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Review Commentary
Super-electrophilic carbenes and the concept of Philicity

Wolfram Sander,* Carsten Kötting and Rolf Hübert

Lehrstuhl für Organische Chemie II der Ruhr-Universität, D-44780 Bochum, Germany

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ABSTRACT: Electron affinities and ionization potentials were calculated for a number of carbenes and compared with the carbene philicity scale m_{CXY} defined by Moss. It is suggested that a two-dimensional rather than a one-dimensional scale is used to classify the carbenes. Examples of extremely electrophilic carbenes with electron affinities above 2 eV are difluorovinylidene with a singlet ground state and 4-oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene with a triplet ground state. The reactivity of these carbenes towards small molecules under the conditions of matrix isolation is discussed. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: super-electrophilic carbenes; philicity

INTRODUCTION

The reactivity of carbenes is governed by the spin state which is involved in the reaction and by the philicity of the carbene. The philicity of a series of singlet carbenes with substituents X and Y has been quantified by Moss on the basis of the relative rates (selectivities) of the cyclopropanation of electron-rich vs electron-poor olefins.[1,2] The empirical carbene philicity scale m_{CXY} obeys an empirical linear free energy relationship with the Taft substituent parameters $\sigma_{\mathrm{R}}{}^{+}$ and σ_{I}. A very good correlation was found which allows one to calculate the philicity of carbenes R_2C: which are not experimentally accessible:

$$m_{\mathrm{CXY}} = -1.10 \sum_{\mathrm{X,Y}} \sigma_{\mathrm{R}}{}^{+} + 0.53 \sum_{\mathrm{X,Y}} \sigma_{\mathrm{I}} - 0.31$$

Only singlet ground state carbenes bearing at least one electronegative substituent (halogen, OR or NR_2) have been used to define this philicity scale, which limits the range of carbenes investigated and in particular excludes highly electrophilic carbenes. Most of the highly electrophilic carbenes have triplet ground states, and if not are extremely reactive species which are expected to react in a diffusion-controlled manner with olefins and even rapidly with saturated solvents. The m_{CXY} scale cannot be extended to the extremely electronegative carbenes, since these carbenes react unselectively, and it is therefore desirable to have another measure for the philicity which can be applied to the whole range of carbenes.

Moss and co-workers used the FMO theory and correlated differences in HOMO and LUMO energies of carbenes and olefins with the philicity scale m_{CXY}.[3] Although this method has been fairly successful, a problem is that orbital energies are not observable, and particularly the calculated LUMO energies depend considerably on the level of theory used. In principle, the HOMO and LUMO energies are related to the ionization potentials (*IP*) and electron affinities (*EA*), respectively, via Koopmans' theorem.[4] Since *IP* and *EA* have been determined for a number of carbenes and can be readily calculated by standard quantum chemical procedures,[5] we used these quantities to evaluate the philicity of carbenes and as a guide for the search of extremely electrophilic carbenes.

SUBSTITUENT EFFECTS ON THE IP AND EA OF CARBENES

An obvious way to increase the electron demand of carbon centers is to introduce electronegative substituents, especially fluorine. However, according to the philicity scale, difluorocarbene (**1**) is only amphiphilic and less electrophilic than methylene or even dichlorocarbene. This is rationalized by the short CF distance resulting in an efficient overlap of the lone pairs at the fluorine atoms with the vacant π-orbital at the carbon atom, which in turn leads to an increase in the LUMO energy. On the other hand, the lone pair at the carbon atom is strongly stabilized by the σ-electron-withdrawing capability of the fluorine atoms, which results in a decrease in the HOMO energy. Hence F_2C: is expected to be neither strongly nucleophilic nor electrophilic. The *EA* of H_2C: and F_2C: was determined to be 0.630 and

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*Correspondence to: W. Sander, Lehrstuhl für Organische Chemie II der Ruhr-Universität, D-44780 Bochum, Germany.
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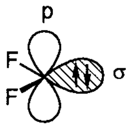
Table 1. Calculated and experimental electron affinities (*EA*) of selected carbenes[a]

