only rarely extrapolated to monoaminocarbenes.[178] Recently, Albéniz, Espinet et al. reported transfer reactions of aminomethyl- and aminophenylcarbenes from tungsten to palladium (Scheme 134).[159b,179] Notably, the ensuing complexes **204** slowly decompose at room temperature via CC coupling of the aminocarbene and pentafluorophenyl fragments, affording the iminium **205**. Such a reductive elimination has also been observed for *N*-heterocyclic carbene complexes[180] and appears as a possible decomposition route during catalytic applications.

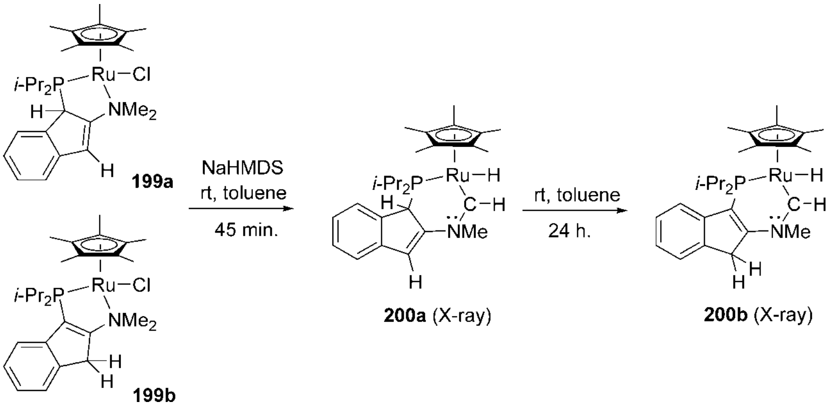
3.5.2. Bonding Situation, Ligand Properties

Among the possible bonding situations typically encountered in carbene complexes (Scheme 101),[181] the presence of at least one π-donating phosphino or amino group at the carbene center favors at first glance Fischer-type complexes with strong $C_{carbene} \rightarrow M$ σ donation, weak $M \rightarrow C_{carbene}$ π backdonation, and an important contribution of the zwitterionic form **Q** (see Scheme 101). This is, in fact, the bonding situation found in all the complexes prepared to date by coordination of stable/persistent acyclic carbenes; despite the broad diversity of carbenes involved, their electronic properties as ligands are rather similar. Nevertheless, DFT calcula-

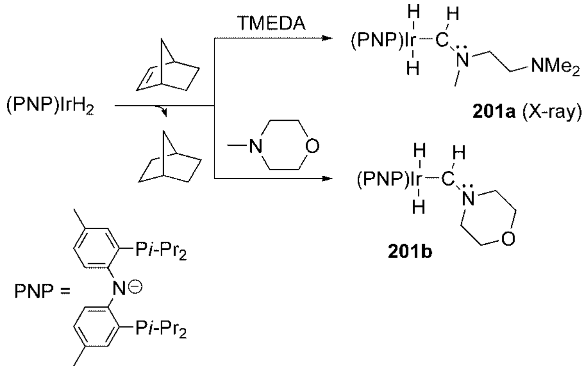
Scheme 130



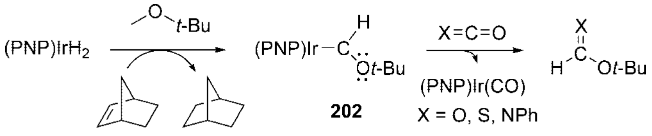
Scheme 131



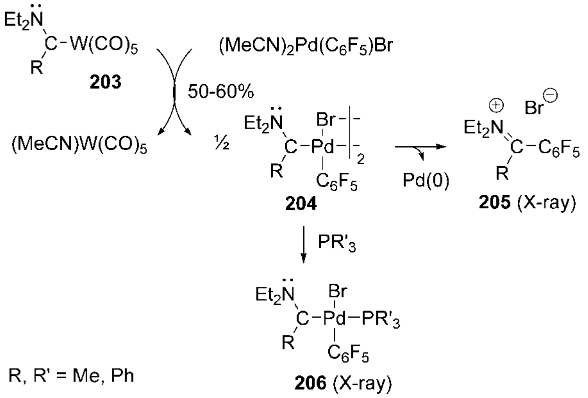
Scheme 132



Scheme 133



Scheme 134



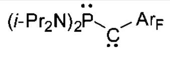
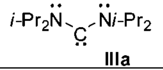
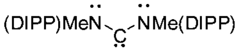
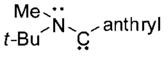
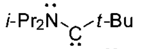
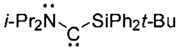
tions suggest that phosphinocarbenes are more flexible electronically than aminocarbenes because of the possible competition between the P → C π donation (which is weaker than N → C π donation) and M → $\mathrm{C_{carbene}}$ π backdonation. Schrock-type complexes are also conceivable with phosphinocarbenes (whose singlet−triplet energy gap typically range from 5 to 15 kcal/mol), but this remains to be illustrated experimentally. As discussed in section 3.5.1, η^2-complexes have been characterized with both phosphino- and aminocarbenes. The weaker π-donating character of phosphorus, associated with its higher ability to accommodate ring strain, makes this η^2-coordination mode much more favorable for phosphinocarbenes and enables them to behave as four-electron ligands even in the absence of a second donating group at the carbene center.

The nature and strength of the carbene−metal interactions are discussed hereafter on the basis of experimental and theoretical data. In addition, the ligand properties of the different carbene skeletons are compared, as well as the η^1/η^2-coordination modes.

