Carbene Complexes of Nonmetals

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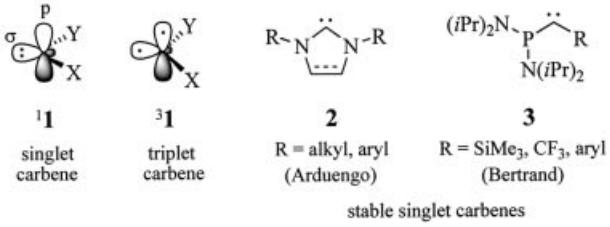
Electrophilic carbenes accept a variety of n- and π-donors. The products range from persistent ylides to matrix-isolated xenon complexes. Ylides can be viewed as carbene complexes if they regenerate carbenes *thermally* or undergo *concerted* methylene transfer reactions. According to these definitions, the present review focuses on oxonium and iodonium ylides. Transient π-complexes appear to be involved in addition reactions of carbenes with arenes (but not with alkenes). Nucleophilic carbenes form adducts with Lewis acids which are, for the most part, stable and have been well characterized structurally. Only recently attention has been directed to reversible systems.

1. Introduction

Carbenes (**1**) are neutral, divalent derivatives of carbon.[1] The carbene carbon has two electrons not involved in bonding which can be spin-paired (singlet state) or unpaired (triplet state). As a rule, carbenes are highly reactive intermediates that can be isolated, at best, in solid matrices at very low temperatures.[2] However, with appropriate substituents, stable singlet carbenes,[3] such as **2** and **3**, and long-lived triplet carbenes have been obtained (Scheme 1).[4]

Complexation is a more versatile method of "taming" a carbene. Transition metal complexes of carbenes have been advanced to a position of prominence in synthetic organic chemistry:

· Stable transition-metal-carbene complexes, as exemplified by **4**, have been employed in a wide range of stoichiometric transformations, which include carbene transfer, cycloaddition, cyclization, and benzoanellation (the Dötz reaction).[5]



Scheme 1. Structure and stability of carbenes

· Transition-metal compounds that are also Lewis acids catalyze dinitrogen extrusion from diazo compounds to form transient metal carbenes, which undergo carbene transfer to multiple bonds and (intramolecular) C−H insertion reactions. Extraordinary levels of enantioselectivity have been achieved through the design of chiral catalysts based on rhodium, copper, and cobalt.[6]

· Alkylidene complexes of tungsten, molybdenum, and ruthenium catalyze the olefin metathesis reaction (Scheme 2).[7] Commercial polymers are made by ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET), while cross metathesis (CM) and ring-opening metathesis (ROM) are applied in organic synthesis. Ring-closing metathesis (RCM), effected by **5**−**7**, is extremely useful for macrocyclization en route to natural products and biologically active compounds.[8]

In transition-metal-carbene complexes, the carbene binds to the metal as a σ-donor/π-acceptor ligand. With heteroatom-substituted carbenes, π-donation from the heteroatom competes with π-donation from the metal. Consequently, in a series of otherwise similar complexes **4**, the length of the metal−carbon bond increases with increasing donor strength of X and Y. Strongly stabilized carbenes,

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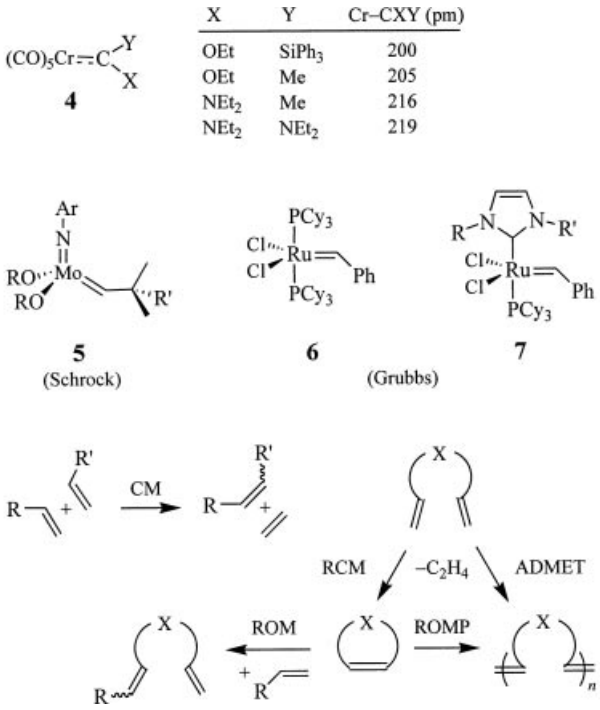


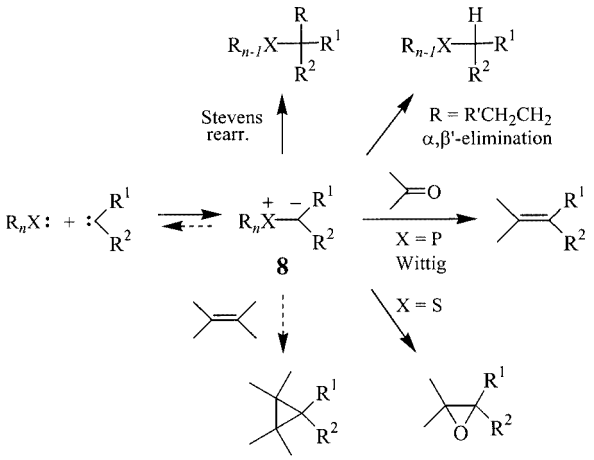
Scheme 2. Metal carbene complexes and olefin metathesis

such as **2**, are believed to bind a metal as almost pure σ-donors. Thus, the Ru=CHPh bond lengths in complexes **7** are between 180−185 pm, while the Ru−CN(N′) bond lengths are between 205−209 pm.[8b] The diaminocarbene ligand of the "second generation" catalyst **7** replaces a phosphane ligand of the "first generation" catalyst **6** with a concomitant increase in activity; in both cases the catalytic site is the Ru=CHPh bond. Similar replacements proved to be very fruitful in various areas of catalysis.[9] As a result of their unique donor properties, diaminocarbenes form complexes even with alkali metals.[10]

Carbene complexes of nonmetals have been investigated extensively though not systematically. The enormous variations in structure, bonding, and reactivity are both fascinating and challenging. The aim of the present review is to organize the scattered data, to localize "blank spots", and to encourage the application of these complexes in synthesis and catalysis. The focus is on (derivatives of) carbon, nitrogen, phosphorus, oxygen, sulfur, the halogens, and xenon. Metalloids (semimetals) such as boron, silicon, germanium, arsenic, selenium, and tellurium have also been covered, though less exhaustively.

2. Carbene Complexes versus Ylides

Heteroatoms with nonbonding electron pairs accept electrophilic carbenes to produce ylides **8** (Scheme 3).[11] Alternatively, ylides are made by deprotonation of onium ions. Isolable ylides have been obtained with X = N, S, P, and I if R^1 and/or R^2 are electron-withdrawing groups. Less stable ylides undergo [1,2]-shifts of R (Stevens rearrangement) and α,β′-elimination. With allylic R groups, [3,2]-shifts compete or predominate. Useful intermolecular ylide reactions include the conversion of ketones into alkenes (X = P, Wittig reaction) and oxiranes (X = S).



Scheme 3. Formation and reactions of ylides

The general view of bonding in ylides is that the heteroatom donates electron density to the carbene carbon atom. The computed bond lengths (Table 1) depend only slightly on the theoretical method (HF,[12−14] MP2,[13−18] B3LYP,[17−19] QCISD[20]) and the basis set employed. Double-bond character is occasionally assigned to the short C−X bonds of phosphonium and sulfonium ylides.[21] Alternatively, the ylidic bonds to P and S are thought to be shortened due to the attraction between the oppositely charged C and X. Accordingly, the C−P and C−S bonds of "stabilized" ylides (where negative charge is withdrawn from C by electron acceptors) are longer than those of non-stabilized analogues (Table 1).[22−24] When X is a highly electronegative atom (N, O), the C−X bond is longer than a single bond. Here, the positive charge of the R_nX fragment resides mainly on R when X is negatively charged, leading to electrostatic repulsion between C and X. Electron-withdrawing groups on carbon tend to shorten such C−X bonds.[25]

Table 1. Bond lengths ($^+$X−C$^-$) of ylides **8**

X	Computed pm	rel.[a]	ref.	Experimental pm	rel.[b]	ref.
N	155−159	1.07	[13−15,18]	147−150[c]	1.01	[25]
O	171−183	1.25	[13,17,18,20]			
P	167−168	0.89	[12−14,17,18]	166−170[d]	0.91	[23]
				170−173[c]	0.93	[22]
S	164−168	0.90	[12−14,17,18]	171−175[c]	0.95	[24]
I	216−230	1.00−1.07	[19]	204−213[c]	0.95−1.00	[26]

[a] Computed bond lengths of R*n*X−CR^{1}R^2 (R, R^1, R^2 = H, Me) relative to bond lengths of H*n*X−CH$_3$ computed by the same method. [b] Bond lengths from crystal structure analyses of ylides relative to common C−X bond lengths. [c]Data for "stabilized" ylides (R^1,R^2 = electron-withdrawing groups). [d] Data for Ph_3PCH_2,[23a] Me_3PCH_2,[23b] and R_3PCHAr.[23c,23d]

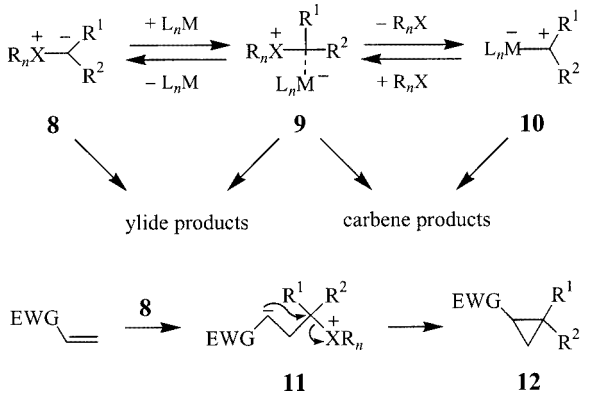
From a structural point of view, ylides can be regarded as carbene complexes if their C−X bonds are significantly longer than single bonds. Oxonium ylides conform to this definition. However, the relative bond lengths of ammonium and iodonium ylides do not differ. Experimentally, iodonium ylides show some evidence of reversibility (see below), whereas ammonium ylides do not. Binding energies (ylide relative to R_nX + R^1R^2C:) should be more relevant. Although the computed binding energies depend on the method employed (Table 2),[13,17] the following trends are observed: (a) the order of binding energies is O ≈ I < N ≈ S < P; (b) ylides Me_nX-CH_2 are more strongly bound than ylides H_nX-CH_2;[17c,17d] (c) for ylides $H_nX-CR^1R^2$, the activation energies for 1,2-H shift are lower than the binding energies.[13,17,20] Such species are, at best, fleeting intermediates in the course of X−H insertion reactions (H_nX + $:CR^1R^2 \rightarrow H_{n-1}X-CHR^1R^2$).

Table 2. Computed binding energies of ylides (most stable conformers)

X	H_nX-CH_2 kJ/mol	method	ref.	Me_nX-CH_2 kJ/mol	method	ref.
O	79	MP2A[a]	[13]			
	40	MP2C[a]	[17a,17b]	87	MP2C[b]	[17d]
	25	QCISD(T)[c]	[20]			
	44	DFT[d]	[17b]			
N	170	MP2A[a]	[13]			
	175	MP2C[b]	[17f]	237	MP2C[b]	[17f]
P	291	MP2A[a]	[13]			
	276	MP2C[b]	[17c]	369	MP2B[e]	[17c]
S	181	MP2A[a]	[13]			
	167	MP2C[b]	[17e]	245	MP2C[b]	[17e]
	147	DFT[f]	[17e]	205	DFT[e]	[17e]
I	25	DFT[g]	[19]	52[h]	DFT[g]	[19]

[a] MP2/6-31G*. [b] MP2/6-311++G(d,p). [c] QCISD(T)/6-311++G**. [d] B3LYP/6-311++G**. [e] MP2/6-31+G(d). [f] B3LYP/6-31+G(d). [g] B3LYP/LANL2DZ. [h] Refers to Ph-I-CH_2.

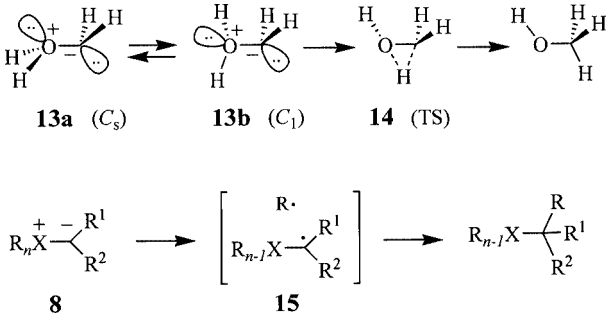
As for reactivity, ylides can be regarded as carbene complexes if they regenerate carbenes *thermally* or undergo *carbene transfer* with alkenes. Alternative routes to carbene-derived products must be excluded: (a) Carbenes can be generated photochemically from stable sulfonium[27,28] and iodonium ylides.[19,29−31] (b) Transition-metal complexes catalyze carbene transfer reactions of sulfonium[11a] and iodonium ylides.[32] The product distributions of these reactions are similar to those obtained by the catalyzed decomposition of diazo compounds,[33] pointing to the intervention of transition-metal-carbene complexes **10**. However, the asymmetric induction observed with nonracemic catalysts[34,35] indicates that transition metal-ylide complexes **9** are also involved in product formation (Scheme 4). (c) Sulfonium ylides form cyclopropane derivatives from electron-deficient alkenes (EWG = COR, CO_2R, CN, SO_2R, and NO_2) by a sequence of Michael addition (→ **11**) and 1,3-elimination (→ **12**, Scheme 4).[36] Even dienes,[37] arylalkenes,[38] and fullerenes[39] appear to react analogously. Nevertheless, some oxonium ylides and iodonium ylides show the attributes of carbene complexes, as will be summarized below.