Carbene	Experiment[b]	B3LYP[c] adiabatic	B3LYP[c] vertical, carbene[d]	B3LYP[c] vertical, anion[e]
FHC:	0.56	0.80	0.47	1.20
Cl_2C:	1.60	1.89	1.46	2.45
F_2C: (**1**)	0.18	0.55	−0.02	1.25
$H_2C{=}C$:	0.49	0.66	0.56	0.76
HFC=C:	1.72	1.96	1.98	2.33
$F_2C{=}C$: (**2**)	2.26	2.53	2.16	2.95

[a] *EA* in eV.
[b] Negative ion photoelectron spectroscopy.[6,7]
[c] B3LYP/6–311 ++ G(d,p).
[d] *EA* at the geometry of the neutral carbene.
[e] *EA* at the geometry of the radical anion.

0.179 eV, respectively,[6] indicating the stabilizing influence of fluorine substitution as discussed above.



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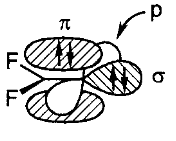

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Fluorine substitution can only increase the electrophilicity of a carbene if the π-overlap is not possible either for reasons of symmetry or because the distance between the carbene center and the fluorine atom is too large. In vinylidenes the vacant p-orbital at the carbene center is located in the molecular plane, and the electron deficiency at the carbene center increases with fluorine substitution. The *EA* of the parent vinylidene $H_2C{=}C$: increases substantially from 0.490 to 2.255 eV in $F_2C{=}C$: (**2**).[7]

DFT calculations have been shown to reliably describe the properties of carbenes,[8,9] and we therefore used the B3LYP method in combination with a large 6–311 ++ G(d,p) basis set to calculate substitution effects on *EA* and *IP* of carbenes. The *EA* is the difference in the energies of the carbene and the corresponding radical anion, and therefore depends on the geometries used in the energy calculations. This can be clearly seen by comparing the *EA* calculated for the relaxed geometries of carbene and radical anion [*EA* (adiabatic)] with that obtained by using the carbene [*EA* (vertical, carbene)] or radical anion [*EA* (vertical, anion)] geometries for the energy calculations (Table 1). The largest effect was found for CF_2 with a difference between *EA* (vertical, carbene) and *EA* (vertical, anion) of 1.27 eV. This results from the widely different FCF bond angles in the carbene and the anion. In the vinylidenes the differences in the geometries are smaller and the carbene center is less affected, and consequently *EA* (vertical, carbene) and *EA* (vertical, anion) differ by only a few tenths of an electronvolt. There are smaller deviations between *EA* (vertical, carbene) and *EA* (adiabatic), and both values are in reasonable agreement (within the error of the theoretical method) with the experimental data, although in the experiments the adiabatic *EA* was determined (Table 1). Since the calculation of *EA* (vertical, carbene) is less time consuming, which is of importance especially for the larger carbenes, we only use these values in the following discussion of the properties of carbenes.

It is interesting to study the influence of substituents X and Y on the *EA* and *IP* of the carbenes XYC: and XYC=C: and compare these values with the m_{CXY} values (Table 2). The *EA* of the carbenes investigated in this study vary between −0.6 and +3.6 eV and the *IP* between 12 and 7 eV, covering the whole range from electrophilic to nucleophilic carbenes. For halocarbenes (X, Y = F, Cl, Br) *EA* and m_{CXY} are nicely correlated, and Br_2C: with $EA = 1.84$ eV shows the smallest value of $m_{CXY} = 0.65$. F_2C: is much less electrophilic with $EA = -0.02$ eV (experimental value 0.18 eV) and $m_{CXY} = 1.47$. The *IP* increases from 9.65 eV in Br_2C: to 12.31 eV (experimental value 11.4 eV) in F_2C:, and if *IP* is taken as a measure for the nucleophilicity of a carbene, F_2C: is not only less electrophilic but also less nucleophilic than Br_2C:. This should result in an overall lower reactivity towards both electron-rich and electron-poor olefins, which is not reflected in m_{CXY}, since this only measures the relative rates.