The metrical parameters obtained from X-ray diffraction studies have provided valuable information regarding the nature of the metal−carbene bond. A variety of carbene complexes have been structurally characterized (M = Pd, Ni, Cr,...). The discussion will be focused on [(carbene)-RhCl(diene)] complexes, for which a series of analogous compounds have been prepared with the push−pull phosphinoarylcarbene **VIIa**, the push−push diaminocarbenes **IIIa**,**i**, and the push−spectator monoaminocarbenes **IXe**, **Xa**, and **XIIa** (Table 13). The key geometric features clearly indicate Fischer-type structures for these complexes with strong $\mathrm{C_{carbene}}$ → M σ donation and weak, if any, M → $\mathrm{C_{carbene}}$ π backdonation. The $\mathrm{C_{carbene}Rh}$ bond lengths (1.99−2.10 Å) are in the range typical for C−Rh single bonds, while the $\mathrm{PC_{carbene}}$ (1.67 Å) and $\mathrm{NC_{carbene}}$ (1.31−1.36 Å) bond lengths are short, indicating multiple bond character (zwitterionic form **Q**; see Scheme 101). The carbene ligands exert a significant *trans* influence, as apparent from the elongation of the $\mathrm{RhC_{diene}}$ bonds by ~10 pm. Thus, a rather uniform ligand behavior is observed, despite the broad variety of substitution patterns, stabilization modes, and chemical reactivities of these carbenes. Notably, the geometry of aminocarbenes is only marginally affected upon coordination (the $\mathrm{NC_{carbene}}$ bond length varies by only a few pm, and the carbene bond angle varies by only a few degrees), whereas the complexation of the phosphinoarylcarbene **VIIa** induces a noticeable elongation of the $\mathrm{PC_{carbene}}$ bond [from 1.544(3) to 1.673(7) Å] and a dramatic contraction of the $\mathrm{PC_{carbene}C}$ bond angle [from 162.1(3) to 119.5(4)°]. Upon coordination, the carbene lone pair n_σ strongly interacts with the metal center and no longer interacts with the aryl group, so that the cumulenic character of the carbene disappears and the $\mathrm{C_{carbene}C}$ bond elongates [from 1.390(4) to 1.513(9) Å].

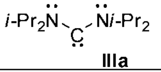
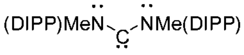
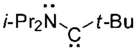
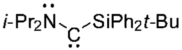
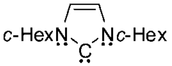
The electronic properties of the carbene ligands have been further investigated by looking at the carbonyl stretching frequencies (Table 14) of the corresponding carbonyl complexes (see section 3.5.1 for their preparation) and compared

Table 13. Geometrical Data for Carbene Complexes ($(R_2E-\ddot{C}-R')RhCl(L_2)$) (E = P or N, L_2 = nbd or cod), As Determined by X-ray Diffraction Analyses

carbene $R_2E-\ddot{C}-R'$[a,b]	$C_{carbene}Rh$ (in Å)	$EC_{carbene}$ (in Å)	RhC_{cis} (in Å)	RhC_{trans} (in Å)	$EC_{carbene}R'$ (in °)	Ref
 **VIIa**	2.096(7)	1.673(7) [1.544(3)][d]	2.108(8)[c]	2.181(7)[c]	119.5(4) [162.1(3)][d]	141
 **IIIa**	2.041(2)	1.360(3)[c] [1.372(6)][c,d]	2.114(2)[c]	2.225(2)[c]	118.0(2) [121.0(5)][d]	142
 **IIIi**	2.086(8)	1.352(9)[c]	2.114(9)[c]	2.183(8)[c]	119.5(6)	35
 **IXe**	2.043(7)	1.326(9)	2.131(8)[c]	2.233(8)[c]	114.8(6)	53
 **Xa**	2.039(2)	1.317(3) [1.298(2)][d]	2.114(2)[c]	2.223(2)[c]	121.1(2) [120.5(1)][d]	58
 **XIIa**	1.994(2)	1.316(2)	2.121(2)[c]	2.240(2)[c]	124.0(1)	62

[a] Ar_F = 2,6-$(F_3C)_2$-C_6H_3. [b] DIPP = 2,6-*i*-$Pr_2-C_6H_3$. [c] Average value. [d] Corresponding value in the free carbene.

Table 14. Carbonyl Stretching Frequencies of $[RhCl(CO)_2]$ Complexes Derived from (Di)Aminocarbenes, As Determined Experimentally

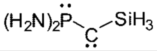
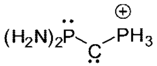
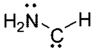
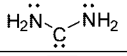
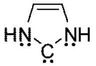
carbene[a,b]	ν_{CO} (in cm^{-1})	Ref
 **IIIa**	2057, 1984	142
 **IIIi**	2068, 1989	35
 **Xa**	2070, 1989	58
 **XIIa**	2072, 1989	62
	2081, 1996	142
	2076, 2006	142

[a] DIPP = 2,6-*i*-$Pr_2-C_6H_3$. [b] Mes = 2,4,6-$Me_3-C_6H_2$.

with those of *N*-heterocyclic carbenes. Overall, the acyclic diaminocarbenes appear more donating than NHCs (imidazol-2-ylidenes as well as imidazolidin-2-ylidenes). Monoaminocarbenes also behave as strong σ-donor ligands despite the presence of a single π-donating substituent, with their electronic properties being intermediate between those of acyclic and cyclic diaminocarbenes. The bis(diisopropylamino)carbene **IIIa** exhibits the strongest σ-donor character, in agreement with that discussed in section 3.2.1 concerning the Brönsted basicity. The introduction of two aryl groups at the nitrogen atoms slightly decreases the donor character (from **IIIa** to **IIIi**), while the electronic properties of monoaminocarbenes seem virtually independent of the nature of the spectator group (*tert*-butyl in **Xa** versus diphenyl-*tert*-butyl silyl in **XIIa**). Although experimental data is lacking about the electronic properties of phosphinocarbenes, the carbonyl stretching frequencies predicted theoretically for $Cr(CO)_5$ and $Ni(CO)_3$ complexes suggest that (di)aminocarbenes are better donors than phosphinocarbenes.[182]

Schoeller and co-workers reported in 2000 the first theoretical comparative study of phosphino- and aminocarbene complexes.[183] The formation of Fischer-type complexes by coordination of different model carbenes to the $[W(CO)_5]$ fragment was examined (Table 15). The complexation only