Scheme 4. Alternatives to direct carbene transfer from ylides

2.1. Oxonium Ylides

The water-methylene complex, H_2O-CH_2 (**13**), is the simplest oxonium ylide. Neutralization−reionization studies of $H_2O-CH_2^{\bullet+}$ in a tandem mass spectrometer indicated that an appreciable fraction of **13** must have survived the microsecond lifetime of the experiment.[40] According to computational studies,[17a,17b,20] the potential energy surface for **13** is very flat. Local minima that differ by 1−4 kJ/mol were found for the C_s conformer **13a** and for the C_1 conformer **13b** (Scheme 5). The computed barrier to 1,2-H shift (2−7 kJ/mol) is only a fraction of the binding energy (Table 2). Hence regeneration of CH_2 from **13** *in the gas phase* is unlikely. However, a small to negligible barrier was computed (3−21G) for direct methylene transfer from **13** to ethylene.[41] Water as a *solvent* raises the computed barrier for 1,2-H shift to 27−29 kJ/mol, whereas the binding energy of **13** is only slightly affected (polarizable continuum model).[17b,20] The QCISD//MP2 level of theory predicts competitive dissociation and 1,2-H shift of **13** *in water*.[20]

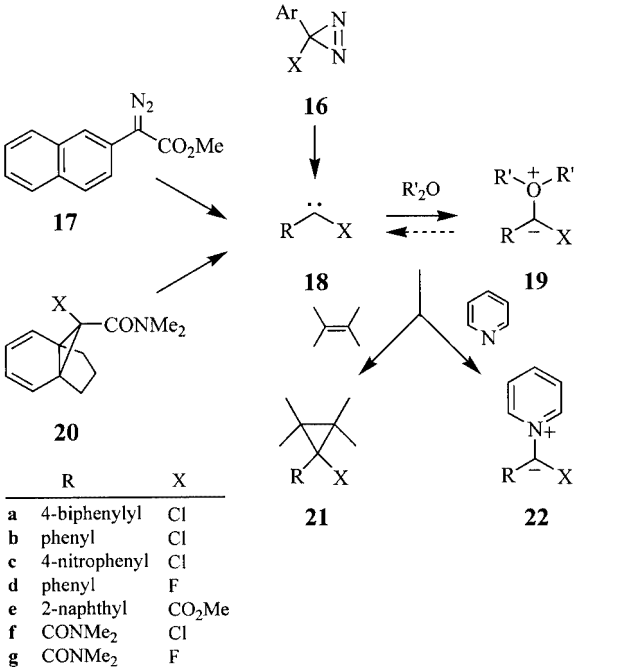


Scheme 5. Rearrangement of ylides

As a rule, oxonium ylides of the type $R_2O-CR^1R^2$ (R = alkyl, aryl) do not rearrange readily. The exceptions include ylides derived from strained cyclic ethers (oxiranes, oxetanes), which undergo ring expansion.[42] A wealth of experimental evidence points to a bond homolysis/radical recombination pathway for 1,2-shifts of ammonium and sulfonium ylides (Scheme 5).[11] This view has also been supported computationally for N[43] and P ylides.[44] In the

oxonium ylide series, the detection of radical-derived products (e.g. R−R) and a migratory aptitude of R that correlates with radical stability are indicative of the homolysis/radical recombination mechanism as well.[45] Ylides derived from acetals and ortho esters are thought to rearrange by way of ionic intermediates.[46]

The intervention of oxonium ylides in carbenoid reactions has been studied by time-resolved spectroscopy. Laser flash photolysis (LFP) of (biphenyl-4-yl)chlorodiazirine (**16a**) in isooctane generated the carbene **18a** ($\lambda_{max.}$ = 360 nm, Scheme 6). In the presence of THF, the absorption shifted to 375 nm, and the reaction rates of **18a** with tetramethylethylene (TME) and with pyridine decreased moderately.[47] The data were interpreted in terms of a carbene-ylide equilibrium with $K = 0.5\ M^{-1}$. (Analogous experiments with propionitrile[48] and 2-vinylpyridine[49] gave K = 0.45 M^{-1} and $K = 80\ M^{-1}$, respectively). Various arylhalocarbenes, **18b**−**d**, were investigated by means of time-resolved IR spectroscopy (TRIR).[50] Ethers were found to affect the C−X vibrations and the reaction rates with TME only slightly.[50,51] Arylhalocarbenes have singlet ground states, due to electron-donation from the halogen atoms to the divalent carbon. Therefore, complexation with external donors does not contribute strongly to the stability of these species.

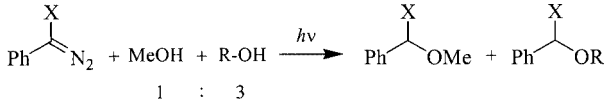


	R	X
a	4-biphenylyl	Cl
b	phenyl	Cl
c	4-nitrophenyl	Cl
d	phenyl	F
e	2-naphthyl	CO_2Me
f	$CONMe_2$	Cl
g	$CONMe_2$	F

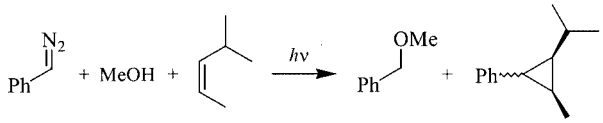
Scheme 6. Oxonium ylides studied by time-resolved spectroscopy

In contrast, 2-naphthyl(methoxycarbonyl)carbene (**18e**) is a spin-equilibrated carbene with a small singlet/triplet energy gap ($\Delta G \approx 0.8$ kJ/mol).[52] LFP of the diazo precursor **17** in the presence of THF generated a long-lived ylide **19e** whose rate of formation was proportional to the concentration of THF.[53] However, the intermolecular reactivity of **19e** was not explored. More evidence was adduced from LFP studies of **20**.[54] By means of TRIR, and of computed IR frequencies, the carbenes **18f** ($\nu_{C=O}$ = 1635 cm^{-1}) and **18g** ($\nu_{C=O}$ = 1650 cm^{-1}) were distinguished from the analogous ylides **19f**,**g** ($\nu_{C=O}$ = 1560−1610 cm^{-1}). The THF-derived ylides **19f** and **19g** reacted with TME ($k = 1.8 \times 10^6\ M^{-1}s^{-1}$ and $2.8 \times 10^7\ M^{-1}s^{-1}$, respectively) more slowly than the carbenes **18f** and **18g**, by factors of 23 and 7, respectively. The data point to stronger complexation of **18f**,**g**, relative to **18a**−**d**, but do not reveal the mechanism by which the ylides **19f**,**g** react with TME.

Indirect evidence for carbene complexation comes from product distributions, as influenced by the presence of ethers. Both solvent effects and directing effects of alkoxy substituents have been studied. The discrimination of arylcarbenes between pairs of alcohols, and between methanol and alkenes, was found to be affected by ethers (Scheme 7).[55] The unique effect of 1,4-dioxane was attributed to its low basicity, relative to THF.[56] Weak bonding of the carbene is thought to promote carbene transfer, whereas strong bonding leads to ylide rearrangement. However, the O−H insertion reactions of carbenes are intricate processes[57] whose rates are controlled, among other factors, by aggregation (hydrogen bonding) of the alcohols.[58] Thus, aside from carbene complexation, there are additional ways for ethers to intervene.



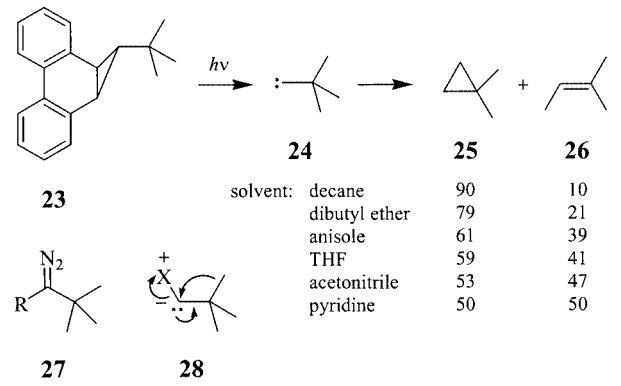
	X	R	additive (60%)	$k_{MeOH} : k_{ROH}$
a	H	*t*Bu	none	1.85
			THF	3.92
			1,4-dioxane	16.5
	H	*i*Pr	none	1.45
			1,4-dioxane	6.57
b	CO_2Me	*t*Bu	none	6.87
			THF	7.21
			1,4-dioxane	17.8



additive (60%)	$k_{MeOH} : k_{add}$
none	1.04
benzene	1.14
1,4-dioxane	6.49

Scheme 7. Modification of arylcarbene reactivities by ethers

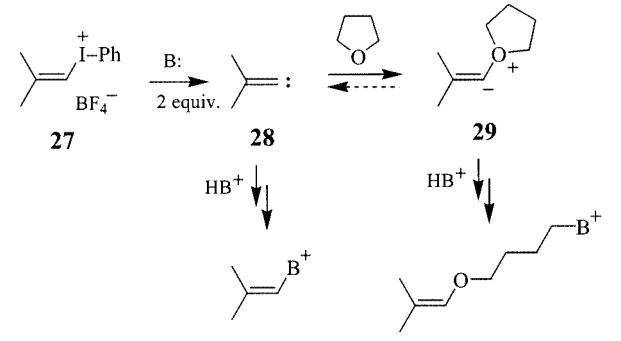
The competing intramolecular reactions of *tert*-butylcarbene (**24** → **25** + **26**) were also found to be affected by donor solvents, including ethers (Scheme 8).[59] Similar effects were seen on photolysis of the carbene precursor **23** and on thermolysis of (*tert*-butyl)diazomethane (**27**, R = H). The enhanced formation of alkene **26** was attributed to a concerted migration−elimination of the ylide **28**, although there is little precedent for such a mechanism (as a rule, methyl groups migrate to the vacant carbene p-orbital).[60] However, all carbene-stabilizing substituents R (Ph,[61] Cl,[62] CO_2Et,[63] $COCMe_3$ [64]) lower the cyclopro-



Scheme 8. Solvent effects on the reactivity of *tert*-butylcarbene

pane to alkene ratio obtained from **27** relative to that of the parent compound (R = H). This effect can be explained in terms of the Hammond postulate: the formation of **26** is more exothermic than that of **25** by 32−34 kJ/mol, hence more alkene will be produced as the activation barriers increase and the transition states become more product-like. Complexation of carbene **24** should induce analogous changes.

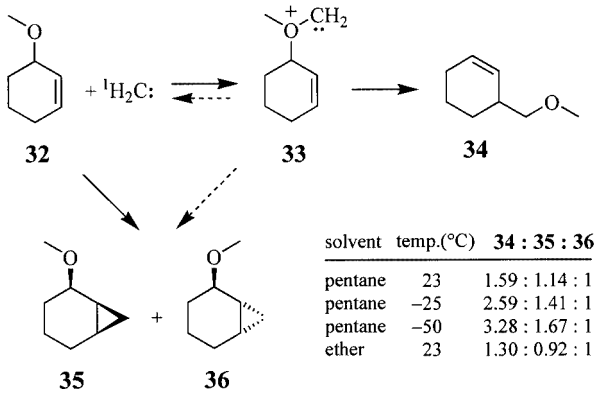
Treatment of the iodonium salt **27** with base generates 2-methylpropenylidene (**28**) by way of an α-elimination (Scheme 9).[65] In the presence of THF, the major products were **30** and **31**, the latter is clearly derived from the ylide **29**. The product ratios were found to depend strongly on temperature, lower temperatures favor **31**. These findings were explained in terms of *reversible* ylide formation. At elevated temperatures, **29** is thought to dissociate with regeneration of **28**, thus enhancing the fraction of product **30**.



B:	Temp. (°C)	30	31
Et_3N	25	45	55
	-20	29	71
	-78	19	81
DBN	25	47	53
	-78	5	95
DBU	25	31	69
	-78	3	97

Scheme 9. Reversible ylide formation of dimethylvinylidene with THF

The reaction of 3-methoxycyclohexene (**32**) with singlet methylene afforded three major products, which result from a [3,2] sigmatropic shift of the ylide **33** (→ **34**) and from cyclopropanation of the double bond (**35** +**36**) (Scheme 10).[66] Three different methylene precursors were used, each of which showed a small preference for *syn* addition to the methoxy group (the data in Scheme 10 are for diazomethane). Steric considerations would predict a preference for *anti* addition, as observed with 3-methylcyclohexene. The ratio of **35** to **36** was found to increase with decreasing temperature, concomitant with an increase in **34**. The data suggest that ylide **33** (or a weaker complex of **32** with methylene) transfers CH_2 to the *syn* face of the double bond. A lower *syn*/*anti* ratio and a smaller fraction of **34** were obtained in the presence of ether, consistent with competing complexation of CH_2 by solvent. With 3-methylcyclohexene, the *syn*/*anti* ratio (0.95) was found to be independent of solvent and temperature. Therefore, a specific reversible interaction of methylene with the methoxy group of **32** has been clearly demonstrated. When methylene was added to 7-methoxynorbornene, similar effects were seen.[66a] However, the results are less conclusive, owing to the inherent *exo* preference of the norbornene skeleton.