The substituents RO and R_2N are more efficient in reducing *EA* than halogen, and in most cases negative values are predicted for these carbenes. With $EA = -0.62$ eV the smallest value is observed for $(MeO)_2C$:, and with $EA = -0.44$ eV $(Me_2N)_2C$: is fairly close. A much larger difference, however, is found for *IP*, which in $(Me_2N)_2C$: is only 7.1 eV, almost 2 eV less than in $(MeO)_2C$:. This is in line with the observed high nucleophilicity of carbenes of Arduengo/Wanzlick type, which is more pronounced than that of alkoxycarbenes.

As mentioned above, the *EA* of $H_2C{=}C$: increases substantially on fluorination, and chlorine is almost as effective as fluorine. In contrast, the *IP* is almost unaffected by fluorination (11.4 eV in both $H_2C{=}C$: and **2**) and decreases only slightly on chlorination. Thus, vinylidene and its halogenated derivatives should exhibit a very low nucleophilicity and the halogenated derivatives should be extremely electrophilic. Substitution with NH_2 reduces both *EA* and *IP* by several electronvolts, and $(H_2N)_2C{=}C$: is predicted to be more nucleophilic than electrophilic. However, this vinylidene shows a large deviation from C_{2v} symmetry caused by a strong interaction of one of the nitrogen lone pairs with the vacant p-orbital at the carbene center.

A compilation of the calculated *EA* and *IP* values allows several classes of carbenes to be identified (Table 2, Fig. 1). (i) Strongly nucleophilic carbenes with large m_{CXY} values are found at the bottom left part of the diagram. These carbenes exhibit a small or negative *EA* and a low *IP*. Substitution with NR_2 results in an *IP*

Table 2. Electron affinities (*EA*)and ionization potentials (*IP*) of a series of carbenes

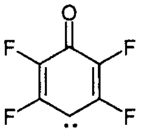
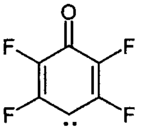
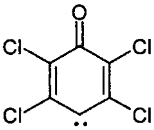
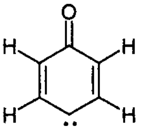
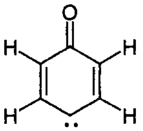
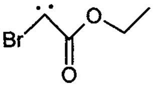
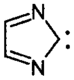
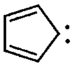
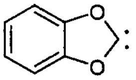
			EA (eV)		*IP*(eV)		
Carbene[a]	No.	Symmetry	B3LYP[b]	Exp.[c]	B3LYP[b]	Exp.[c]	m_{CXY}[d]
	S-**3**	$C_{s'}$, $^1A'$	3.61		9.71		
	T-**3**	$C_{2v'}$, $^3B_1$	3.32		9.82		
	T-**5**	$C_{2v'}$, $^3B_1$	3.08		9.02		
	S-**4**	$C_{s'}$, $^1A'$	2.35		8.47		
	T-**4**	$C_{2v'}$, $^3B_1$	2.05		10.05		
$F_2C{=}C$:	**2**	$C_{2v'}$	2.16	2.26	11.42		
$Cl_2C{=}C$:		$C_{2v'}$	2.11		10.37		
Br_2C:		$C_{2v'}$	1.84		9.65		0.65
FHC=C:		$C_{s'}$	1.62	1.72	11.92		
	**6**	C_1	1.61		9.24		0.29
PhClC:		C_1	1.52		8.18		
Ph_2C		C_1	1.48		6.77		0.46
Cl_2C:		$C_{2v'}$	1.46	1.60	10.16	9.27	0.97
	**7**	$C_{s'}$	1.40		10.06		
H_2C:		$C_{2v'}$, $^1A_1$	1.20		10.54		−0.31
H_2C:		$C_{2v'}$, $^3B_1$	0.23	0.63	10.45	10.4	
	**8**	C_1	1.19		8.67		
PhFC:		C_1	1.11		8.59		0.89
ClFC:		$C_{s'}$	0.84		11.08	10.7	1.22
ClMeC:		C_1	0.68		9.16		0.58
	**9**	$C_{2v'}$	0.57		9.34		
$H_2C{=}C$:		$C_{2v'}$	0.56	0.49	11.38		
FHC		$C_{s'}$	0.47	0.54	10.70	10.1	0.58
$(H_2N)_2C{=}C{=}C$:		C_2	0.16		8.69		
FMeC:		C_1	0.00		9.71		0.84
F_2C:	**1**	$C_{2v'}$	−0.02	0.18	12.31	11.4	1.47
	**10**	C_2	−0.18		8.17		