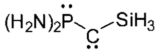
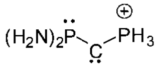
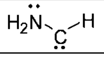
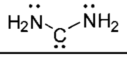
Table 15. Geometrical Data and Bonding Energies for Fischer-type Complexes $(Carbene)W(CO)_5$, As Predicted by DFT Calculations

carbene	$C_{carbene}W$ (in Å)	$EC_{carbene}$ (in Å)[a]	$EC_{carbene}R'$ (in °)[a,b]	ΣE_α (in °)[a]	D_0 (in kcal/mol)[c]
	2.224	1.713 [1.590][d]	113.9 [133.1][d]	336.6 [360.0][d]	41.4
	2.086	1.828 [1.556][d]	105.7 [175.6][d]	308.5 [360.0][d]	36.8
	2.171	1.341 [1.338][d]	107.9 [104.8][d]	360.0 [360.0][d]	58.6
	2.256	1.359 [1.362][d]	113.6 [111.9][d]	360.0 [360.0][d]	52.8
	2.241	1.376 [1.383][d]	102.1 [100.2][d]	360.0 [360.0][d]	54.9

[a] E = P or N. [b] Carbene bond angle. [c] Bonding energy associated with the coupling of the ground-state fragments ^{1}(carbene) and $^1(W(CO)_5)$. [d] Corresponding value predicted for the free carbene.

Figure 23. Schematic representation of the π-interaction in Fischer-type complexes of phosphino- and aminocarbenes.

Table 16. Geometrical Data and Bonding Energies for Schrock-type Complexes (Carbene)WCl_4, As Predicted by DFT Calculations

carbene	$C_{carbene}W$ (in Å)	D_0 (in kcal/mol)[a]
 $(H_2N)_2\ddot{P}-\ddot{C}-SiH_3$	1.823	38.0
 $(H_2N)_2\ddot{P}-\ddot{C}-PH_3^{\oplus}$	1.856	−16.2
 $H_2\ddot{N}-\ddot{C}-H$	1.940	–16.0
 $H_2\ddot{N}-\ddot{C}-\ddot{N}H_2$	1.993	–28.8

[a] "Bonding" energy associated with the coupling of the ground-state fragments ^{1}(carbene) and ^{3}(WCl_4).

marginally modifies the geometry of acyclic or cyclic (di)aminocarbenes, and the corresponding bonding energies are rather large ($D_0 \approx 55$ kcal/mol). In contrast, the coordination of phosphinosilyl- and phosphinophosphoniocarbenes is accompanied by a noticeable elongation of the $PC_{carbene}$ bond and significant pyramidalization of the phosphorus environment, which suggests that P → C π donation and M → $C_{carbene}$ π backdonation are both occurring (Figure 23). In addition, the carbene bond angle of the phosphinocarbenes contracts by 20−70° upon coordination, as the result of the interaction of the carbene lone pair with the metal center. These important geometric distortions lead to weaker bonding energies for phosphinocarbenes ($D_0 \approx 40$ kcal/mol) than for aminocarbenes.

The formation of Schrock-type complexes has also been investigated with the triplet (WCl_4) fragment (Table 16).[184] As expected, shorter $C_{carbene}W$ bond lengths were predicted, in particular for the phosphinocarbene complexes, something consistent with more double-bond character of the $C_{carbene}M$ bond and higher contribution of form **O** (see Scheme 101). The interaction between the ground-state fragments is favorable energetically only for the phosphinosilylcarbene $(H_2N)_2P-\ddot{C}-SiH_3$, with a bonding energy ($D_0 = 38.0$ kcal/mol) similar to that predicted for the corresponding Fischer-type $W(CO)_5$ complex ($D_0 = 41.4$ kcal/mol). The carbene/WCl_4 interaction is not favorable for the other carbenes, because of the energetic costs required to bend the phosphinophosphoniocarbene on one hand and to overcome the strong N → C π donation in (di)aminocarbenes on the other hand. In general, phosphinocarbenes are more prone to form Schrock-type complexes than aminocarbenes, but this bonding situation remains to be illustrated experimentally (with early transition metals in high oxidation states, only η^2-complexes have been prepared to date[9,185]).

Fischer-type rhodium(I) complexes of phosphino- and aminocarbenes [(carbene)$RhCl(L_2)$] have also been investigated computationally, allowing for a better understanding of the nature and strength of the $C_{carbene}-Rh$ bond (Table 17).[186] This study involves the *cis* and *trans* isomers of complexes $[\{(H_2N)_2PCH\}RhCl(C_2H_4)_2]$, which adopt very similar structures ($C_{carbene}Rh \approx 1.90$ Å, $PC_{carbene} \approx 1.80$ Å, $\Sigma P_\alpha \approx 320°$) and are quasi-isoenergetic. Replacement of the ethylene coligands for carbonyl groups induces rather large modifications: the *cis* complex exhibits a longer $RhC_{carbene}$ bond (2.107 Å), a shorter $PC_{carbene}$ bond (1.648 Å), and a trigonal planar environment around phosphorus (resonance form **Q**, Scheme 101). Overall, its geometry strongly resembles that observed experimentally in complex **141** and indicates strong $C_{carbene}$ → Rh σ donation and weak, if any, Rh → $C_{carbene}$ π backdonation. The related *trans* complex is less perturbed by the modification of the coligand but lies ∼12 kcal/mol higher in energy than the *cis* form. The most stable structure for $[\{(H_2N)_2PCH\}RhCl(CO)_2]$ corresponds to an original *cis* form featuring a secondary Cl → $C_{carbene}$ interaction.[187] The three forms of the complex $[\{(H_2N)_2PCH\}RhCl(CO)_2]$ nicely illustrate the electronic flexibility of phosphinocarbene ligands, associated with the various possible interactions for the p_π orbital at the carbene center (Figure 24). In comparison, all complexes derived from the aminocarbene $H_2N-\ddot{C}-H$ adopt very similar geometries, with strong N → $C_{carbene}$ σ interaction and weak, if any, Rh → $C_{carbene}$ π backdonation (the NC bond is short and the nitrogen atom is in a planar environment). From an energetic point of view, the interaction between the carbene and metal fragments is only slightly less favorable for phosphino- than for aminocarbenes ($\Delta E = E_{complex} - E_{carbene} - {}^1/_2E_{Rh\ dimer} \approx 25-30$ versus 35 kcal/mol).