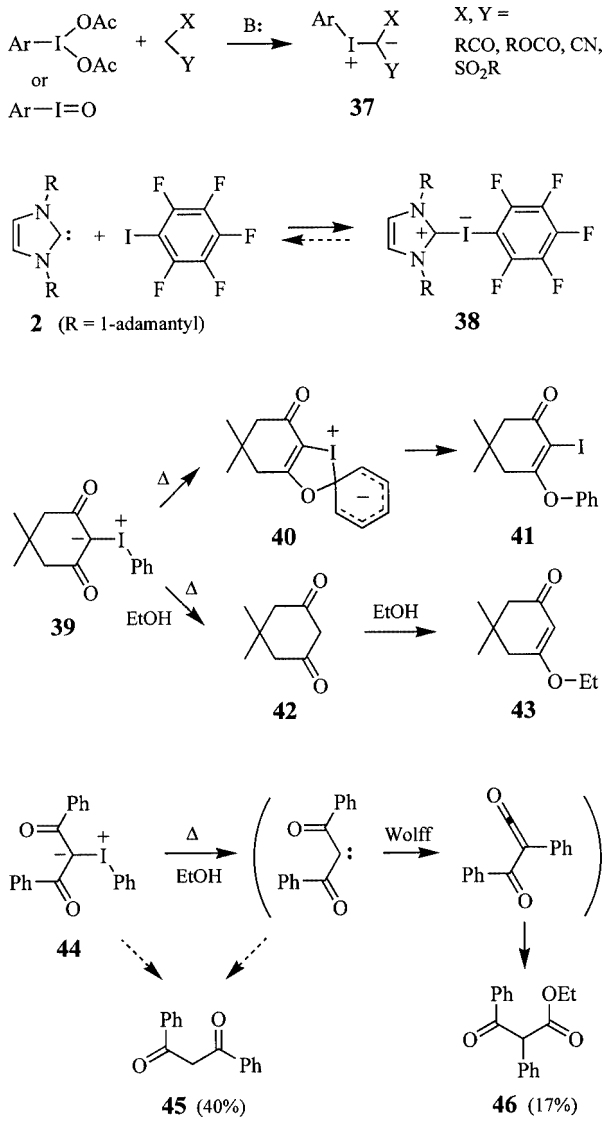


solvent	temp.(°C)	34 : 35 : 36
pentane	23	1.59 : 1.14 : 1
pentane	−25	2.59 : 1.41 : 1
pentane	−50	3.28 : 1.67 : 1
ether	23	1.30 : 0.92 : 1

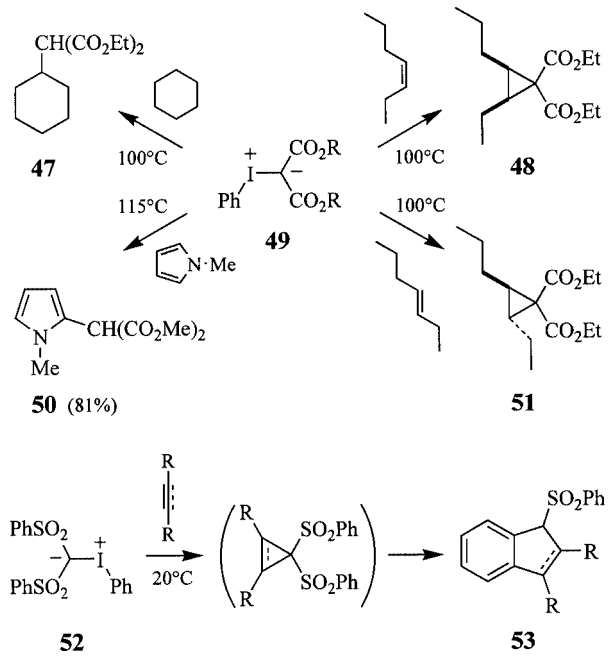
Scheme 10. Stereodirecting effect of a substrate methoxy group

2.2. Iodonium Ylides and Related Species

In contrast to the fleeting oxonium ylides, many iodonium ylides are isolable compounds.[32] The method of choice for the efficient preparation of "stabilized" iodonium ylides **37** is the reaction of iodosoarenes or iodosoarenediacetates with 1,3-dicarbonyl compounds or -disulfones (Scheme 11). The $Rh_2(OAc)_4$-catalyzed decomposition of 2-diazo-1,3-dicarbonyl compounds in the presence of aryl iodides also affords **37**.[67] The ylides **37** can be viewed as complexes of *electrophilic* carbenes with aryl iodides. On the other hand, the *nucleophilic* carbene **2** reacts with pentafluoroiodobenzene to give the reverse ylide **38**, which is stable in solid form.[68] The iodanide character of **38** is reflected by a nearly linear structure, whereas the C−I−C angles of **37** range from 85 to 99°. In solution, **38** equilibrates with free carbene and iodoarene (NMR spectroscopy). Reversibility is more difficult to demonstrate with **37**. While photolysis[19,29−31] and catalysis[29,32−35,69] readily induce the carbenic reactivity of **37**, examples of thermal dissociation are rare. Thermolysis of the dimedone-derived ylide **39** in aprotic solvents led to rearrangement, **39** → **41**,[70] by way of a five-membered transition state **40**.[71] On heating **39** in ethanol, 15% of **41** was formed, along with dime-



Scheme 11. Ylides derived from aryl iodides



Scheme 12. Reactions of iodonium ylides with C−H and C=C bonds

done (**42**, 10%) and its ethyl ether (**43**, 32%).[29] The latter products arise by hydrogen transfer from the solvent. Reduction prevailed in the thermolysis of ylide **44** in ethanol (→ **45**, 40%), but the ester **46** (17%) was also formed.[29] The Wolff rearrangement, **44** → **46**, points to intervention of a carbonylcarbene.

Ylide **49** was found to decompose in cyclohexane at 100 °C, affording the C−H insertion product **47** (46%) along with iodobenzene (80%) (Scheme 12).[19] The high-yielding reaction of **49** with the α-position of *N*-methylpyrrole, **49** → **50**, was employed in a synthesis of the anti-inflammatory agent tolmetin.[72] Thermolysis of **49** in the presence of (*Z*)- and (*E*)-3-heptene afforded the cyclopropanes **48** and **51**, respectively, in a stereospecific reaction (less than 2% of the "wrong" isomer was formed).[19] C−H insertion and stereospecific cyclopropanation, proceeding under the same conditions, strongly suggest the intermediacy of a singlet carbene. On the other hand, ylide **52** reacts at 20 °C with alkenes, particularly norbornenes,[30b,73] and alkynes[30b] to eventually give indanes/indenes **53**. The mild conditions argue against dissociation of the ylide. Alternative mechanisms have been proposed that involve a stepwise electrophilic addition of the iodonium center to the double bond, followed by reductive elimination of aryl iodide.[69b,69e,69h]

In summary, the reactions of iodonium ylides are mechanistically more intricate than computed binding energies would suggest. Kinetic studies should help to demonstrate the thermal generation of carbenes from iodonium ylides unequivocally. Scant evidence exists for carbene complexes of other organic halides. 3-Chlorocyclohexene showed directive effects in reactions with methylene, similar to those observed with 3-methoxycyclohexene (Scheme 10).[66] The preference for tertiary to primary C−H insertion by ^{1}:CH−CO_2Et was enhanced in the presence of perfluorohexane.[74] Calculations support the formation of carbene-fluoroalkane complexes as a possible origin of the solvent effect.

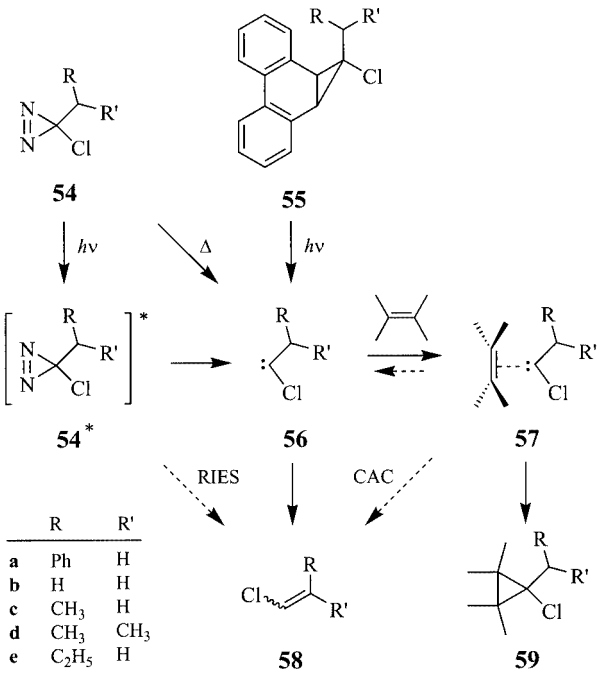
3. Complexation with π-Systems

3.1. Alkenes

The addition to alkenes, with the formation of cyclopropanes, is the most important and best-studied reaction of carbenes. The intervention of carbene-alkene complexes (CAC) was first postulated on the basis of absolute rate constants, measured by time-resolved spectroscopy.[75] Arrhenius plots with a positive slope were obtained for certain carbene-alkene addition reactions, e.g. Ph−C−X (X = F, Cl, Br),[75] $PhCH_2$−C−Cl,[76] and $PhCH(CH_3)$−C−Cl[77] with tetramethylethylene (TME). A positive slope implies a negative E_a, which was initially thought to exclude

a single-step reaction. However, Houk pointed out that a negative E_a can be the consequence of a highly exothermic *bimolecular* reaction. Here, ΔH decreases from the start while ΔG reaches a maximum due to the increase in $-T\Delta S$.[78] This interpretation does not require a CAC en route to cyclopropanes.

The debate on carbene-alkene complexes was revived by studies with 3-alkyl-3-chlorodiazirines (**54**).[79] The alkylchlorocarbenes **56** generated from **54** undergo 1,2-H shift (→ **58**) and addition to alkenes (→ **59**) competitively (Scheme 13). If **56** was the only intermediate, the ratio **59/58** would increase linearly with the concentration of alkene. However, curved plots were obtained on photolysis of **54**,[80] as shown for **54a** − TME in Figure 1. The curvature



Scheme 13. Mechanisms proposed for alkylchlorocarbene chemistry

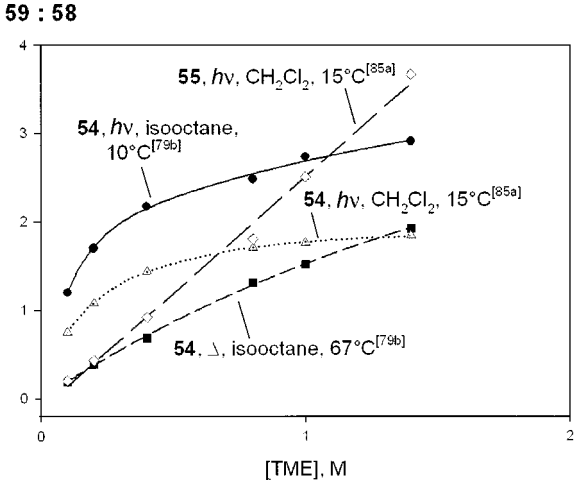
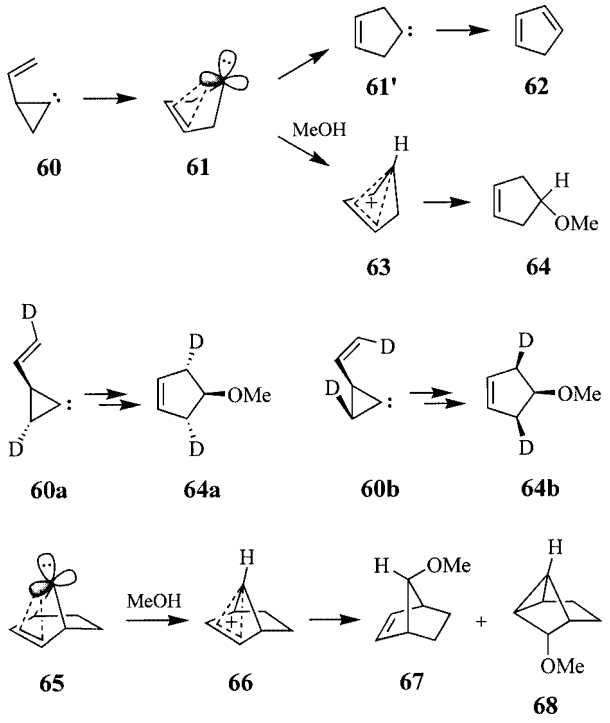


Figure 1. Plots of product ratio **59a/58a** versus concentration of tetramethylethylene (TME), obtained with precursors **54a** and **55a** of benzylchlorocarbene (**56a**)

implies a (second) precursor to **58** that is not scavenged by alkene, even at infinite concentration. Liu and Bonneau assigned this role to CAC **57**,[80][81] while rearrangement in the excited state (RIES) of the diazirine (1,2-H shift in concert with extrusion of nitrogen) was advocated by Goodman,[82] Platz,[83] and Moss.[84] The yields of carbenes **56** generated by photolysis of **54** were found to depend on the strength of the α-C−H bond, for example, **54b/54c/54d** = 0.52:0.28:0.024.[83a] These and other observations support RIES, but do not necessarily exclude CACs. The problem was eventually solved by means of the non-nitrogenous carbene precursor **56**, which gave a linear plot of **59/58** vs. [alkene] (Figure 1).[85] Clearly, RIES is the major source of "excess" **58** in photolyses of **54**; few data remain that are not readily explained by RIES.[81b,81d] Diazirines **54** photoisomerize to give diazo compounds, but this inefficient process ($\Phi = 0.08-0.15$)[85a,86] is not likely to affect the product distribution.

Theoretical studies describe the addition reaction of carbenes with alkenes as a concerted but highly asynchronous process, involving electrophilic (p-π) and nucleophilic (σ-π*) interactions. The "π-approach" of electrophilic carbenes, first proposed by Skell[87] and Moore,[88] was confirmed computationally by Hoffmann (EHT)[89] and Kutzelnigg (CEPA-2).[90] Kinetic isotope effects (^{13}C, ^{2}H) provide experimental evidence for a nonlinear attack of dichlorocarbene at 1-pentene.[91] Later calculations showed that halocarbene-alkene complexes could appear as broad, shallow wells in the reaction enthalpy profile, whereas these complexes did not represent minima on the free energy surfaces (CF_2 + ethylene,[92] CCl_2 + ethylene,[93] CHCl + ethylene,[94] Cl−C−CH_2Cl + ethylene and TME[95]).