Table 2. continued

			EA (eV)		*IP*(eV)		
Carbene[a]	No.	Symmetry	B3LYP[b]	Exp.[c]	B3LYP[b]	Exp.[c]	m_{CXY}[d]
Cl(MeO)C:		$C_{s'}$	−0.18		9.60		1.59
	**11**	$C_{2v'}$	−0.21		9.77		
$(H_2N)_2C{=}C$:		C_1	−0.32		8.70		
$(Me_2N)_2C$:		C_2	−0.44		7.10		
	**12**	$C_{s'}$	−0.44		7.94		
$Me(Me_2N)C$:		C_1	−0.48		7.40		2.91
	**13**	$C_{2v'}$	−0.52		8.15	7.68	
$(MeO)_2C$:		C_1	−0.62		9.01		2.22

[a] The closed-shell singlet states were calculated if not stated otherwise.

[b] Calculated at the B3LYP/6–311 ++ G(d,p) level of theory. The energies of the radical cations and anions were calculated at the carbene geometries (vertical energies).

[c] Experimental values (adiabatic energies) taken from Ref. 42.

[d] Philicity scale defined by Moss.[1]

around 7 eV, which increases to 9 eV with RO and to 12 eV with F as substituents. The stable Arduengo/Wanzlick carbenes are characterized by both low *IP* and low *EA*, and thus high nucleophilicity. F_2C shows the same low *EA*, but in addition a high *IP*, and the overall reactivity of this carbene is small. (ii) Halogenated vinylidenes are among the carbenes with the highest *EA* and *IP*. These carbenes are extremely electrophilic and show no nucleophilicity. (iii) Carbenes with a high *EA* and low *IP* generally have a small S–T gap and thus triplet ground states. Only few examples, such as **4**, were investigated in this study.

Although the philicity scale m_{CXY} defined by Moss is based on kinetic data for carbene cycloaddition reactions, there is some relation to the *EA* and *IP* of carbenes, defining a two-dimensional philicity scale. We therefore used these data for the search of extremely electrophilic carbenes.

PROPERTIES OF DIFLUOROVINYLIDENE AND 4-OXO-2,3,5,6-TETRAFLUOROCYCLOHEXA-2,5-DIENYLIDENE

In accordance with the theoretical predictions, difluorovinylidene (**2**)[10] and 4-oxo-2,3,5,6-tetrafluoro-

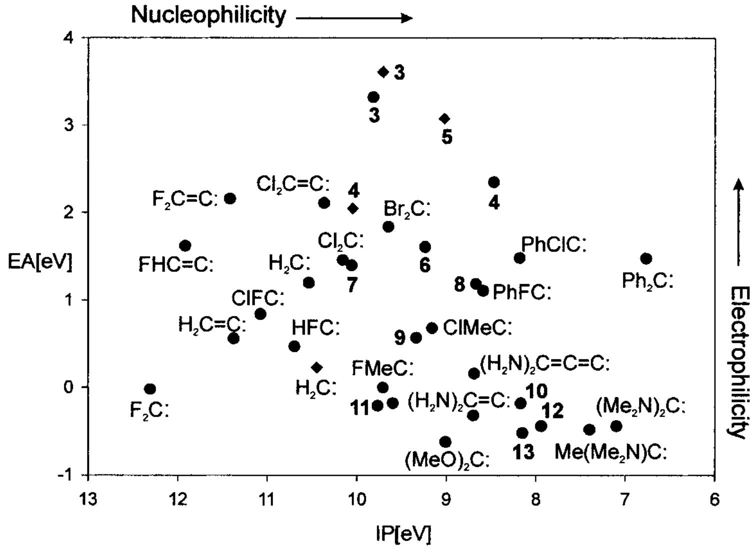
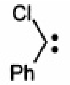
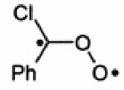
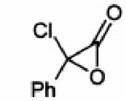
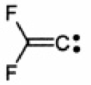
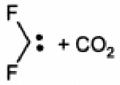
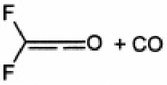
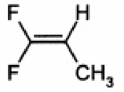
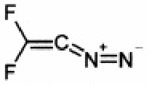
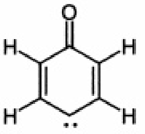
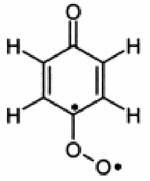
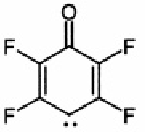
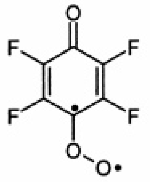
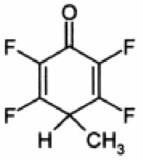