A detailed study has also been carried out by Hu et al. on $[Cr(CO)_5]$ complexes derived from monoamino- and diaminocarbenes (Table 18).[144] As in related $[W(CO)_5]$ complexes, rather long $C_{carbene}Cr$ bond lengths were predicted, especially with the bis(diisopropylamino)carbene **IIIa** (2.245 Å). The carbonyl stretching frequencies well-reproduce the variation of the donor character (acyclic diaminocarbenes ≥ acyclic monoaminocarbenes ≥ cyclic diaminocarbenes) observed experimentally for the $[RhCl(CO)_2]$ complexes. This trend has been correlated with intrinsic properties of the carbenes such as the proton affinity (PA) and the electronegativity χ, defined as (IP + EA)/2 (with IP = ionization potential and EA = electron affinity). In addition, the bonding energy

Table 17. Geometrical Data and Bonding Energies for Fischer-type Complexes (Carbene)$RhCl(L)_2$, As Predicted by DFT Calculations

complex	$C_{carbene}Rh$ (in Å)	$EC_{carbene}$ (in Å)[a]	ΣE_α (in °)[a]	ΔE (in kcal/mol)[b]
trans-$[(H_2N)_2PCH]RhCl(C_2H_4)_2$	1.890	1.817	315.9	−0.4
cis-$[(H_2N)_2PCH]RhCl(C_2H_4)_2$	1.909	1.774	322.1	0
trans-$[(H_2N)_2PCH]RhCl(CO)_2$	1.925	1.799	317.5	12.4
cis-$[(H_2N)_2PCH]RhCl(CO)_2$	2.107	1.648	357.8	0
cis-$[(H_2N)_2PCH]RhCl(CO)_2$[c]	2.054	1.837	310.8	−2.2
trans-$(H_2NCH)RhCl(C_2H_4)_2$	1.927	1.352	360.0	3.2
cis-$(H_2NCH)RhCl(C_2H_4)_2$	1.973	1.330	360.0	0
trans-$(H_2NCH)RhCl(CO)_2$	1.962	1.347	360.0	9.5
cis-$(H_2NCH)RhCl(CO)_2$	2.053	1.321	360.0	0

[a] E = P or N. [b] Relative energies. [c] Associated with Cl → $C_{carbene}$ interaction.

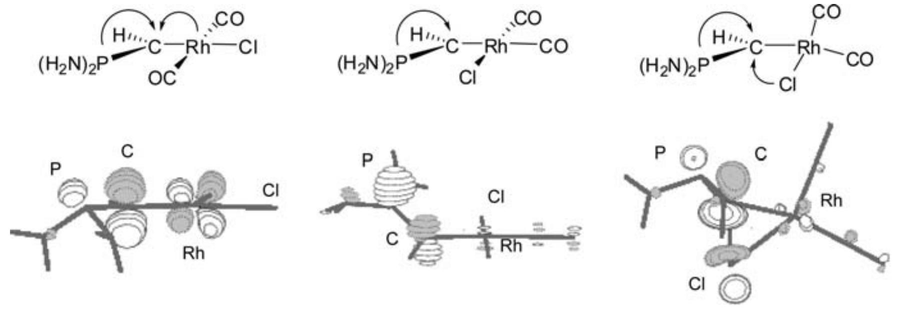
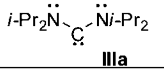
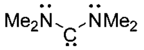
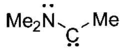
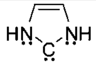
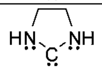


Figure 24. Plots of the p_π-centered molecular orbitals for complexes $[\eta^1\text{-}\{(H_2N)_2PCH\}RhCl(CO)_2]$. Reprinted with permission from ref 186. Copyright 2000 Wiley.

Table 18. Geometric Data, Carbonyl Stretching Frequencies (Totally Symmetric Mode), and Bonding Energies for $[Cr(CO)_5]$ Complexes Derived from (Di)Aminocarbenes, As Predicted by DFT Calculations

carbene	$C_{carbene}Cr$ (in Å)	ν_{CO} (in cm^{-1})	D_0 (in kcal/mol)[a]
 **IIIa**	2.245	2122	42.4
 **IIIf**	2.186	2129	40.1
	2.136	2135	49.0
	2.107	2137	53.7
	2.101	2137	54.4

[a] Bonding energy associated with the coupling of the ground-state fragments ^{1}(carbene) and $^1(Cr(CO)_5)$.

between the carbene and $Cr(CO)_5$ fragments was found to slightly increase from the acyclic diaminocarbenes $R_2N-\ddot{C}-NR_2$ **IIIa**,**f** (R = *i*-Pr, Me) ($D_0 \approx 40$ kcal/mol) to the acyclic monoaminocarbene $Me_2N-\ddot{C}-Me$ ($D_0 = 49$ kcal/mol), and to *N*-heterocyclic carbenes ($D_0 = 55$ kcal/mol). This study has also been recently extended to phosphino- and aminocarbenes.[182] Slightly larger bonding energies were found for push−spectator than push−pull phosphinocarbenes (with D_0 from 45−50 to 30−35 kcal/mol), consistent with the required bending of the push−pull systems. Model monoaminocarbenes were also found to strongly bind to the $Cr(CO)_5$ fragment (with D_0 of ~40−50 kcal/mol). However, the rather large differences observed between the aminocarbenes $Me_2N-\ddot{C}-Me$ ($D_0 = 49$ kcal/mol), $Me_2N-\ddot{C}-(t\text{-Bu})$ ($D_0 = 34$ kcal/mol), and $(t\text{-Bu})MeN-\ddot{C}-(t\text{-Bu})$ ($D_0 = 18$ kcal/mol) point out the critical influence of steric factors. In this respect, it is certainly difficult to make fine comparisons between different carbene ligands using only model systems, and more sophisticated calculations would be required.