In summary, conclusive evidence for carbene-alkene complexes has not been obtained, whether by experiment or computation. *Intermolecular* encounter of the reactants leads immediately to the formation of cyclopropanes. *Intramolecular* complexation, however, is more likely. With carbenes such as 3-cyclopentenylidene (**61**) and 7-norbornenylidene (**65**), addition to the internal C=C bonds cannot proceed to completion as the products would be prohibitively strained. Recent computations have shown that the Skattebøl rearrangement[96] of 2-vinylcyclopropylidene (**60**) initially produces the π-complex **61** (Scheme 14).[97] A barrier ($\Delta G^{\neq}$) of 16 kJ/mol protects **61** against conversion into the planar structure **61′**, which is computed to be more stable than **61** by 19 kJ/mol. A 1,2-H shift of **61′** eventually affords cyclopentadiene (**62**). Qualitatively similar conclusions had been drawn earlier from the fact that labeled **61** was scavenged stereoselectively (≥ 95%) with methanol (**60a** → **64a**, **60b** → **64b**).[98] These findings clearly exclude a planar intermediate on the reaction path from **60** to **64**. 7-Norbornenylidene (**65**) has attracted the attention of theoreticians as early as 1968.[99] Recent computations have shown that C-7 of **65** leans toward the double bond, and the C-2−C-7 distance (189 pm) is much shorter than the C-6−C-7 distance (266 pm).[100] Therefore, **65** can be viewed as a π-complex or as a homoaromatic carbene. The bonding in **61** and **65** is similar to that in the analogous



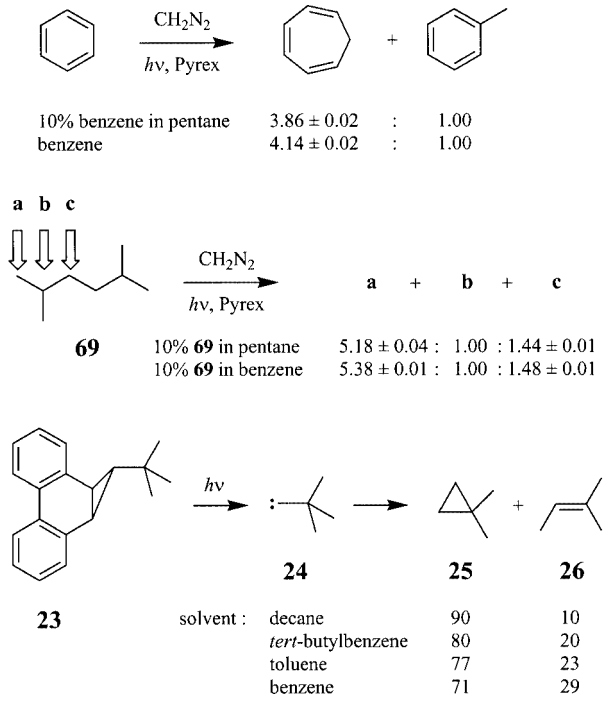
Scheme 14. Intramolecular π-complexation, homoaromatic carbenes

carbocations **63** and **66**, respectively. In fact, the reactions of **61** and **65** with methanol are thought to involve proton transfer as the first step.[101] In the case of **65**, the formation of **68** along with **67** attests to the intervention of **66**.[102]

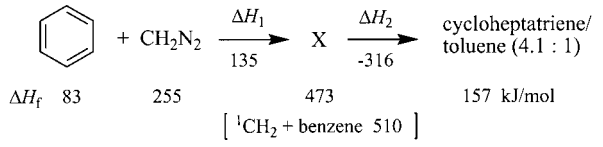
3.2. Arenes

Benzene affects the reactivity of singlet carbenes, including methylene. Early observations[103] were later confirmed by precise measurements.[104][105] When diazomethane was photolyzed in benzene-solvent mixtures, the ratio of cycloheptatriene to toluene was found to increase with the concentration of benzene (Scheme 15). Benzene also exerts a small effect on the insertion of methylene into the primary, secondary, and tertiary C−H bonds of 2,5-dimethylhexane (**69**).[104] The competing reactions of *tert*-butylcarbene (**24**), γ-C−H insertion (→ **25**), and 1,2-methyl shift (→ **26**) are more strongly influenced by aromatic solvents.[59] The data for *tert*-butylbenzene, an aromatic-aliphatic "composite", are intermediate between those for decane and benzene.

Khan and Goodman studied the thermochemistry of the methylene-benzene reaction by means of picosecond optical grating calorimetry.[106] LFP of diazomethane in benzene results in two heat depositions, corresponding to a fast (<100 ps) and a "slow" ($k = 2.4 \times 10^9$ s^{-1}) chemical process. ΔH_1 (135 kJ/mol) is associated with the formation of intermediate X, whereas ΔH_2 (−316 kJ/mol) refers to the conversion of X into products. Addition of ΔH_1 to the heats of formation of diazomethane and benzene leads to ΔH_f (X) = 473 kJ/mol (Scheme 16). The same number is obtained from ΔH_2 with the heats of formation of cycloheptatriene and toluene (4.1:1). As ΔH_f (X) is lower than the



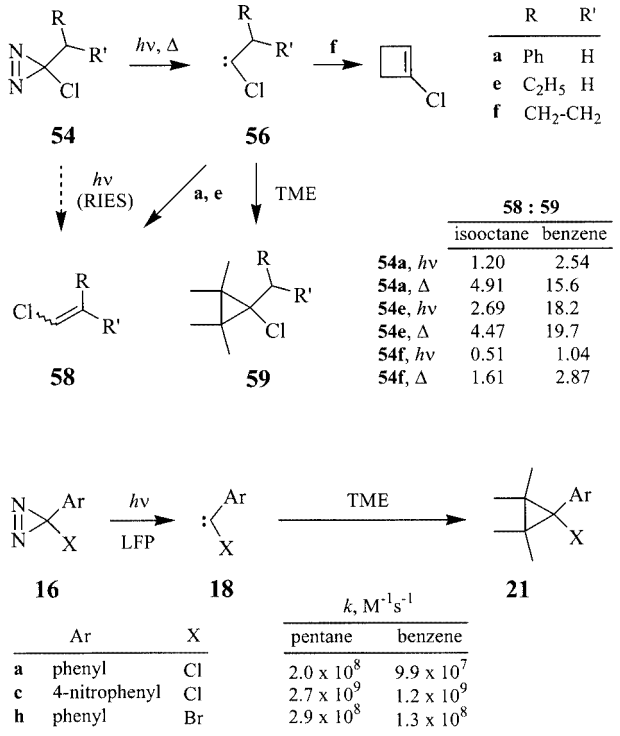
Scheme 15. Complexation of methylene and *tert*-butylcarbene with benzene



Scheme 16. Thermochemistry of the methylene-benzene reaction

sum of ΔH_f ($^1CH_2$) and ΔH_f (benzene) by 37 kJ/mol, it was concluded that X must be a methylene-benzene complex. However, ΔH_f values for CH_2N_2 have been computed (285 and 281 kJ/mol)[107][108] that exceed Goodman's. On the product side, the isomerization of norcaradiene to give cycloheptatriene ($k_{298} \approx 10^7$ s^{-1})[109] may not be complete on the time scale of the calorimetric experiment. In each case, the energy gap between X and $^1CH_2$ + benzene would become smaller.

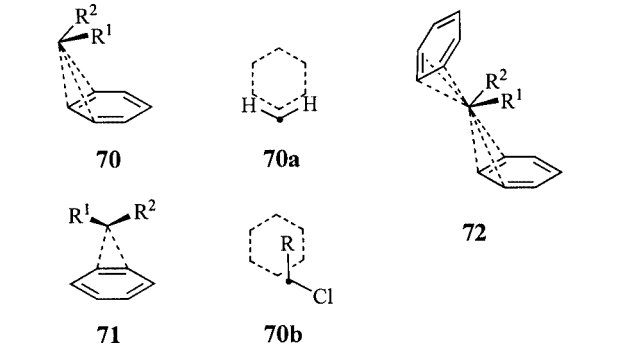
Rearrangement versus addition product studies for alkylchlorocarbenes (**56**) in several solvents have been reported (Scheme 17).[110] With carbenes **56a** and **56e**, the extent of 1,2-H shift increases, relative to the addition of TME, as the solvent is changed from isooctane to benzene. The behavior of carbene **56f** indicates that the effect also extends to ring expansion. The excited state contribution to rearrangement (RIES) cannot account for the solvent effect as RIES was found to be *greater* in isooctane than in benzene. Moreover, the solvent effect is pronounced with thermally generated carbenes. Therefore, the changes in product distribution are attributed to transient carbene-benzene complexes that interfere with intermolecular addition. In fact, the reaction of arylhalocarbenes **18** with TME proceeded more slowly in benzene than in aliphatic hydrocarbons, by factors of 2−3.[51] The C−X vibrational fre-



Scheme 17. Complexation of halocarbenes with benzene

quencies of arylhalocarbenes, on the other hand, are not significantly affected by the presence of benzene.[50]

The interaction of carbenes with benzene has also been scrutinized computationally. Two weak complexes of methylene, **70** and **71** ($R^1 = R^2 = H$), were located, which show the carbene center interacting either with a specific benzene carbon atom (**70**) or with the π-cloud above a C−C bond (**71**) (Scheme 18).[106] At the MP2/6-31G*//HF/6-31G* level of theory, **70** and **71** were found to be stabilized by 30 and 24 kJ/mol, respectively, relative to singlet methylene + benzene (no BSSE, vibrational or thermal corrections). The minimum energy conformation **70b** of the CCl_2-benzene system presents no overall molecular symmetry.[94] Relative to **70a**, the CCl_2 unit is rotated, with one Cl atom oriented toward the center of the benzene ring, and one Cl pointing away. The interaction energy of **70** ($R^1 = R^2 = Cl$) was estimated to be 10 kJ/mol [MP2(BSSE)/6-311+G**]. The benzene complex of chloro(methyl)carbene (**70**, R^1 = Cl, R^2 = Me) was found to be similar in geometry and stabilization (15 kJ/mol). As indicated in **70b**, the methyl group points to the center of the benzene ring. Stationary points were also located for 1:2 carbene-benzene complexes (**72**), which show about twice the stabilization energy of **70**.[94]

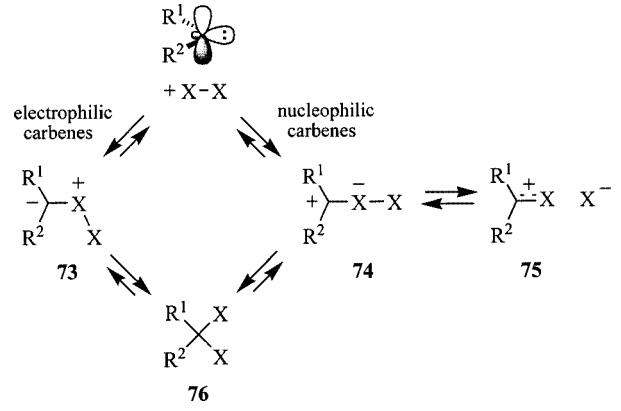


Scheme 18. Computed structures of carbene-benzene complexes

To summarize, both experimental and computational evidence of carbene-benzene π-complexes has been obtained, in contrast to carbene-alkene complexes. The addition of methylene to ethylene ($\Delta_r H = -427$ kJ/mol) is more exothermic than that to benzene ($\Delta_r H = -329$ kJ/mol). Chlorocarbenes react with arenes less efficiently[111] and less rapidly[112] than with alkenes. Most benzene derivatives are inert toward dihalocarbenes. Therefore, it has been suggested that carbene-benzene complexes may be more robust "because their continuation to product formation will be energetically less favorable".[110]

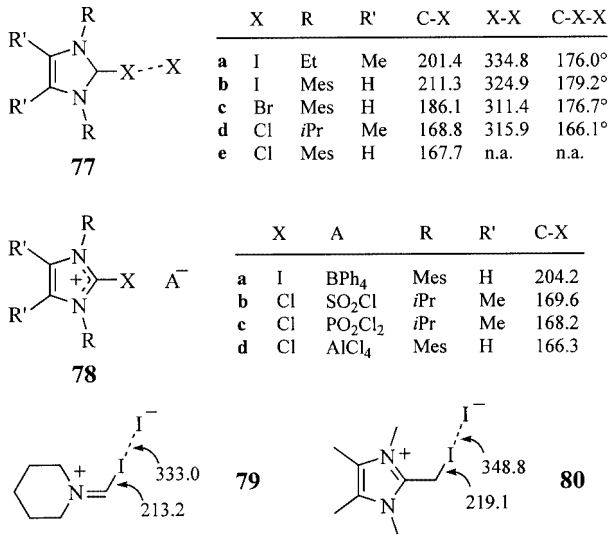
4. Complexation with Halogens

Two limiting cases can be defined for the interaction of carbenes with halogens: (a) The p-orbital of electrophilic carbenes attacks a lone electron-pair (more specifically, the π*-orbital = HOMO) of the halogen with formation of halonium ylides **73** (Scheme 19, left side).[113] A 1,2-shift of **73** eventually leads to geminal dihalides **76**. (b) The σ lone pair of nucleophilic carbenes interacts with the σ*-orbital (LUMO) of the halogen, generating the reverse ylide (halanide) **74** (Scheme 19, right side).[114] With amino groups as substituents R^1, R^2, the eventual product is likely to be ionic (**75**) rather than covalent (**76**).