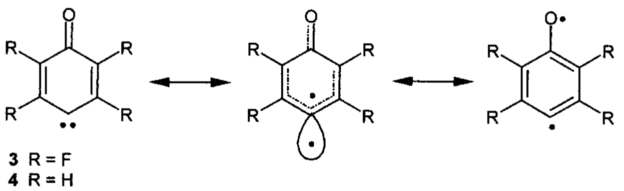
Figure 1. Electron affinities (*EA*) and ionization potentials (*IP*) of a series of carbenes calculated at the B3LYP/6–311 ++ G(d,p) level of theory (see Table 2)

Table 3. Comparison of reactions of carbenes with several trapping reagents under the conditions of matrix isolation

	${}^3O_2$	CO_2	CH_4	N_2
	 slow reaction		no reaction	no reaction
	 fast reaction	 fast reaction	 fast reaction	 fast reaction
 **4**	 fast reaction	no reaction	no reaction	no reaction
 **3**	 fast reaction	-	 fast reaction	no reaction

cyclohexa-2,5-dienylidene (**3**)[11,12] are prototypes of highly electron-deficient singlet and triplet carbenes, respectively, and show an unusual reactivity even in low-temperature matrices. These carbenes could be synthesized in argon matrices in high yields and characterized by IR spectroscopy in combination with DFT calculations. The chemistry of **2** has been described in several publications,[10,13–17] and here only the most striking differences to other carbenes are discussed.

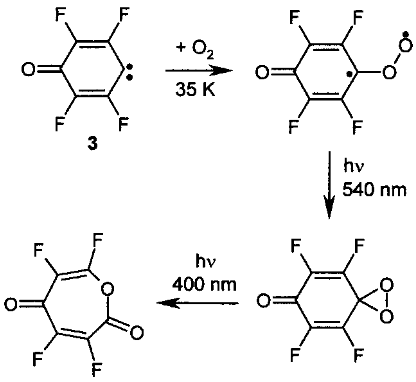
4-Oxocyclohexadienylidene (**4**) and its derivatives are triplet ground-state carbenes which are easily generated by photolysis from their corresponding quinone diazides. The electronic structures of these species resemble that of the phenyl radical for the σ-system and that of the phenoxyl radical for the π-system.[18–23] A typical reaction of **4** is the addition of ${}^3O_2$ to give *p*-benzoquinone *O*-oxide,[20,21] and the addition of CO to give the corresponding ketoketene. Fluorination or chlorination of **4** increases both the *EA* and *IP* of these carbenes, corresponding to an increase in the electrophilicity and decrease of nucleophilicity. The perfluorinated **3** is predicted to exhibit extreme electrophilicity in both its triplet ground state and its low-lying closed-shell singlet state.[11,12]