In the η^1-complexes described above, the phosphino- and aminocarbenes act as two-electron donors. Because of the presence of the heteroatom lone pair in the α position to the carbene center, these carbenes can also act as four-electron donors, and a few η^2-complexes have indeed been prepared (see section 3.5.1). These two coordination modes have been compared theoretically for complexes $[(carbene)RhCl(L_2)]$ (L = C_2H_4, CO, PH_3).[186] The η^2-complexes deriving from the model phosphinocarbene $(H_2N)_2P-\ddot{C}-H$ exhibit $PC_{carbene}$ (~1.76 Å) and $C_{carbene}Rh$ (~1.88 Å) bond lengths at the lower limit of those observed for the corresponding η^1-complexes. The PRh bond lengths (~2.35 Å) are in the range of those observed for $Rh-PH_3$ bonds, consistent with dative bonds. From an energy point of view, the 18-electron η^2-complexes are only slightly higher in energy than the related 16-electron η^1-complexes ($\Delta E \leq 13$ kcal/mol). The two coordination modes are even quasi-isoenergetic with PH_3 as a coligand. The presence of strong σ-donor ligands at Rh increases M → C backdonation, and thus, the phosphorus lone pair of the carbene is more available for P → Rh interaction. Energy minima associated with η^2 coordination have also been found for the related complexes featuring the aminocarbene $H_2N-\ddot{C}-H$. The $NC_{carbene}$ bonds (~1.44 Å) are substantially longer than in the related η^1-complexes, lying in the range typical for single bonds, while the $C_{carbene}Rh$ bonds (~1.81 Å) are noticeably shortened, consistent with some double-bond character. Energetically, the η^2 form lies at least 40 kcal/mol higher in energy than the corresponding η^1 structure, whatever the coligand. Although nitrogen has a lower ability to accommodate the strain associated with the η^2 coordination, this can only partly explain such a difference in behavior between amino- and phosphinocarbenes. The major factor is probably once again the stronger π-donating ability of amino versus phosphino groups, with the change from η^1 to η^2 coordination being associated with a change from π to σ donation between the heteroelement and the carbene. Overall, phosphinocarbenes thus have a higher propensity than aminocarbenes to adopt η^2 coordination, in agreement with experimental observations. With aminocarbenes, the η^2 coordination requires a second donor substituent at the carbene, which can interact with the carbene [as in the η^2-(NC) diaminocarbene complexes **149a**−**c**] or the metal itself [as in the η^2-(PC) aminophosphinocarbene complexes **162**−**164**]. Note last that the diaminocarbene $H_2N-\ddot{C}-NH_2$ and monoaminocarbene $Me_2N-\ddot{C}-Ph$ have been predicted theoretically to behave essentially as pure σ-donor ligands toward the $(BeCl)^+$ and $SmCl_3$ fragments.[188]

3.5.3. Applications in Catalysis

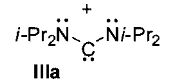
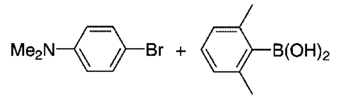
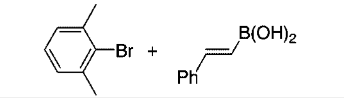
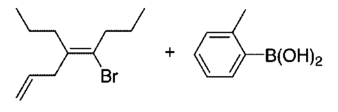
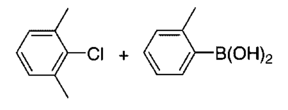
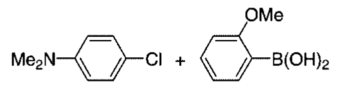
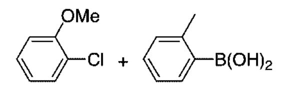
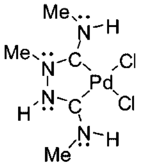
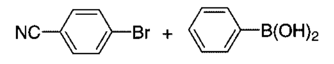
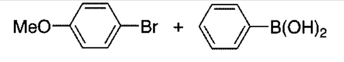
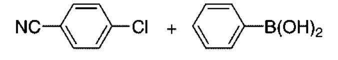
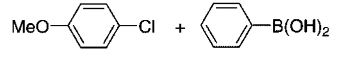
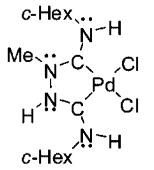
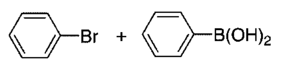
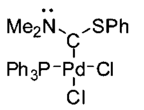
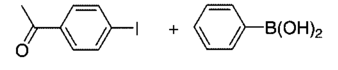
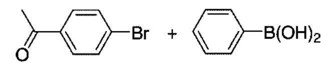
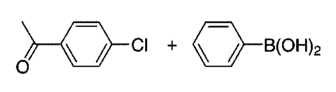
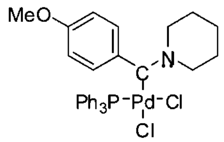
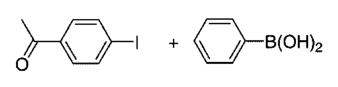
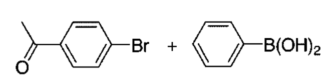
As discussed in the previous section, the electronic properties of acyclic diamino- and monoaminocarbenes roughly parallel those of *N*-heterocyclic carbenes (strong σ-donor, poor π-acceptor). However, the much higher thermal and/or moisture sensitivity of the acyclic variants has limited their application in catalysis. To date, only a few Pd and Ni complexes have been evaluated, but a relatively large array of catalytic transformations have been tested, from C−C and C−N coupling reactions to aza-Claisen rearrangement.

3.5.3.1. Suzuki−Miyaura Reaction. Several aminocarbene complexes were shown to be effective precatalysts for the coupling of aryl halides with aryl boronic acids (Table

Table 19. Selected Examples of Suzuki−Miyaura Coupling Reactions Using Pd Complexes of Acyclic Diamino- And Monoaminocarbenes As Catalysts

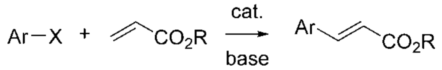
$$\text{R}-\text{X} + \text{Ar}-\text{B(OH)}_2 \xrightarrow[\text{base}]{\text{cat.}} \text{R}-\text{Ar}$$

