Reactions of Difluorovinylidene—A Super-Electrophilic Carbene

Wolfram Sander* and Carsten Kötting[a]

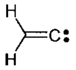
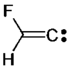
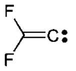
Abstract: Difluorovinylidene is the only vinylidene that could be isolated in low temperature matrices, so far. Its unusual reactivity is governed by its extreme electrophilicity and electron affinity. Thus, it not only adds CO and N_2 without difficulties, but also inserts into CH_4 and even H_2 at temperatures below 40 K. The reaction of $F_2C{=}C$: with $FC{\equiv}CF$ clearly reveals that the formation of methylenecyclopropene proceeds in a stepwise reaction. The most striking example for the electrophilicity of $F_2C{=}C$: is the thermal reaction with Xe to give a charge-transfer complex with a characteristic IR spectrum.

Keywords: carbenes · cycloadditions · insertions · matrix isolation · vinylidene

Introduction

The concept of philicity has proven to be a useful tool to rationalize carbene reactivity.[1, 2] During the last years the nucleophilic carbenes of Arduengo- and Wanzlick-type, which are stable at room temperature and even can be crystallized, attracted much attention.[3, 4] In contrast, electrophilic singlet carbenes are much less well studied. The reason for this is that typical electron-accepting substituents (e. g. $-CF_3$, -CN, $-CO_2R$) at the carbene center lead to triplet ground state carbenes with an entirely different reaction pattern. At least one π-donating substituent (e. g. -halogen, -OR, $-NR_2$), which reduces the electrophilicity of the carbene, is required to stabilize the singlet ground state. Alternatively, the singlet state can be stabilized by reducing the R-C-R bond angle Θ, which for $\Theta = 0°$ finally leads to the vinylidenes. Thus, vinylidenes with strongly electron-accepting substituents should provide electrophilic singlet carbenes. This concept is in line with the electron affinities (EA) of fluorinated vinylidenes measured by Lineberger and co-workers using negative-ion photoelectron spectroscopy.[5–7] The EA of vinylidene (**1**) was determined to 0.490 eV, similar to the EA of methylene (0.63 eV). However, while fluorination of H_2C: decreases the EA to 0.542 eV in HFC: and to 0.179 eV in F_2C:, fluorination of $H_2C{=}C$: has the opposite effect and the EA increases to 1.718 eV in $HFC{=}C$: (**2**), and to 2.255 eV in $F_2C{=}C$: (**3**) (Table 1).

Table 1. Experimental and calculated singlet–triplet splittings (ΔE_{ST}) and electron affinities (EA) of some carbenes.

	ΔE_{ST}[a] [kcal mol^{-1}]	EA[a] [eV]	ΔE_{ST}[b] [kcal mol^{-1}]	EA[b] [eV]
H_2C:	9.08	0.630	11.8	0.73
HFC:	– 14.9	0.542	– 11.5	0.85
F_2C:	– 57.0	0.179	– 51.6	0.61
1 	– 47.5	0.490	– 48.1	0.68
2 	– 30.4	1.718	– 28.0	1.98
3 	– 21.3	2.255	– 14.7	2.56

[a] Experimental values from negative-ion photoelectron spectroscopy (taken from references [5–7]). [b] Calculated at the B3LYP/6–311++G(d,p) level of theory, including the ZPE.

Evidence for the formation of **3** in the gas phase by trapping experiments was published by Strausz and co-workers[8] and by Stachnik and Pimentel,[9] who generated **3** by Hg-sensitized and multi-IR photon decomposition, respectively, of trifluoroethylene. Brahms and Dailey used difluoropropadienone (**4**) as a source of **3**.[10–12] Irradiation ($\lambda > 220$ nm) of **4** in the gas phase produced **3** as an intermediate which could be trapped with cyclopentene to give both the product of the addition to the double bond as well as CH insertion products (Scheme 1).[10] These results indicate that **3** is highly reactive and of low selectivity. In argon matrices **4** could not be photodecarbonylated, since carbene **3** immediately is trapped by the CO formed in the same matrix cage.[11] This was clearly demonstrated by doping the matrix with ^{13}CO which resulted in the incorporation of the label into **4**. In nitrogen matrices difluorodiazoethene (**5**) was produced in low yield (2 %), which again indicates the formation of **3** as a transient species.[11]

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[a] Prof. Dr. W. Sander, Dipl.-Chem. C. Kötting
Lehrstuhl für Organische Chemie II der Ruhr-Universität
D-44780 Bochum (Germany)
Fax: (+49) 234-709-4353
E-mail: sander@neon.orch.ruhr-uni-bochum.de

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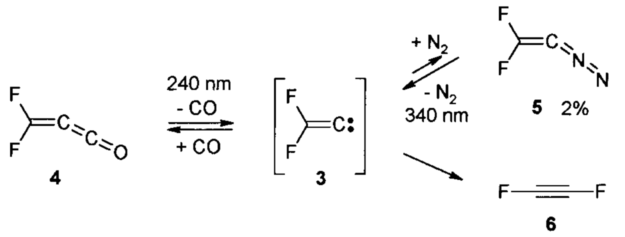


Scheme 1. Reactions of the transient carbene **3**.