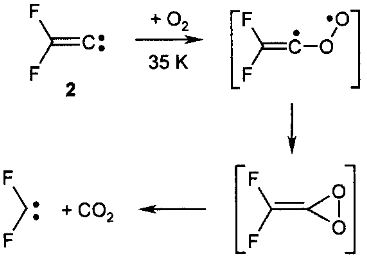
The chemistry of **2** and **3** was investigated by generating the carbenes in argon matrices doped with a trapping reagent. Typical carbene precursor: trapping reagents: argon ratios were 1:10:1000. The photolyses were carried out at 7–10 K. Under these conditions, the mobility of molecules trapped in solid argon is very low and bimolecular thermal reactions are inhibited by the lack of diffusion. Warming an argon matrix to one third to half of its melting point (30–40 K) allows small molecules to diffuse. The thermal energy *kT* at cryogenic temperatures is very small and therefore only reactions with very low activation barriers ($<$1–2 kcal mol^{-1}) are observed. Since reactions in matrices are solid-state reactions, it is very difficult to determine the intrinsic reaction kinetics. Here, we only qualitatively compare the reactivities of **2** and **3** with those of phenylchlorocarbene and oxocyclohexadienylidene (**4**) as examples of less electrophilic singlet and triplet carbenes, respectively. Typical reactions are the oxidation with ${}^3O_2$, the carboxylation with CO_2, the insertion into CH_4 and the addition of N_2 (Table 3).

Reaction with oxygen

In oxygen-doped matrices, triplet carbenes such as Ph_2C:, **3** or **4** react very rapidly (diffusion-controlled) with ${}^3O_2$. The primary products of these formally spin-allowed reactions are carbonyl *O*-oxides.[24] This high reactivity is independent of the electrophilicity of the carbene. In contrast, reactions of singlet carbenes with $^3O_2$ are formally spin-forbidden, and in most cases these reactions are very slow or do not occur. Thus, under the conditions of matrix isolation, F_2C: does not react with $^3O_2$[25] and the reaction of PhClC: is very slow.[26] Since the oxygenation is an electrophilic addition at one of the oxygen atoms of O_2, electron-withdrawing groups at the phenyl group of PhClC: increase the reactivity.[27] This has also been observed in LFP experiments.[28,29]

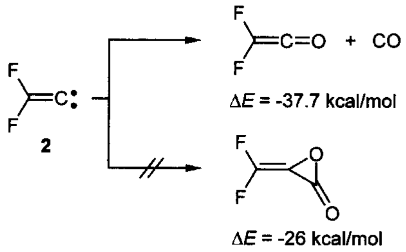


Vinylidene **2** reacts extremely rapid with $^3O_2$, but no carbonyl *O*-oxide is formed, which in this case would be a ketene oxide. The major products are F_2C: and CO_2, presumably formed via a ketene *O*-oxide and a methylenedioxirane as intermediates.[15] However, in contrast to most other carbene oxygenations, these intermediates could not be stabilized in low-temperature matrices.