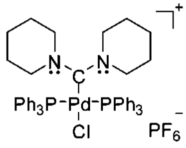
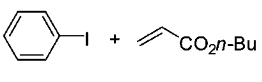
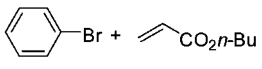
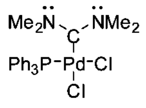
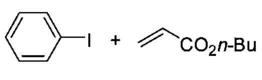
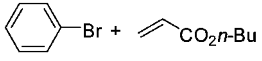
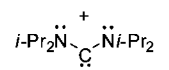
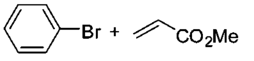
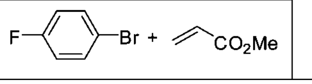
R = aryl, vinyl

catalyst	substrates	conditions	yield	ref
$Pd_2(dba)_3$ (0.5 mol%) +  **IIIa** (1.25 mol%)		n-Bu_4NBr (1.25 mol%) Cs_2CO_3 (2 eq.) toluene/THF RT, 16h	79%	189
			89%	
			88%	
		n-Bu_4NBr (1.25 mol%) Cs_2CO_3 (2 eq.) toluene/THF 45°C, 16h	80%	
			85%	
			92%	
 **176$_{Me}$** (1 mol%)		K_3PO_4 (1.5 eq.) DMA 120°C, 24h	97% (N_2) 97% (air)	163f
			89% (N_2) 62% (air)	
			93% (N_2)	
			4% (N_2)	
 **176$_{c\text{-}Hex}$** (1 mol%)			99% (N_2) 93% (air)	163d
 **173b** (1 mol%)		K_2CO_3 (2.8 eq.) THF 65°C, 16h	82%	156
			78%	
		K_2CO_3 (2.8 eq.) toluene 110°C, 16h	81%	
 **173c** (1 mol%)		K_2CO_3 (2.8 eq.) THF 65°C, 16h	80%	
			78%	

19). Thadani et al. investigated catalysts derived from acyclic diaminocarbenes and $Pd_2(dba)_3$.[189] Only carbenes featuring bulky substituents at the nitrogen atoms, such as the bis(diisopropylamino)carbene **IIIa**, were found to give satisfactory yields of the biaryl products, highlighting the influence of ligand sterics on the coupling reaction. Note

Table 20. Selected Examples of Heck Coupling Reactions Using Pd Complexes of Acyclic Diaminocarbenes As Catalysts



catalyst	substrates	conditions	yield	ref
 **174a$_{Pd}$** (1 mol%)		Cs_2CO_3 (2 eq.) NMP, 120°C, 16h	92%	156
			77%	
 **173e** (1 mol%)			82%	
			56%	
$Pd_2(dba)_3$ (0.5 mol%) +  **IIIa** (1.25 mol%)		n-Bu_4NBr (1.25 mol%) Cs_2CO_3 (2 eq.) DMA, THF, 110°C, 8h	78%	189
			85%	

that similar yields of biaryl products were obtained from preformed and in situ-generated bis(diisopropylamino)carbene **IIIa**. The coupling of nonactivated mono- and di-*ortho*-substituted aryl bromides occurs at room temperature with 1 mol % of Pd in good-to-excellent yield (79−95%). At 45 °C, nonactivated mono- and even di-*ortho*-substituted aryl chlorides are efficiently coupled in good yields (80−92%).

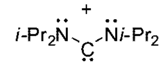
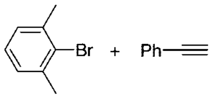
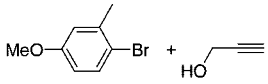
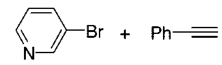
Chelating Chugaev-type palladium complexes **176**, developed by Slaughter et al., also proved to be efficient precatalysts for the Suzuki−Miyaura reaction, although a higher temperature was required (120 °C) to achieve good conversions.[163d−f] The yields of biaryl products are strongly influenced by the substitution pattern of the carbene ligand. The best results were obtained with **176**$_{Me}$ derived from *N*-methyl hydrazine. With 1 mol % of precatalyst, aryl bromides featuring an electron-donating or electron-withdrawing group in the *para* position were coupled to phenyl boronic acid in high yields (85−100%). Aryl chlorides substituted with an electron-withdrawing group (p-NO_2, *p*-CN) are also reactive substrates, affording the biaryl derivatives in good yield (79−93%). However, these Chugaev-type complexes were not efficient for the coupling of chlorobenzene or *para*-chlorotoluene with phenyl boronic acid (10 and 3% yield, respectively). Interestingly, minimal loss of yield and little formation of homocoupled byproduct were observed when the coupling reactions were conducted open to air. This reaction represents a rare example of an oxygen-tolerant catalytic system for the Suzuki−Miyaura reaction.

Preliminary results obtained by Fürstner et al. have evidenced that monoaminocarbene complexes such as the aminooxycarbene complex **173a**, the aminothiocarbene complex **173b**, and the aminoarylcarbene complexes **173c** and **173d** act as efficient precatalysts for the coupling of 4-bromoacetophenone with phenyl boronic acid in moderate-to-good yields (55−81% at 1 mol % loading in refluxing THF).[156] Interestingly, the aminothiocarbene complex **173b** was found to be effective in promoting the coupling of 4-chloroacetophenone at 120 °C.

3.5.3.2. Heck Reaction. Cationic as well as neutral cyclic diaminocarbene Pd complexes have been explored for the Heck reaction. With preformed catalysts,[156] moderate-to-good yields have been obtained in the coupling of iodo- and bromobenzene with *n*-butyl acrylate using 1 mol % of the precatalyst at 120 °C (Table 20). In situ reaction of the bis(diisopropylamino)carbene **IIIa** with $Pd_2(dba)_3$ was also found to generate an active precatalyst capable of coupling bromobenzene and *p*-fluorobromobenzene with methyl acrylate at 110 °C using 1 mol % of Pd.[189]

Table 21. Selected Examples of Sonogashira Coupling Reactions Using an In Situ-Generated Pd Complex of the Bis(Diisopropylamino)Carbene IIIa as Catalyst

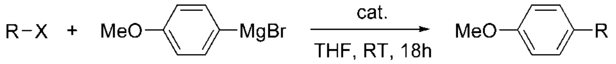
$$R{-}Br + R'{-}{\equiv} \xrightarrow[\text{toluene/THF, RT, 16h}]{\text{cat., } Cs_2CO_3 \text{ (2eq.)}} R{-}{\equiv}{-}R'$$

catalyst	substrates	yield	ref
$[PdCl(allyl)]_2$ (1.5 mol%) +  **IIIa** (4 mol%)		80%	189
		80%	
		90%	

3.5.3.3. Sonogashira Reaction. The application of the bis(diisopropylamino)carbene **IIIa** in Sonogashira reactions was also examined in the presence of $[Pd(allyl)Cl]_2$ (Table 21).[189] The coupling of aryl bromides with terminal alkynes, including propargyl alcohol, proceeds with good yields (80−91%) at room temperature. Note that the reaction occurs efficiently with *ortho*-disubstituted aryl bromides as well as with 3-bromopyridine derivatives.