Recently we found that photochemistry of difluoroacetylene (**6**)[29] at 193 nm provides a simple and highly efficient method to synthesize **3** in more than 90% yield. Under the conditions of matrix isolation carbene **3** is stable, which allows its spectroscopic properties and its unique reactivity with a variety of small molecules to be studied.

Electronic Structure of Difluorovinylidene

Difluorovinylidene (**3**) and its rearrangement to acetylene **6** has been subject to several theoretical studies: Strausz et al. in 1973,[13] Goddard in 1981,[14] Pople and Schleyer et al. 1981,[15] Schaefer III et al. in 1990,[16] and Thiel et al. in 1997.[17] All these studies agree that **3** is separated from **6** by a huge barrier, although the rearrangement is predicted to be strongly exothermic. At the CCSD(T)cc-pVQZ level of theory the barrier is predicted to 36.4 kcal mol^{-1} and the energy of reaction to 29.5 kcal mol^{-1}.[17] Thus, **3** is kinetically stable towards rearrangement even at room temperature.

The C–C stretching vibration of **3** in argon at 7 K is located at 1672 cm^{-1} and thus only 50 cm^{-1} red-shifted compared to that of 1,1-difluoroethylene. This indicates an almost normal C–C double bond in **3**. The HOMO is the bonding π-orbital, calculated (MP2/6-311++G(d)) at −11.50 eV, corresponding to an electron-rich olefin (Figure 1). Quite unusual is the low-lying carbene n-orbital (−13.72 eV), which falls below the π-orbital and indicates the low nucleophilicity of **3**. The LUMO is described best as the in-plane p-orbital at the terminal carbon atom with only small contributions at the other atoms. Most of the chemistry of **3** is governed by the interaction of this low-lying virtual orbital (0.04 eV) with occupied orbitals of the reaction partner.

With a calculated dipole moment of 1.1 D (MP2/RCEP,TZ2Pf) vinylidene **3** is of modest polarity only. The negative charge (natural population analysis charges are used in this discussion) at the fluorine atoms (−0.27) is almost completely compensated by the carbon atom directly bound to the fluorine atoms (+0.44), and the carbene center is only slightly positively charged (+0.11).

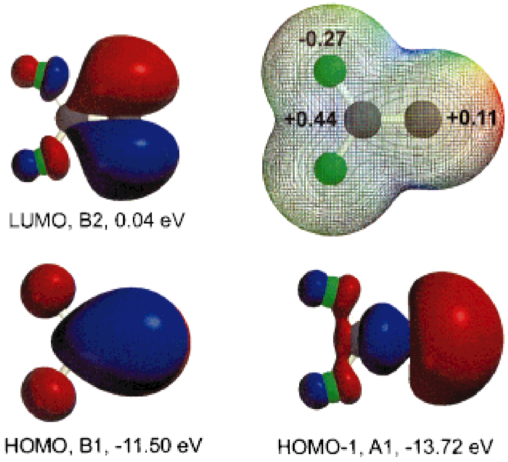
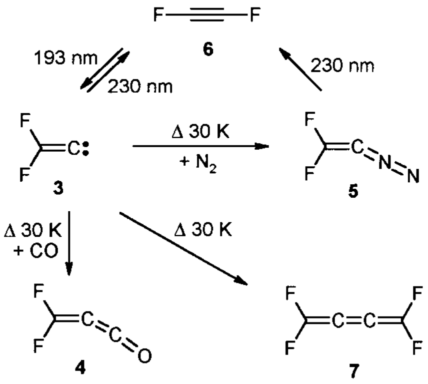


Figure 1. Plots of the HOMO-1, HOMO, LUMO, and the electron density surface encoded with the electrostatic potential (in color, blue corresponds to electrophilic, red to nucleophilic areas on the surface) of difluorovinylidene (**3**). Calculations were done at the MP2/6–311++G(d) level of theory. NPA charges (MP2/TZ2Pf, Ref. 25) are given at the atoms.