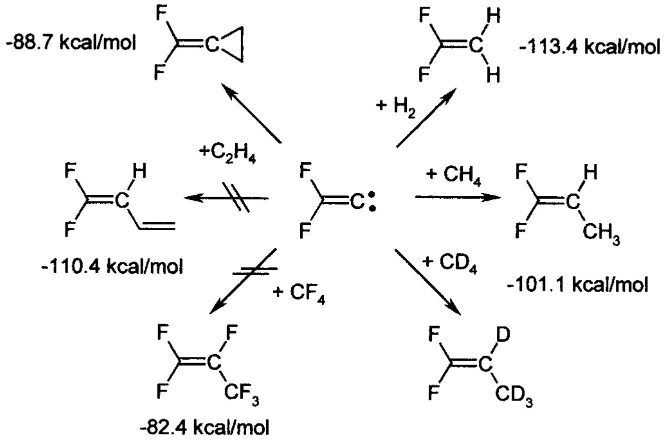
Reaction with CO_2

The key step of the carboxylation of a carbene is the nucleophilic attack of the carbene center at the CO_2 carbon atom. In this reaction no spin restriction is observed and singlet carbene PhClC: reacts as rapid as triplet diphenylcarbene.[27] The carboxylation depends on the nucleophilicity of the carbene, and thus electron-withdrawing groups at the phenyl ring of PhClC: reduce the reactivity. Owing to their low nucleophilicity, neither **3** nor **4** is carboxylated in CO_2-doped matrices, and **4** could even be isolated in solid CO_2. From that it is extrapolated that the strongly electrophilic **2** is also not carboxylated. Indeed, although vinylidene **2** rapidly reacts with CO_2, it is not carboxylated but rather abstracts an oxygen atom from CO_2. This reaction has not been observed with any other carbene. The first step is the electrophilic attack at one of the oxygen atoms, followed by the oxygen atom transfer under formation of $F_2C{=}O$ and CO.[15] Both the oxygen atom transfer and the carboxylation are calculated [B3LYP/6–311G(d) + ZPE] to be exothermic, but the latter reaction obviously is prevented by a significant activation barrier.



Insertion into CH bonds

Many singlet and triplet carbenes are stable in hydrocarbon glasses at temperatures below 77 K.[30] In CH_4-doped argon matrices (0.5–1% CH_4 in Ar) at temperatures up to 45 K, carbenes such as Ph_2C:, PhClC: and **4** are completely unreactive. Methylene is one of the few carbenes that has been described to react with CH_4 in matrices, although it is not completely clear if ethane and other hydrocarbons are formed in a thermal or photochemical reaction.[31,32] The barrier for the insertion of PhClC: into tertiary CH bonds was determined to 3 kcal mol^{-1} by LFP methods, which is significantly lower than that calculated at the B3LYP/6–31G(d) level of theory (7 kcal mol^{-1}).[33] The insertion into the CH bond of methane is expected to proceed with an even higher barrier, and consequently in low-temperature matrices no reaction with CH_4 is observed. The barrier of the insertion of CF_2 into H_2 was calculated to be about 33 kcal mol^{-1}.[34] The extremely electrophilic carbenes **2**[10] and **3**,[11] on the other hand, rapidly insert into the CH bond even at cryogenic temperatures, which suggests very small or even absent activation barriers for these insertions. This is in agreement with DFT calculations [B3LYP/6–311G(d,p)] of the insertions of **2** into H_2 and CH_4, which predict zero barriers for both reactions and reaction energies of −113 and −101 kcal mol^{-1}, respectively (Scheme 1).[17] With −91 and −79 kcal mol^{-1} [B3LYP/6–31G(d,p)] the insertion of **3** into H_2 and CH_4 is about 20 kcal mol^{-1} less exothermic (Scheme 2). The addition of carbenes **2** and **3** to ethene to give the corresponding cyclopropane is much less dependent on the nature of the carbene and exothermic by 89 and 85 kcal mol^{-1}, respectively. In both cases the cyclopropane, and not the insertion product, is formed. For the

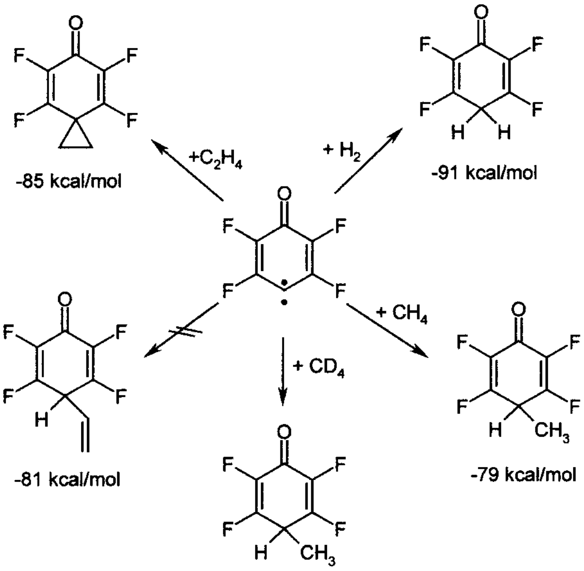


Scheme 1. Some reactions of vinylidene **2** investigated in argon matrices doped with 0.5–1% of a trapping reagent. The reaction energies were calculated at the B3LYP/6–311G(d,p) + ZPE level of theory

insertion of **2** into the CH bond of ethene an activation barrier of 3 kcal mol^{-1} has been calculated, while the addition reaction proceeds without barrier.[17] The activation barrier for insertions into H_2 and CH clearly depends on the electrophilicity of the carbene, while the spin state seem to be less important. Insertion reactions into H_2 and hydrocarbons at cryogenic temperatures can thus serve as a qualitative measure for the carbene philicity.