3.5.3.4. Kumada−Corriu reaction. Diaminocarbene nickel complexes **174a**$_{Ni}$ and **174b**$_{Ni}$ are effective precatalysts for the Kumada−Corriu coupling reaction of bromobenzene, chlorobenzene, and 2-chloropyridine with *para*-methoxyphe-

Table 22. Selected Examples of Kumada−Corriu Coupling Reactions Using Ni Complexes of Acyclic Diaminocarbenes As Catalysts



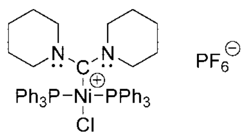
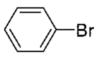
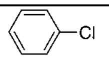
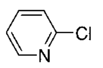
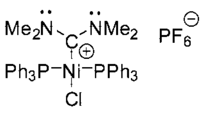
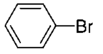
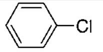
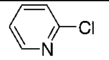
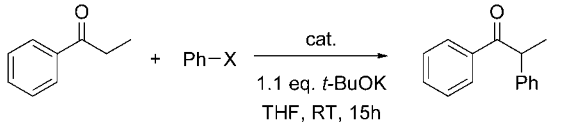
catalyst	RX	yield	ref
 **$174a_{Ni}$** (3 mol%)		81%	156
		77%	
		76%	
 **$174b_{Ni}$** (3 mol%)		67%	
		61%	
		74%	

Table 23. Examples of α-Arylation of Propiophenone Using a Pd Complex of Acyclic Aminobiphenylcarbene As Precatalyst



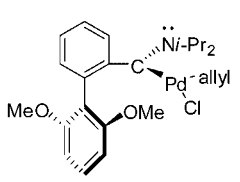
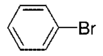
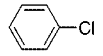
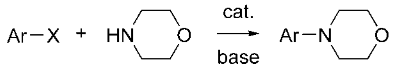
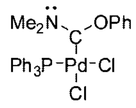
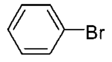
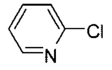
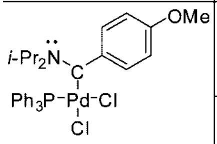
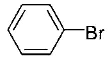
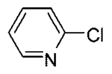
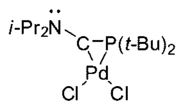
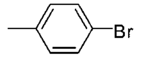
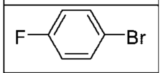
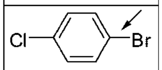
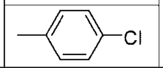
catalyst	PhX	conversion	ref
 **157** (2 mol%)		100%	54
		30%	

Table 24. Selected Examples of Amination Reactions of Morpholine with ArX Using Pd Complexes of Monoaminocarbenes As Precatalysts



catalyst	ArX	conditions	yield	ref
 **173a** (1 mol%)		*t*-BuONa (2 eq.) DME, 5h	82% (70°C)	156
			100% (rt)	
 **173d** (1 mol%)			73% (70°C)	
			100% (rt)	
 **162** (0.5 mol%)		*t*-BuONa (1.4 eq.) xylene 110°C	90% (1 h)	147b
			85% (20 h)	
			90% (20h)	
			20% (1 h)	

nylmagnesium bromide at room temperature (61−81% yields) (Table 22).[156] Small amounts of 4,4′-dimethoxybiphenyl, resulting from the homocoupling of the Grignard reagent, were invariably observed.

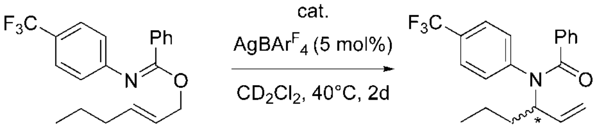
3.5.3.5. α-Arylation of Ketones. A preliminary investigation into the applicability of the aminobiphenylcarbene palladium complex **157** for the α-arylation of propiophenone revealed some promising features (Table 23).[54] Indeed, bromobenzene could be quantitatively coupled at room temperature with a 2 mol % loading of catalyst, which is comparable to the most active phosphine-based catalyst for that reaction. Interestingly, chlorobenzene could be coupled at room temperature, albeit in low yield (30%).

3.5.3.6. Amination Reaction. Encouraging results have been reported for the Buchwald−Hartwig coupling of aryl halides with morpholine (Table 24). With Pd complexes of monoaminocarbenes featuring an oxy, thio, or aryl substituent, good yields (73−92%) were obtained with bromobenzene and 2-chloropyridine.[156] Similarly, the chelating aminophosphinocarbene complex **162** has been shown to be an efficient precatalyst for the amination of bromobenzenes featuring electron-donating as well as electron-withdrawing groups in the *para*-position (80−90% yields).[147b] Unfortunately, nonactivated aryl chlorides, such as 4-methyl chlorobenzene, were not efficiently coupled under these conditions (only 20% conversion after 1 h), which is consistent with the selective coupling of 4-chlorobromobenzene via the Ar−Br bond.

3.5.3.7. Aza-Claisen Rearrangement. Chelating bis(acyclic diaminocarbene) palladium complexes **177a** derived from C_2-symmetric diamines were recently shown to promote the aza-Claisen rearrangement of the allylic benzimidate **207** into the allylic amide **208** in the presence of $AgBAr^F_4$ (Table 25).[164b] Small amounts of the 1,3-rearrangement and elimination byproducts were observed, but the desired allylic amide was obtained in significantly higher yield and with higher selectivity with the chelating bis(acyclic diaminocarbene) precatalysts **177a** compared to a related bis(*N*-heterocyclic carbene) palladium complex. Moreover, the readily available enantiopure precatalysts **177b** led to encouraging enantioselectivities (up to 59% ee).