Scheme 19. Interactions of carbenes with halogens

Crystalline adducts of dihydroimidazol-2-ylidenes with iodine,[115,116] bromine,[117] and chlorine[117,118] have been obtained. The nature of these compounds can be derived from their molecular structures (Scheme 20). Only a near linear geometry of C−X−X, as observed for **77a**−**c**, is compatible with the reverse ylide formula **74**. The chlorine adduct **77d** deviates from linearity,[118b] and **77e** does not display any close Cl−Cl contact.[117] The C−Cl bond lengths in **77d**,**e** agree closely with those in well-defined 2-chloroimidazolium salts **78b**−**d**,[117,119] thus confirming the saltlike nature of the chlorine adducts **77d**,**e**. On the other



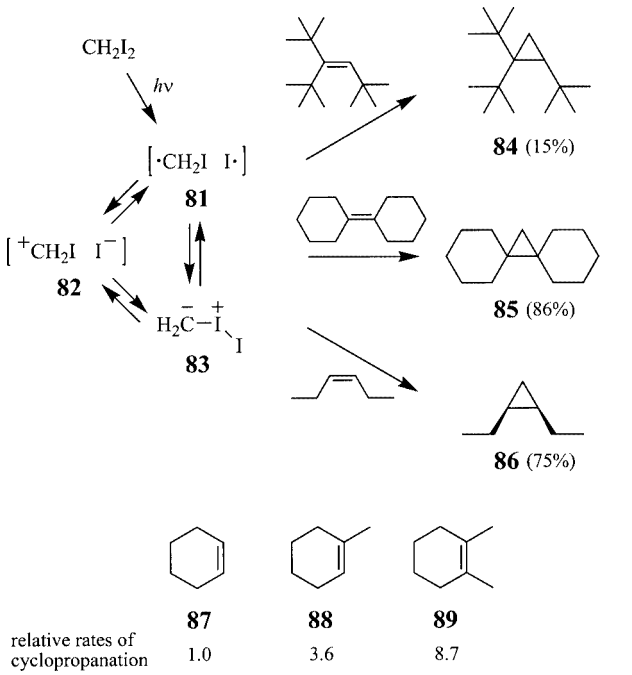
	X	R	R'	C-X	X-X	C-X-X
a	I	Et	Me	201.4	334.8	176.0°
b	I	Mes	H	211.3	324.9	179.2°
c	Br	Mes	H	186.1	311.4	176.7°
d	Cl	*i*Pr	Me	168.8	315.9	166.1°
e	Cl	Mes	H	167.7	n.a.	n.a.

	X	A	R	R'	C-X
a	I	BPh_4	Mes	H	204.2
b	Cl	SO_2Cl	*i*Pr	Me	169.6
c	Cl	PO_2Cl_2	*i*Pr	Me	168.2
d	Cl	$AlCl_4$	Mes	H	166.3

Scheme 20. Halogen adducts of nucleophilic carbenes and related structures (interatomic distances in pm)

hand, the C−I bond of **77b** is slightly longer than that of the analogous salt **78a**.[116] With I_2 adducts of thiones, phosphanes, etc., a broad spectrum of structures and I−I distances was found, ranging from D···I_2 (272−285 pm) over D−I−I (of about 290 pm) to $^+$D−I···I^- (> 300 pm).[120] According to these standards, the bonding in **77a**,**b** is classified as $^+$D−I···I^-, with largely covalent C−I and largely ionic I−I bonds. This conclusion is reinforced by comparing **77a**,**b** with **79**[114] and **80**.[121] Formally, these compounds are diaminocarbene−I_2, aminocarbene−I_2, and alkene [2-(methylene)tetrahydroimidazole]−I_2 adducts, respectively. In spite of the divergent nature of the "donors", the C−I and I−I distances of **77a**,**b**, **79**, and **80** differ only slightly. This is incompatible with D···I_2 or D−I−I structures for any of these compounds. Therefore, the adducts **77a**,**b** are best described as 2-iodoimidazolium iodides with hypervalent (n−σ*) I−I contacts.

Halonium ylides **73** cannot be generated from electrophilic carbenes as the carbene precursors (diazo compounds, ketenes) react readily with halogens. However, the reverse approach, starting from geminal dihalides **75**, has been successfully pursued. In the 1960s, the photolysis of diiodomethane in the presence of alkenes was found to give cyclopropanes (Scheme 21).[122] Similarly, triiodomethane afforded iodocyclopropanes.[123] As a preparative method, the photolysis of diiodomethane never enjoyed the popularity of the Simmons−Smith reaction (CH_2I_2 + Zn/Cu, Zn/Ag, or ZnR_2).[124] Light absorption by iodine slows the conversion of diiodomethane. Moreover, photoexcited iodine reacts with solvent to produce hydrogen iodide, which tends to isomerize cyclopropanes. For a complete and clean reaction, the CH_2I_2/alkene/solvent mixture must be stirred with aqueous $Na_2S_2O_3$/$NaHCO_3$ while being irradiated.[125] Under these conditions, some 20 alkenes formed cyclopropanes with yields that range from 15% for **84** to 86% for **85**. The addition is stereospecific (see **86**) and less sensitive to steric effects than the Simmons−Smith method (which does not



Scheme 21. Cyclopropanation reactions with photoexcited diiodomethane

afford **84**). The methylene transfer agent produced by photolysis of diiodomethane behaves as an electrophile (see relative rates of **87**−**89**). It is distinguished from singlet methylene by its enhanced selectivity and by the lack of C−H insertion. After considerable speculation about the potential role of the iodomethyl radical (**81**), the iodomethyl cation (**82**), and the iodonium ylide **83**,[126] the nature of the intermediate was recently explored by means of spectroscopic and computational methods.

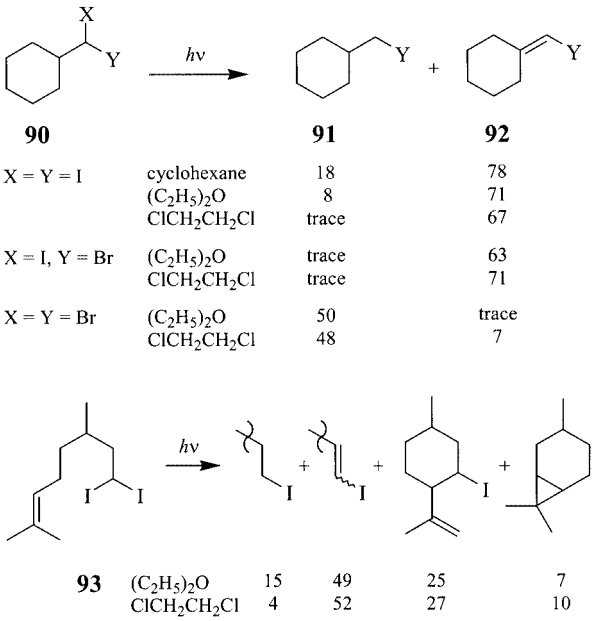
Photolysis (313 nm) of diiodomethane in an argon matrix at 12 K gave rise to a colored species ($\lambda_{max.}$ = 745 and 438 nm), which was assigned as "isodiiodomethane" **83** by comparison of the observed and computed IR spectra.[127] Warming or irradiation (366 or 545 nm) of matrix-isolated **83** led to partial regeneration of diiodomethane. Similar results were obtained with other dihalomethanes CH_2XY (X, Y ≠ F),[127] and even with tetrachloromethane.[128] If two different halogens were present, the heavier halogen migrated (the weaker C−X bond was broken).

Ultraviolet excitation of diiodomethane in solution produces transient absorption bands (λ_{max} ≈ 385 and 570 nm), which have been assigned to a number of different species.[129] Nanosecond[130] and picosecond[131] transient resonance Raman investigations demonstrated that isodiiodomethane **83** is mostly responsible for the intense absorption band at about 385 nm. Both **83** and the $CH_2I_2^+$ cation appear to contribute to the weak transient absorption band at approximately 570 nm.[132] At high concentrations of CH_2I_2, a CH_2I_2···I molecular complex has also been observed.[133] With the use of time-resolved resonance Raman spectroscopy, isodiiodomethane **83** was found to react with cyclohexene on the 5−10 ns time scale. Iodine is produced, which almost immediately forms a I_2···cyclohexene com-

plex.[134] These results suggest that **83** is the methylene-transfer agent in light-induced cyclopropanation reactions of CH_2I_2 with alkenes. DFT investigations confirm that **83** reacts with ethylene to give cyclopropane in a one-step process with a barrier height of approximately 12 kJ/mol.[135] The reactions of iodomethyl radical (**81**) and iodomethyl cation (**82**) with ethylene show two-step profiles with larger potential barriers,[135] whereas $CH_2I_2\cdots I$ transfers iodine rather than CH_2.[133] The potential utility of **83** for the cyclopropenation of alkynes has also been explored computationally.[136] Isodiiodomethane **83** was found to react with methanol and with water, by way of O−H insertion/HI elimination, on the 1−5 ns time scale.[137]

Experimental and computational studies have been extended to a series of isopolyhalomethanes (Table 3). Picosecond resonance Raman spectra indicated that CH_2Cl-I ($\lambda_{max.} \approx 460$ nm) is mainly produced on 267 nm excitation of chloroiodomethane in acetonitrile.[138] This species appears to decay and form the more stable isomer CH_2I-Cl ($\lambda_{max.} \approx 370$ nm) after a few hundred ps. Similarly, fs and ps spectroscopy of bromoiodomethane led to the observation of CH_2Br-I,[139] whereas only CH_2I-Br was detected on the ns time scale.[140] The computed barriers for the reaction of CH_2X-X with ethylene are 12, 28, and 37 kJ/mol for X = I, Br, and Cl, respectively.[141] For the regeneration of CH_2X_2 from CH_2X-X, the computed barrier heights are 60, 49, and 38 kJ/mol for X = I, Br, and Cl, respectively. These data correlate well with experimental observations on light-induced methylene transfer, which works efficiently with CH_2I_2, poorly with CH_2Br_2, and not at all with CH_2Cl_2.[122,125] Computed barrier heights also indicate that CH_2Br-I should be superior to CH_2I-Br, and CH_2Cl-I superior to CH_2I-Cl, as a methylene−transfer agent.[142] Photolysis of CHI_3 generates $ICHI-I$[143] whose lifetime was found to be approximately 1.8 and 0.2 μs in cyclohexane and acetonitrile, respectively.[144] In contrast to the results obtained for CH_2I-I, the computed barrier height for the concerted reaction of ethylene with $ICHI-I$ (43 kJ/mol) exceeds that for the stepwise reaction with $^{\cdot}CHI_2$ (36 kJ/mol).[143] Therefore, the mechanism of iodocyclopropanations[123] is not clearly defined.

The conclusions drawn from dihalomethane studies are not applicable to the photoreactions of 1,1-dihaloalkanes (Scheme 22). As illustrated with (dihalomethyl)cyclohexanes **90**,[150] the major photolysis products arise by reduction (→ **91**)[151] and elimination of HX (→ **92**). The ratio of these products depends strongly on the nature of the halogen and of the solvent. In the case of a quaternary β-carbon atom, rearrangement was observed (Me_3C-CHI_2 → $Me_2C=CHMe$).[150,152] Photoexcited 1,1-dihaloalkanes do not undergo intermolecular cyclopropanation reactions, and intramolecular cyclopropanation is only a minor process with 8,8-diiodo-2,6-dimethyl-2-octene (**93**).[150] The products indicate that haloalkyl radicals **81** and haloalkyl



Scheme 22. Photolysis products of 1,1dihaloalkanes

Table 3. Computed structural and energetic parameters (kJ/mol) for isopolyhalomethanes

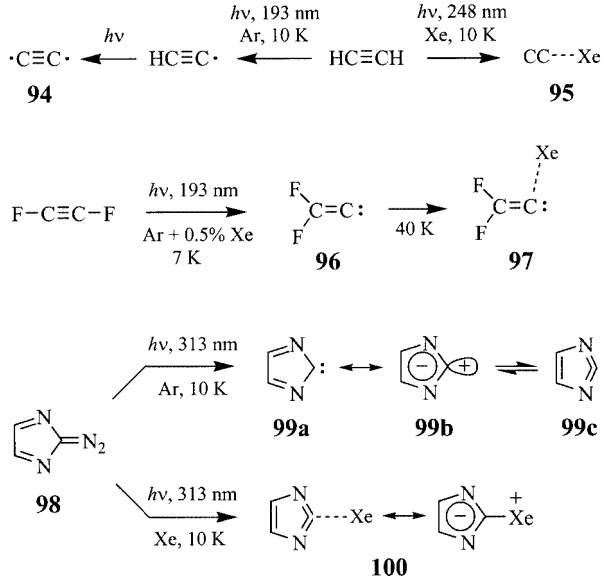
Species	Spectroscopy ref.	∠C−X−Y[a]	*E*, relative to polyhalomethane	Barrier to ethylene addition	Computation ref.
CH_2I-I	[130−133]	116.8°[b]	175[c]		[145]
		121.8°	169	12	[141,146]
CH_2I-Br	[140]	121.0°	173	13	[142]
CH_2I-Cl	[138]	120.6°	188	14	[142]
CH_2Br-I	[139]	123.5°	191	10	[142]
CH_2Br-Br	[147]	122.3°	204	28	[141]
CH_2Br-Cl		122.3°		16	[148]
CH_2Cl-I	[138]	123.7°	209	10	[142]
CH_2Cl-Cl		121.4°	246	37	[141]
$ICHI-I$	[143]	131.0°	129	43	[143,146]
$BrCHBr-Br$	[146]	128.4°[d]	179[d]		[146]
$ClCHBr-Br$	[148]	127.2°[d]			[148]
$HO_2CCHBr-Br$	[149]	118.9°			[149]
$Br_2CBr-Br$	[146]	149.1°[d]	137[d]		[146]

[a] B3LYP/Sadlej-pVTZ unless noted otherwise. [b] MP2/6-31G(d). [c] G2. [d] B3LYP/6-31G(d,p).

cations **82** predominate over carbene-halogen complexes **83** in the photochemistry of 1,1-dihaloalkanes.