Reactions with nitrogen and xenon

Only highly electrophilic and thermodynamically unstable carbenes are expected to react exothermically with N_2 to give the corresponding diazo compounds. The fragmentation of diphenyldiazomethane into Ph_2C: and N_2 has been determined by time-resolved photoacoustic calorimetry to be thermoneutral ($\Delta H_R = 0 \pm 1.7$ kcal mol^{-1})[35] and that of phenylchlorodiazirine to PhClC: and N_2 to be endothermic ($\Delta H_R = +11.1 \pm 1.6$ kcal mol^{-1}).[36] Therefore, the photolysis of diazo compounds and diazirines is the most important method for the synthesis of carbenes, and in many cases carbenes can be matrix isolated in solid N_2 without formation of the corresponding diazo compounds. Methylene has been reported to be trapped by N_2,[37] and recently the reaction of singlet 2*H*-imidazol-2-ylidene (**7**) with N_2 was reported.[38] Despite its high electrophilicity, triplet carbene **3** does not react with N_2,[11] while **2** is very efficiently trapped even by traces of N_2 in the matrix. The latter reaction is highly exothermic and proceeds in a diffusion-controlled reaction with no activation barrier.



Scheme 2. Some reactions of carbene **3** investigated in argon matrices doped with 0.5–1% of a trapping reagent. The reaction energies were calculated at the B3LYP/6–31G(d,p) + ZPE level of theory

The complexation of xenon has only been observed for **2, 7** and C_2. All these ground-state singlet molecules are electrophilic with an *EA* of 2.26,[7] 1.4 (calculated) and 3.27 eV,[39] respectively. The xenon complexes show a significant charge transfer from xenon to the carbene, and the binding energies of the complexes are of the order of several kcal mol^{-1}. Several IR absorptions show significant red shifts compared with the uncomplexed carbenes, which allows the complexes to be identified spectroscopically. Triplet carbenes, even **3**, do not show a similar interaction with Xe resulting in significant shifts of IR bands.

CONCLUSION

The *EA* and *IP* of carbenes can be reliably calculated with DFT methods and provide a measure of the philicity of carbenes. The advantage of *EA* and *IP* over LUMO and HOMO energies is that experimental values have been determined for a number of carbenes and therefore experiment and theoretical prediction can be directly compared. There is a reasonable correlation between *EA* and m_{CXY} which allows *EA* to be used as guide for the search for extremely electrophilic carbenes. Vinylidene **2** and tetrafluorocyclohexadienylidene **3** are examples of such carbenes exhibiting unusual reactivity. Both carbenes insert into the CH bond of CH_4 without a measurable activation barrier. This highly exothermic reaction is most characteristic for strongly electrophilic carbenes and is not observed with other, less electrophilic carbenes.

EXPERIMENTAL

Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Messer-Griesheim, 99.9999%) on top of a CsI window at 8 K at a rate of approximately 0.15 mmol min^{-1}. Mixtures of argon with gaseous compounds (typically 0.5%) were produced in a vacuum line. IR spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range 400–4000 cm^{-1}. Irradiations were carried out with the use of an ArF excimer Laser ($\lambda = 193$ nm) (Lambda Physik COMPex 100) or Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the mercury high-pressure arc lamp was absorbed by a 10 cm path of water. Schott cut-off filters were used (50% transmission at the wavelength specified) in combination with dichroic mirrors.

Calculations were performed with the Gaussian 98 program package.[5] Geometries, energies and vibrations of the neutral species were calculated at the B3LYP/6–311 ++ G(d,p) level of theory. These geometries were used for single-point calculations [UB3LYP/6–311 ++ G(d,p)] of the radical anions and radical cations, respectively. The thermochemistry of **2** and **3** was calculated at the B3LYP/6–311G(d,p) and B3LYP/6–31G(d) level of theory, respectively, and includes zero point energies.

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