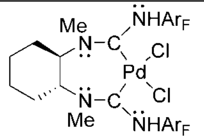
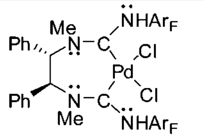
Compared to NHCs, much less data is available concerning the use of acyclic aminocarbenes as ligands for transition metal based catalysis. As reported in this section, encouraging results were obtained in C−C and C−N bond-formation processes as well as for aza-Claisen type rearrangements.[190] However, acyclic carbene-based ligands so far have failed to compete with their cyclic analogues, which are usually both more readily accessible and less sensitive. Further developments in this area would require the preparation of more robust precatalysts, which is a goal that could be reached by exploiting the high structural modularity of the acyclic backbone. In particular, monoaminocarbenes featuring a spectator group present a certain degree of freedom in substituent variation.

Table 25. Examples of *aza*-Claisen Rearrangements Using Chiral Pd Complexes of Bis(Acyclic diaminocarbenes) As Catalysts



$Ar^F = 3,5\text{-}(F_3C)_2C_6H_3$

207 **208**

catalyst	yield	ee	ref
 (±) **177a** (5 mol%) $Ar_F = p\text{-}CF_3C_6H_4$	70%	-	164b
(1*R*-2*R*)-**177a** (5 mol%)	50%	30% (*S*)-(+)	
 (1*S*,2*S*)-**177b** (5 mol%) $Ar_F = p\text{-}CF_3C_6H_4$	34%	59% (*S*)-(+)	

4. Conclusions and Outlook

This review reports the major progress that has been achieved over the past few years in the isolation and reactivity of stable noncyclic carbenes. The increasing variety of available noncyclic carbenes has allowed for better insight into the stabilization of these otherwise reactive intermediates. In addition, their intrinsic reactivity has made them valuable synthons in organic synthesis and has enabled their use in transition-metal mediated catalysis.

Two different types of carbenes can be distinguished, namely, phosphino- and aminocarbenes, where the nature of the predominant stabilizing substituent dictates the electronic properties and chemical reactivity of stable noncyclic carbenes. For example, because of rather weak $P \rightarrow C_{carbene}$ π donation, phosphinocarbenes have a small singlet−triplet energy gap. Therefore, they are both nucleophilic and electrophilic, and their reactivity typically matches that of transient carbenes. Aminocarbenes are stabilized by strong $N \rightarrow C_{carbene}$ π donation and, thus, have a larger singlet−triplet energy gap, and their formally vacant p_π orbital is less energetically accessible. Besides the push−pull and push−push stabilization modes illustrated by the phosphinosilylcarbenes **I** and diaminocarbenes **III**, respectively, carbenes featuring a spectator group (such as an aryl or alkyl substituent) were isolated in the early 2000s, opening access to a significantly broader variety of substitution patterns.

Better understanding has been gained on the factors controlling the dimerization of diaminocarbenes and the cyclopropanation of phosphinocarbenes. Stable carbenes have also allowed the facile preparation of otherwise synthetically challenging or even unknown compounds. Striking examples are the aminoketenes, methylene phosphonium salts, diphosphinocarbocations (in their open and closed forms), and phosphonium ylides. Last but not least, reactivity patterns without equivalent for transient species have been evidenced such as radical fragmentation of aminohydrazinocarbenes, reaction at the periphery of the carbene center of aminophosphinocarbenes, and nucleophilic substitution at the carbene center of aminophosphoniocarbenes. In addition, the ability of aminoalkylcarbenes to activate H_2 and NH_3, in an analogous manner to transition metals, emphasizes the interest in fine-tuning the degree of carbene perturbation.

The coordination chemistry of noncyclic carbenes has also attracted considerable attention. The direct synthesis of phosphinocarbene complexes by complexation of a stable phosphinoarylcarbene has been reported, and significant progress has been achieved in the preparation of aminocarbenes complexes, both by direct coordination of stable/persistent carbenes and by generation of the carbene moiety within the coordination sphere of metals. The nature and strength of the carbene−metal bonds have been assessed experimentally and theoretically, revealing common features but also noticeable differences between phosphino- and aminocarbenes. The use of acyclic aminocarbenes as ligands in transition metal mediated catalysis is still in its infancy, compared to *N*-heterocyclic carbenes. However, the encouraging results obtained over the past few years should stimulate further investigations in this area, in order to take advantage of the structural modularity and electronic and coordination flexibility of acyclic carbenes.

Although the variety of stable/persistent acyclic carbenes has been spectacularly increased over the past few years, numerous challenges are still to be overcome and are likely to stimulate synthetic and/or computational chemists in the future: (i) diversify the π-donating group to group 16 elements and to carbon-based moieties (phosphonium and sulfonium ylides have already been used in cyclic versions,[191] and push−pull allenes have been shown to have some carbene character[192,193]); (ii) diversify the withdrawing group in push−pull stabilized carbenes to carbon-based moieties (carbonyl, cyano,...) and group 13 elements; (iii) prepare push−pull stabilized aminocarbenes; (iv) prepare push−spectator stabilized carbenes featuring other leaving groups than a phosphonio group (ammonium, sulfonium, iodonium,...); (v) prepare new polyfunctional compounds combining carbenes and classical (in)organic functionalities; (vi) prepare hydrogeno- and halogenocarbenes that would be isolatable or at least characterizable under standard conditions; and (vii) further decrease the degree of carbene perturbation to allow the isolation or at least characterization under standard conditions of carbenes in both the singlet and triplet states.[194]

The increasing variety of available carbenes, combined with the fine-tuning of stability/reactivity, will clearly contribute to new developments, not only in carbene chemistry itself but also in the synthetic applications of these new compounds. In particular, further achievements can be expected in the use of acyclic carbenes as synthons for organic synthesis and as ligands for transition metals. Their involvement as organo-catalysts and their ability to react with small molecules also seem most promising.

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