5. Complexation with Xenon

In low-temperature matrices, "super-electrophilic" carbenes[153] form complexes with xenon. Dicarbon (C_2, **94**) is a powerful electrophile (EA = 3.27 eV)[154] with a singlet ground state ($X^1\Sigma g^+$). The carbenelike behavior of C_2 is due to a doubly occupied, weakly antibonding HOMO ($2\sigma_u$) and a low-lying LUMO ($3\sigma_g$).[155] Irradiation (193 nm) of acetylene in an argon matrix produced C_2H and C_2 consecutively (Scheme 23). In contrast, only the xenon complex C_2Xe (**95**) was observed upon photolysis of acetylene at 248 nm in a xenon matrix.[156] The most remarkable feature of **95** is the CC stretching fundamental (1767.0 cm^{-1}, IR-active) which is close to that of C_2^- (1757.8 cm^{-1}) and is red-shifted by 60.5 cm^{-1} relative to that of C_2 (1827.5). The linear structure of C_2Xe is consistent with electron donation from xenon into the vacant $3\sigma_g$-orbital that is oriented along the internuclear axis.[156,157] The computed C−Xe bond length of C_2Xe (approximately 270 pm)[157] is much shorter than the sum of the van der Waals radii (386 pm) but is significantly longer than the experimental C−Xe bond length in $(C_6F_5)_2Xe$ (235−239 pm).[158]



Scheme 23. Xenon complexes of highly electrophilic carbenes

Irradiation of difluoroacetylene at 193 nm generates difluorovinylidene (**96**) by way of a 1,2-F shift.[159] Difluorovinylidene is a strong electrophile (EA = 2.26 eV)[160] whose LUMO is described best as the in-plane p-orbital at the terminal carbon. In a 0.5% Xe-doped argon matrix at 7 K, **96** ($\nu_{C=C}$ = 1672 cm^{-1}) was produced, which reacted with Xe on annealing of the matrix at 40 K to give the complex **97** ($\nu_{C=C}$ = 1620 cm^{-1}).[159b,159c] The bent structure (∠ C−C−Xe = 102°) computed for **97** is consistent with electron donation from xenon into the in-plane vacant p-orbital of **96**.

Experiment[161] and theory[153][162] support the electrophilic character of imidazol-2-ylidene (**99**), as visualized by the resonance structure **99b**. However, the computed N−C−N angle of 143° suggests a major contribution of the strained carbodiimide **99c** to the overall structure.[162] Photolysis of 2-diazo-2*H*-imidazole (**98**) in an argon matrix generated **99**, which was identified by comparison with the computed IR spectrum. Irradiation of **98** in xenon matrices led to several new IR bands, some of which were assigned to the xenon complex **100**. Computations indicate that the N−C−N angle of **99** becomes smaller (about 130°) through complexation with Xe. This effect causes the N−C−N stretching vibration to shift from ca. 1707 cm^{-1} in **99** to ca. 1520 cm^{-1} in **100**.[162]

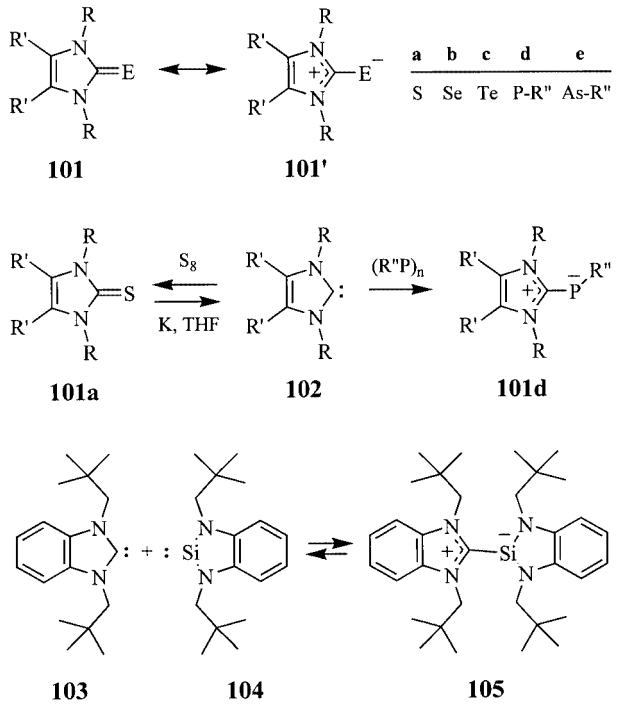
6. Miscellaneous Complexes of Nucleophilic Carbenes

With few exceptions, complexes of electrophilic carbenes are elusive species that are difficult to detect and characterize. In contrast, nucleophilic carbenes form stable adducts with a large variety of electrophiles.[3c,163] Cyclic diaminocarbenes **2** have been the most popular substrates. As a rule, dihydroimidazol-2-ylidenes persist as monomers. Tetrahydroimidazol-2-ylidenes tend to dimerize unless they are kinetically stabilized by bulky substituents.[164] Monomer-dimer equilibria have also been observed.[165] Adducts of these carbenes with aryl iodides **38** and halogens **77** have been mentioned in previous sections, and many more will be reviewed below. Some of these adducts undergo reversible dissociation while others do not, or have not been studied to that end.

6.1. Adducts with Nominal Double Bonds

Nominal C=E double bonds are created if chalcogens (S, Se, Te) or pnictinidenes (PR, AsR) are attached to the divalent carbon atom (**101**, Scheme 24). The contribution of ylidic structures **101′** depends on the nature of E. The C−S bond lengths of dihydroimidazol-2-thiones **101a** (167−168 pm) are more similar to those of C=S double bonds (about 160 pm) than to those of C−S single bonds (about 182 pm).[166] In contrast, the C−Te bond lengths of **101c** (205−209 pm) approach that of a C−Te single bond (about 212 pm).[167] The nominal P=C double bond of **101d** (176−179 pm) is long for typical phosphaalkenes (about 167 pm) and slightly shorter than the P−R′′ (R′′ = Ph) single bond (182−184 pm).[168] The geometry of the imidazole ring in **101d** (∠ N−C−N = 104−105°) is intermediate between that of the carbene **102** (∠ N−C−N = 101.5°) and that of imidazolium ions (∠ N−C−N = 108−109°). The NMR spectra of **101d**,**e** indicate rapid rotation about the C−E bond at room temperature.

Dihydroimidazole-2-thiones (**101a**) can be prepared by various routes,[169] including the reaction of **102** with cyclooctasulfur.[170] Compounds **101b**−**e** have been obtained exclusively by the reaction of **102** with $(E)_n$.[167,168,171] No evidence for thermal regeneration of **102** from **101** has been



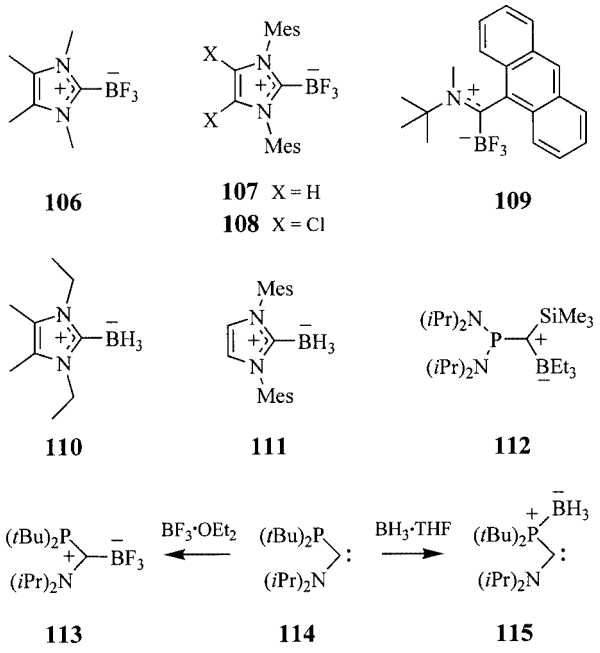
Scheme 24. Adducts of dihydroimidazol-2-ylidene adducts with chalcogens, pnictinidenes, and silylenes

reported, although desulfurization of **101a** with potassium is a useful route to **102**.[164,172]

Stable silylenes[173] failed to react with **102**[174] although adducts of **102** with GeI_2,[175] $SnCl_2$,[176] and $SnAr_2$ [177] have been reported. However, mixing of the benzodihydroimidazol-2-ylidene **103** with the isoleptic silylene **104** afforded the adduct **105**.[178] According to the crystal structure of **105**, the long central bond of 216.2 pm is strongly twisted, the carbon atom is in an almost planar environment but the silicon in a pyramidal environment.[178a] Silenes (C=Si ≈ 170 pm) and even silanes (C−Si ≈ 190 pm) have shorter C−Si distances. Variable-temperature ^{13}C and ^{29}Si NMR spectra of **105** revealed the presence of a dissociative equilibrium in solution; dissociation of **105** into **103** and **104** was nearly complete at ca. 85 °C. Similar observations were made with germylene and stannylene adducts of **103**, the order of stability is Sn > Ge ≥ Si.[178b]

6.2. Reverse Ylides

In the preceding section (6.1.), reverse ylides (**101′**, **101d**, **105**) appeared as resonance structures of C=E double bonds. The present section covers reverse ylides that cannot engage in multiple bonding. Scheme 25 shows a selection of carbene-borane adducts (**106**−**111**) for which crystal structures were obtained. The C−B bond lengths of **106**[179] and **107**[180] are similar to those of reference compounds $[RBF_3]^-M^+$ (Table 4). The C−B bond in **108** (166.9 pm) is slightly longer than that in **107** (163.5 pm), which may indicate weaker bonding in **109** due to the electron-withdrawing Cl atoms.[180] A rather long C−B bond (168.8 pm) was also found in **109**, an amino(aryl)carbene complex with only one



Scheme 25. Carbene-borane adducts obtained from the components

stabilizing amino group.[181] The C−B bonds of the BH_3 adducts **110**[182] and **111**[183] are comparable with those of $[RBH_3]^-M^+$ (Table 4). Judging from the bond lengths, the adducts **106**−**111** are reasonably represented as ylides (Scheme 25). However, the N−C−N bond angles of **106**−**108**, **110**, and **111** (104−105°) are contracted relative to those of imidazolium ions (108−109°), as would be expected of carbene complexes. Compounds **106**−**111** were obtained from the appropriate carbenes with BF_3·OEt_2,,[179,180] BF_3·THF,[181] BH_3·SMe_2 [182] and BH_3·THF,[183] respectively. None of the aminocarbene-borane adducts gave evidence of dissociation at ambient temperature.

Table 4. Carbon−boron bond lengths (pm) of carbene-borane adducts and reference compounds

Compound	C−B (pm)	ref.	Compound	C−B (pm)	ref.
106	163.8	[179]	$[MeBF_3]K$	157.5	[186]
107	163.5	[180]	$[PhBF_3]K$	161	[187]
108	166.9	[180]			
109	168.8	[181]			
110	160.3	[182]	$[MeBH_3]Li$	159.7	[188]
111	159.6	[183]	$[(tBu)_2BH_2]K$	164.3	[188]
118	159.6	[191]			
120	164.5	[192]	$[Ph_4B][NR_4]$	164-165	[189]
121	163.4	[193]	Ph_3B-NR_3	162-164	[189]
125	162.3	[194]		163.2	[190]
127	163.3	[195]			

Borane adducts of phosphanylcarbenes proved to be less robust. The adduct **112**, derived from a phosphanyl(silyl)-carbene, was observed by NMR spectroscopy at −80 °C, but decayed rapidly due to elimination of Et_2BNR_2.[184] Bifunctional behavior was reported for the amino(phosphanyl)-

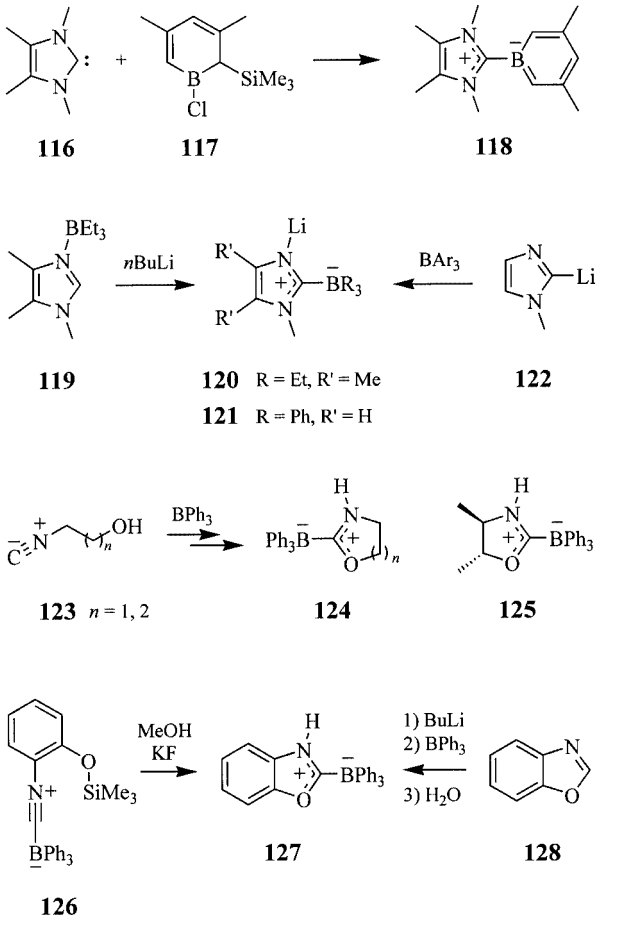
carbene **114**: selective interaction of BF_3 with the carbene center (**113**) was demonstrated by NMR spectroscopy, whereas coordination of the softer Lewis acid BH_3 occurred at the phosphorus atom (**115**, crystal structure).[185]

Complexation has served to stabilize otherwise elusive boranes and carbenes. A borabenzene-dihydroimidazol-2-ylidene adduct was obtained by reaction of borabenzene precursor **117** with carbene **116** (Scheme 26).[191] Borane adducts of *N*-lithiated dihydroimidazol-2-ylidenes (**120**, **121**) were prepared either from imidazol-borane complexes **119** with butyllithium,[192] or from 2-lithiated imidazoles **122** and triarylboranes.[193] When ω-hydroxyalkyl isocyanides **123** were treated with triarylboranes, the transient complexes of **123** cyclized rapidly to give borane adducts of dihydrooxazol-2-ylidene (**124**, $n = 1$) and perhydrooxazin-2-ylidene (**124**, $n = 2$).[194] The silyl ethers of **123** gave stable borane adducts whose reaction with KF-MeOH afforded **124**. The same procedure was used to convert **126** into the dihydrobenzoxazin-2-ylidene-borane adduct **127**.[195] Compound **127** was also obtained from benzoxazole (**128**) by a route that is analogous to the conversion of **122** into **121**.[196] Dihydrooxazol-2-ylidenes [= amino(oxy)carbenes] would be expected to be weaker donors than dihydroimidazol-2-ylidenes (= diaminocarbenes). However, the C−B bond lengths of their borane adducts are nearly the same, as attested by crystal structures of **125**[194b] and **127** (Table 4).[195]

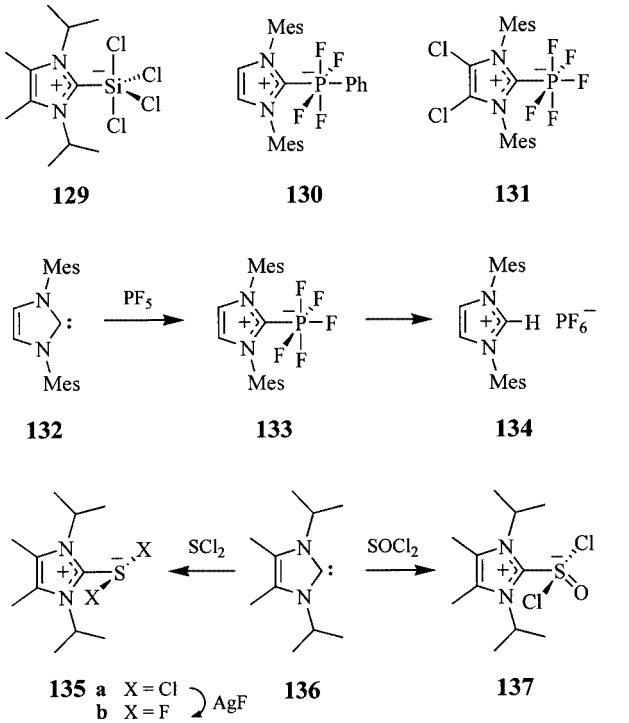
Several dihydroimidazol-2-ylidenes **102** afforded adducts with $SiCl_4$, $SiMe_2Cl_2$, $SiPh_2Cl_2$, and $SnPh_2Cl_2$.[197] The crystal structure of **129** shows that Si is in a trigonal-bipyramidal environment, the carbene ligand assuming an equatorial position (Scheme 27). Both the C−Si bond length (191.1 pm) and the N−C−N angle (107.1°) are unexceptional.[197]

The carbene **132** and $PhPF_4$ were found to give the stable adduct **130** with an octahedral geometry.[198] The carbene−phosphorus bond of **130** (191.0 pm) is somewhat longer than the phosphorus−phenyl bond (184.2 pm), and the N−C−N angle (105.0°) is intermediate between those in **132** (101.4°) and in the imidazolium salts (108−109°). In the reaction of **132** with PF_5, the adduct **133** was a minor product, which readily decomposed to give of the imidazolium salt **134**.[180] The 4,5-dichloro derivative of **132** provided the stable PF_5 adduct **131** (P−C 189.8 pm) in 60% yield; analogous adducts of AsF_5,[180] SbF_5,[180] and $Sb(CF_3)_3$ [199] were also obtained. Few trivalent phosphorus compounds have been studied: a stable adduct was formed from the carbene **136** and Mes−N=PCl,[200] whereas the transient adducts generated from carbenes **103** and **116** with phosphaalkynes were transformed into 1,2,4-triphospholes, 1,2,3-triphosphetenes, and azaphospholenes.[201]

The carbene **136** reacted with SCl_2 and $SOCl_2$ to give the adducts **135a** and **137**, respectively.[202] The crystal structure of **135a** shows a T-shaped geometry. The Cl−S−Cl angle is 175.9° and the Cl−S−Cl plane intersects the N−C−N plane at an angle of 84.5°. In **137**, the oxygen atom assumes an equatorial position, formally replacing a nonbonding electron pair of **135a**. The C−S bond length of **137** (181.1



Scheme 26. Carbene-borane adducts obtained by indirect routes

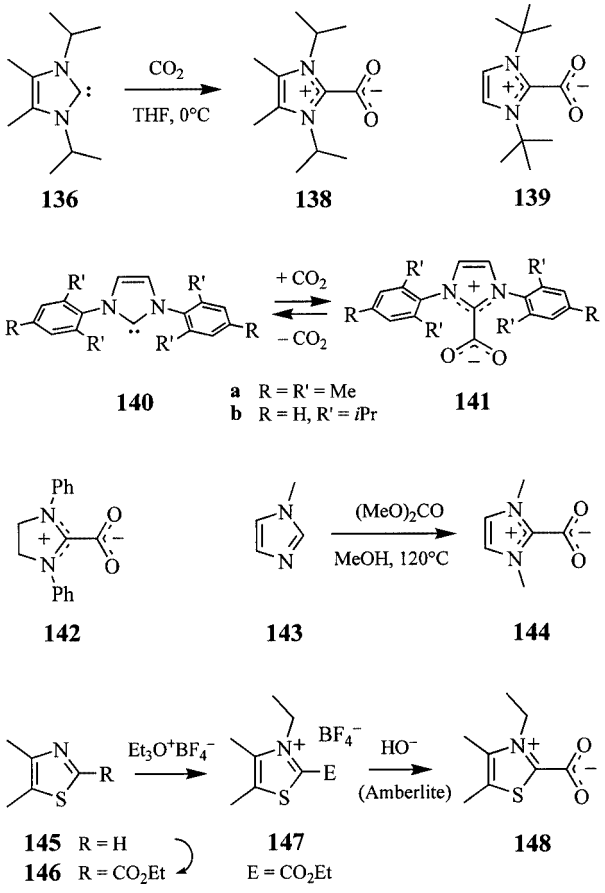


Scheme 27. Adducts of dihydroimidazol-2-ylidenes with halides of silicon, phosphorus, and sulfur

pm) is typical of a single bond, whereas that of **135a** (173.2 pm) is somewhat shorter. The N−C−N angles of both **135a** (108.3°) and **137** (109.3°) are similar to those of imidazolium ions. Adduct **135a** fragments with dissociation of the S−Cl bonds (rather than the C−S bond) to give an imidazol-2-thione (**101a**). Conversely, bromination of **101a** produced bromine analogues of **135** (X = Br).[203] Compound **135b**, the nominal adduct of **136** with SF_2, was prepared by exchanging the chlorine atoms of **135a** with fluorine. Reactions of **136** with SF_4, SO_2ClF, and SO_2F_2 gave rise to 2-fluoroimidazolium salts rather than to adducts.[202]

6.3. Betaines

Nucleophilic carbenes accept various heterocumulenes X=C=Y with formation of betaines. Thus carbon dioxide was found to react with carbene **136** at 0 °C, affording the imidazolium-carboxylate **138** (Scheme 28).[204] The betaines **139**[205] and **141**[206] were also obtained from the appropriate carbenes and CO_2. Indirect and non-carbenic routes to such betaines are also available. Hydrolysis of a carbene-isocyanate adduct (see below) afforded **142**.[207] Heating of 1-methylimidazole (**143**) with dimethylcarbonate provided 1,3-dimethylimidazolium-2-carboxylate (**144**).[208] This one-pot procedure should proceed similarly to the stepwise preparation of 3-ethyl-4,5-dimethylthiazolium-2-carboxylate (**148**) from 4,5-dimethylthiazole (**145**) by way of **146** and **147**.[209] The planes of the imidazolium and carboxylate groups are twisted by 29° in **144**,[208] but are nearly perpendicular in **138**[204a] and **141b**,[206] due to the bulky substituents at nitrogen. The C−C bond length (**138**: 153.6 pm, **141b**: 151.1 pm, **144**: 152.3 pm) corresponds to that of a single bond and is not significantly affected by torsion. The betaine **138** has been employed as a neutral bridging ligand for titanium complexes, without significant changes in geometry.[204b]



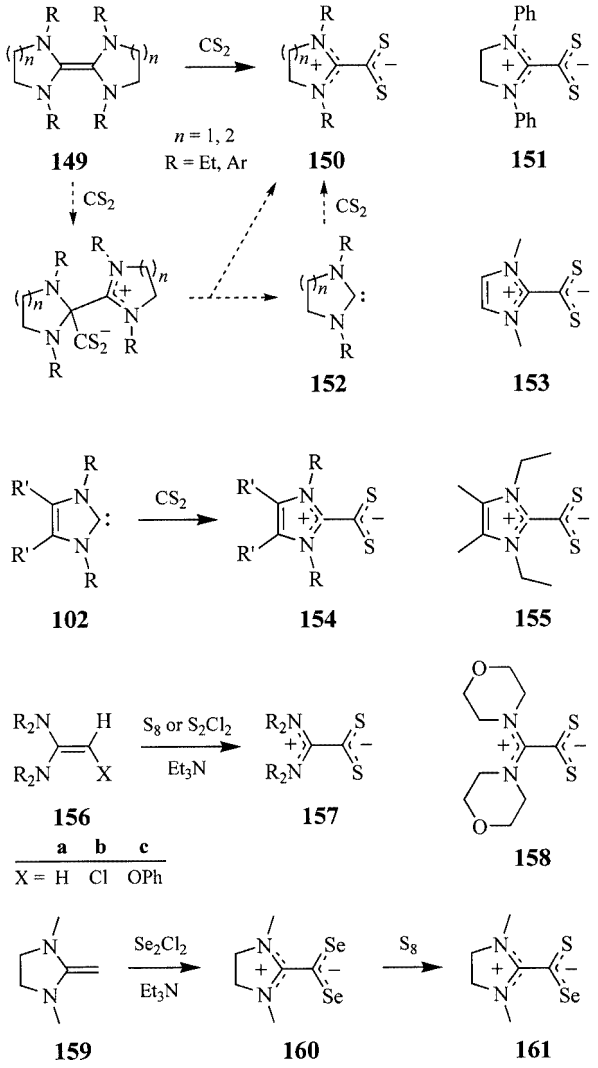
Scheme 28. Betaines derived from nucleophilic carbenes and CO_2

The betaines **138** and **144** were purified by sublimation in vacuo; dissociation was not observed under these conditions. In contrast, the thiazolium betaine **148** is a rather unstable substance, which catalyzes benzoin condensations in solution, presumably due to regeneration of the carbene.[209] Related observations were made in low-temperature matrices. Irradiation of imidazole-2-carboxylic acid (Ar, 10 K, 254 nm) produced a species that was assigned (IR) as a complex of the parent dihydroimidazol-2-ylidene with CO_2.[210] Analogous irradiation of thiazol-2-carboxylic acid gave rise to "free" dihydrothiazol-2-ylidene.[211]

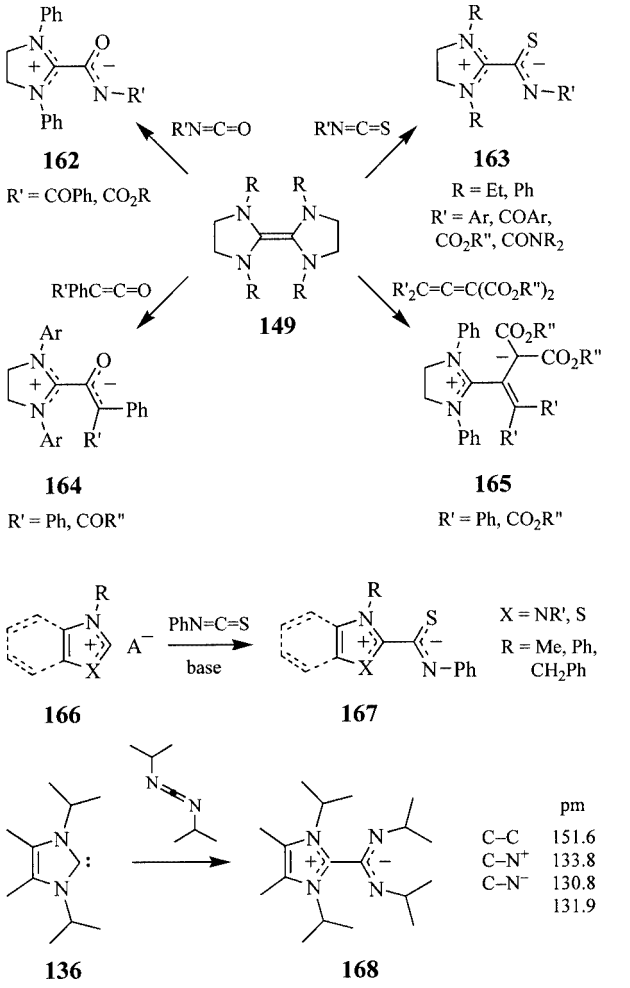
In the case of **141**, the thermal reversion of imidazolium-2-carboxylates to carbene and CO_2 was thoroughly investigated.[206] NMR spectroscopic studies suggested that bound CO_2 in **141b** equilibrates with free $^{13}CO_2$ (1 atm). Thermogravimetric analysis indicated decarboxylation of **141b** at 136−164 °C and of **141a** at 187−203 °C. The addition of **140a** to **141b** led to quantitative formation of **141a** and free **140b**. Similarly, addition of **136** to either **141a** or **141b** resulted in quantitative formation of **138** and **140a** or **140b**, respectively. According to these crossover experiments, the relative order for adduct stability appears to be **138** > **141a** > **141b**.

The carbene−CO_2 "adducts" are outnumbered by their sulfur analogues, which have been known since 1965. In contrast to CO_2, carbon disulfide is capable of cleaving tetraaminoethylenes **149** with formation of diaminocarbenium-dithiocarboxylates **150** (Scheme 29).[207,212] In a first step, the reaction is thought to produce **150** and carbene **152**, which is then captured by CS_2. This approach was later supplemented by the addition of stable dihydroimidazol-2-ylidenes to CS_2, **102** → **154**.[213] A non-carbenic route (to **157**), the sulfurization of enediamines **156**, also dates back to 1965.[214] Improved procedures utilize the reactions of **156b**,**c** with elemental sulfur, or of **156a** with S_2Cl_2.[215] The right hand side of Scheme 29 shows products of these reactions for which X-ray crystal structures have been obtained. In each case, the CS_2^- group is nearly perpendicular to the N−C−N plane. The central C−C bond lengths (**151**: 149.7 pm,[212c] **153**: 149.8 pm,[216] **155**: 149.8,[213a] **158**: 151.0[217]) appear to be slightly shorter than those of the analogous carboxylates.

Complexes of diaminocarbenium-dithiocarboxylates with various metals, which include Mo,[218] W,[219] Re,[220] Ni,[221] Pd,[222] Pt,[222,223] Ag,[222] and Au,[222] have been reported. Various reactions of the dithiocarboxylate group have been studied, such as cycloaddition with alkynes,[212c] bromination and iodination,[213a] alkylation,[215a,224] oxidation[225] and reduction,[224,226] addition of Grignard and organolithium reagents,[227] and formal addition of tosyl ni-



Scheme 29. Betaines derived from diaminocarbenes and CS_2 or CSe_2



Scheme 30. Betaines derived from nucleophilic carbenes and (hetero)cumulenes

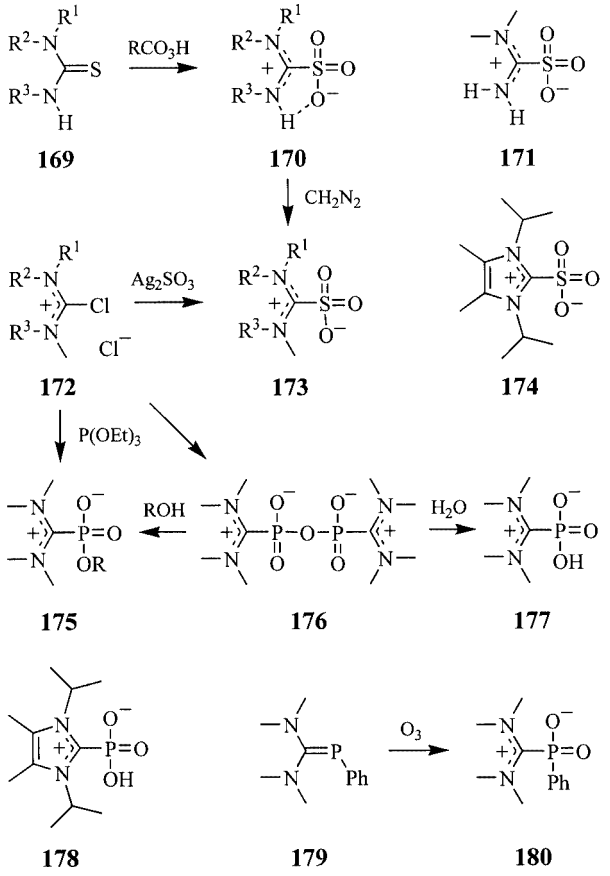
trene.[228] None of these involved the regeneration of diaminocarbenes.

Seleno analogues of **150** have not been approached from **102** or **149**, most probably due to the objectionable properties of CSe_2. The reaction of **156b** (R = Et) with elemental selenium produced compounds with a hexaselenocyclooctane core.[229] However, reaction of the cyclic enediamine **159** with Se_2Cl_2 in the presence of triethylamine provided the desired product **160**.[230] With elemental sulfur, **160** afforded **161** and, eventually, **150** (n = 1). In contrast to the C−Se bonds, the C−CSe_2^- bond proved to be inert: heating of **160** with CS_2 did not produce **150**.

The tetraaminoethylenes **149** react with acylisocyanates to give the betaines **162** (Scheme 30).[207] With R′ = Ar, the isolation of betaines failed due to rapid cycloaddition of **162** with isocyanate.[231] A series of stable betaines **163** have been obtained from **149** with isothiocyanates.[207,212a,231] Ketenes and acceptor-substituted allenes also attack **149** with formation of the betaines **164**[232] and **165**,[233] respectively. The transformation of **149** into "adducts" of tetrahydroimidazol-2-ylidenes (**162**−**165**) proceeds as outlined for CS_2 in Scheme 29. In order to prepare the analogous derivatives **167** of dihydro(benz)imidazol-2-ylidenes, (benz)imidazolium salts **166** have been treated with base (NEt_3, NaH, or BuLi) in the presence of phenylisothiocyanate.[170c,213b,234] The procedure is also applicable to thiazolium salts,[235] but appears to be limited to isothiocyanates. These reactions involve generation of the carbenes in situ; however, the isolable dihydroimidazol-2-ylidene **136** was added to diisopropylcarbodiimide.[236] The resulting imidazolium-amidinate **168** is a strong base whose crystal structure shows nearly perpendicular N−C−N planes. Due to crowding of the isopropyl groups, the amidinate nitrogens are non-equivalent both in the solid state and in solution (NMR spectroscopy).

Various betaines formally derived from diaminocarbenes and inorganic Lewis acids have been reported. Actually most of these compounds have been obtained by indirect routes not involving carbenes. The oxidation of thioureas **169** with hydrogen peroxide or peracids leads to amidiniumsulfonates **170** (thiourea trioxides),[237] which can be viewed as carbene−SO_3 adducts (Scheme 31). The method is applicable to cyclic thioureas[238] and dihydrobenzimidazol-2-

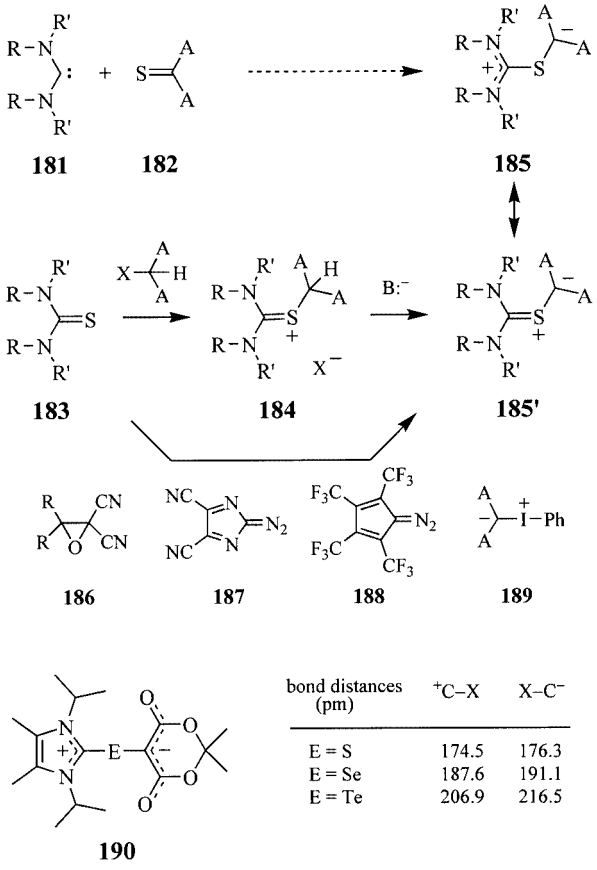
thiones;[239] three (or less) substituents at the nitrogen atoms are tolerated. Tetrasubstituted derivatives **173** have been prepared by methylation of **170** with diazomethane[240] or by reaction of 2-chloroamidinium chlorides **172** with silver sulfite.[241] A similar displacement reaction appears to be involved in the synthesis of **174** from carbene **136** and SO_2X_2 (X = Cl, F).[242] The crystal structures of **171**[243] and **174**[242] show C−S bond lengths (**171**: 182.7 pm, **174**: 182.2 pm) that are nearly the same although the N−C−N angles (**171**: 123.5°, **174**: 108.4°) differ substantially. The C−S bonds of **171** and **174** are only slightly longer than those of arenesulfonates (178−179 pm).[244]



Scheme 31. Amidiniumsulfonates, -phosphonates and -phosphinates

2-Chloro(tetramethyl)formamidinium chloride (**172**, R = Me) served also as the starting material for the preparation of amidiniumphosphonates. Depending on the reaction conditions, the interaction of **172** with triethyl phosphite affords **175** (R = Et)[245] or **176**.[246] The anhydride **176** is converted into **175** by alcoholysis and into **177** by hydrolysis.[246] The imidazolium-phosphonate **178** was obtained from the carbene **136** by reaction with $POCl_3$, followed by hydrolysis.[247] C−P bond lengths of 186−188 pm were estimated from the crystal structures of **176**,[248] **177**,[249]and **178**,[247] and compared with bond lengths of 177−181 pm for alkyl- and arylphosphonates. The amidinium-phosphinate **180** was prepared by oxidation of the phosphaalkene **179**.[250]

Push-pull-stabilized thiocarbonyl ylides[251] **185** can be regarded as adducts of diaminocarbenes **181** with electron-deficient thiones **182** (Scheme 32). So far, compounds **185** have not been made from **181**, nor have they been found to dissociate with formation of **181**. Alkylation of thioureas **183**, followed by deprotonation of the isothiuronium salts **184**, proved to be a versatile route to **185**.[252] Alternatively, oxiranes **186** (R = CF_3,[253] CN[254]), diazo compounds **187**[255] and **188**,[256] and iodonium ylides **189** (A = RCO,[257] $PhSO_2$ [258]) have been employed in methylene-transfer reactions with **183**. Recently, X-ray crystal structures of **190** have been obtained.[252c] The $^+$C−E bonds are only slightly shorter than the E−C$^-$ bonds, and are markedly longer than C=E double bonds, pointing to a minor contribution of the ylide structure **185′**.



bond distances (pm)	$^+$C–X	X–C$^-$
E = S	174.5	176.3
E = Se	187.6	191.1
E = Te	206.9	216.5

Scheme 32. Betaines derived from carbenes and thiones

7. Conclusion and Outlook

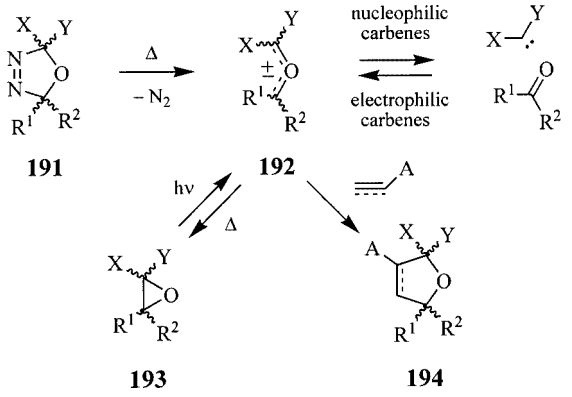
Electrophilic carbenes react irreversibly with good n- and π-donors. The rich and preparatively useful chemistry of both ylides and cyclopropanes does not include thermal regeneration of carbenes. However, photolyses of some ylides and of norcaradienes (see **20**, **23**, and **54**) have served as sources of carbenes. With less potent donors (ethers, aryl iodides), evidence for reversible complexation with electrophilic carbenes has been obtained (sections 2.2. and 2.3.). Moreover, some oxonium ylides (Scheme 6) and carbene-iodine adducts (Scheme 21) undergo methylene transfer re-

actions with alkenes. Attempts at controlling the reactivity of carbenes by weakly complexing solvents (ethers, fluorocarbons) have met with limited success.

The approach of electrophilic carbenes to n- and π-donors may involve long-range stabilizing interactions, prior to formation of covalent bonds. Flat minima on the PES have been observed for the addition reactions of carbenes with arenes (section 3.2.) but not with alkenes (section 3.1.). Ylide formation from ethers and (amidocarbonyl)(halo)-carbenes (**18f**,**g**, Scheme 6) appears to be preceded by weak complexation, whereas dichlorocarbene proceeds immediately to the ylide.[54] Computations proved to be crucial in the exploration of these phenomena, while experimental verification remains challenging. Additional insight may be obtained by studying the interaction of electrophilic carbenes with electron-poor alkenes (e.g. $CF_3CH{=}CH_2$).

Nucleophilic carbenes accept good electrophiles with formation of reverse ylides (section 5.2.) or betaines (section 5.3.). A wealth of structural data for these compounds is available, whereas their chemistry has received much less attention. So far, examples of reversible association are rare (see **105**, Scheme 24, and **141**, Scheme 28). Recently, the focus of research in this area appears to have shifted toward equilibrating species whose application in synthesis and/or catalysis is still in its infancy.

Studies are lacking in which a single (type of) "ligand" is combined with carbenes of divergent electrophilicities and nucleophilicities. There is a notable exception: carbonyl ylides **192** have been approached by addition of electrophilic carbenes to aldehydes and ketones,[259] by nitrogen extrusion from 1,3,4-oxadiazolines **191** (X = alkyl, OR, NR_2; Y = OR, NR_2),[260] and by ring opening of oxiranes **193** (R, X, Y = aryl, CN) (Scheme 33).[261,262] Although some of this work was performed a long time ago and with different objectives, the following trends are obvious: (a) Electrophilic carbenes bind irreversibly to carbonyl compounds. Unless the resulting carbonyl ylides are intercepted by dipolarophiles (**192** → **194**), cyclization affords oxiranes (**192** → **194**). (b) Carbonyl ylides generated from aryloxiranes behave analogously. The sequence of disrotatory photochemical ring opening and conrotatory ring closure leads to *E*,*Z*-isomerization of the substrate.[263] Carbenes are formed only by *photolysis* of the ylides **192**, i.e. on double irradiation of **193** (250 nm and visible light).[264] (c) Carbonyl ylides **192** formally derived from nucleophilic carbenes (but actually generated from **191**) dissociate irreversibly. With (methoxy)(methyl)carbene, evidence for reversible association with acetone has been obtained.[265] In accordance with these findings, computations predict that the reactions of carbonyl compounds with CH_2 should be exothermic, whereas those with $C(OH)_2$ should be endothermic.[266]



Scheme 33. Formation and dissociation of carbonyl ylides

The complexation of *ambiphilic* carbenes invites further investigation. (Alkoxy)(alkyl)carbenes have been generated photochemically from appropriate diazirines[267] and cyclobutanones,[268] in addition to the thermolysis of oxadiazolines **191**. Some of these species can be monitored directly by their UV absorptions.[269] In view of the moderate reactivity of ambiphilic carbenes,[269a,270] good opportunities for reversible ylide formation, and for the detection of long-range interactions, can be envisioned.

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