Reactions of Difluorovinylidene

The reactions of vinylidene **3** with a variety of small molecules were investigated in argon matrices doped with 0.5–1% of the reagent at temperatures below 40 K. In the first step **3** was produced by 193 nm irradiation (ArF Excimer Laser) of acetylene **6** at 7 K. In the second step the matrix was warmed to 20–40 K (depending on the reagent) to allow the diffusion of species trapped in the matrix. Thus, the photochemical preparation of **3** and the subsequent thermal reactions can be separately monitored by IR or UV/Vis spectroscopy. Since the thermal energy available at these cryogenic temperatures is very small, only reactions with vanishing or very small activation barriers are observed.

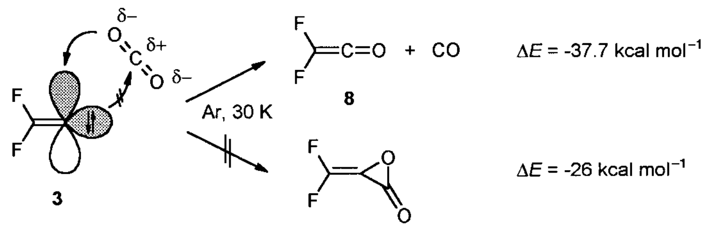
Dimerization and reactions with CO and N_2: Annealing of an argon matrix containing **3** at 30 K results in the formation of tetrafluorobutatriene (**7**) as the major product (Scheme 2). This reaction is calculated (B3LYP/6-311G(d)+ZPE) to be exothermic by 167.3 kcal mol^{-1} (the dissociation energy of butatriene). If the matrix is doped with CO or N_2, propadienone **4** or diazoethene **5** are the dominant products.[17] The formation of these products is strongly exothermic and very efficient, which explains the failure to produce **3** from these precursors.[11] Irradiation of **5** yields acetylene **6**, but not carbene **3**, since the thermal in-cage recombination of **3** and N_2 rapidly leads back to **5**, and only that fraction of **3** that rearranges to **6** is not trapped by nitrogen.



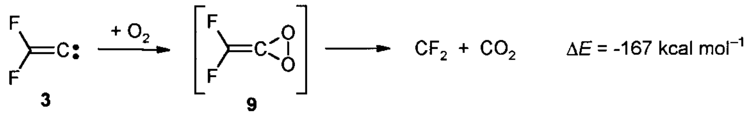
Scheme 2. Reactions of vinylidene **3**.

Oxidation: Vinylidene **3** is easily oxidized with CO_2 to give the highly labile difluoroketene **8** as the only product.[18] In earlier kinetic studies of the reactions of carbenes with CO_2 it was found that α-lactones are the principal products and that this reaction is governed by the nucleophilicity of the carbenes, while the spin state has not much influence.[19] Electrophilic carbenes such as 4-oxocyclohexadienylidene did not react in solid CO_2 at temperatures up to 80 K, and therefore it is surprising that the even more electrophilic **3** rapidly reacts with CO_2. It is tempting to assume that **3** does not react as a nucleophile but rather attacks the CO_2 at the oxygen atom, and thus acts as an electrophile (Scheme 3).

The oxidation of **3** with O_2 is rather complicated, since the oxygen is partially cleaved to highly mobile oxygen atoms by the 193 nm irradiation. As a consequence, thermal and photochemical processes can hardly be differentiated. The major products are CF_2, CF_2O, CO, and CO_2, which reveals that the C=C bond in **3** is cleaved during the oxidation. The most reasonable mechanism to rationalize these products is a route via methylenedioxirane **9**, which subsequently fragments to CF_2 and CO_2 (Scheme 4). The formation of **9** is calculated to be exothermic by 70.5 kcal mol^{-1} and the fragmentation by 96.7 kcal mol^{-1}, which sums up to a total energy of reaction of 167.2 kcal mol^{-1}! CF_2O could either be formed by trapping of the CF_2 by oxygen atoms or by a second oxidation pathway leading to CF_2O and CO.



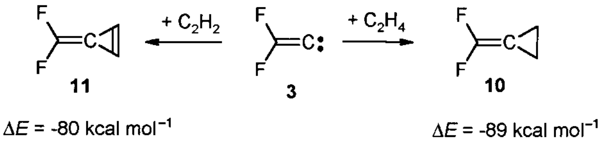
Scheme 3. Oxidation of vinylidene **3** with CO_2. Energy of reaction calculated at the B3LYP/6-311G(d) level of theory.



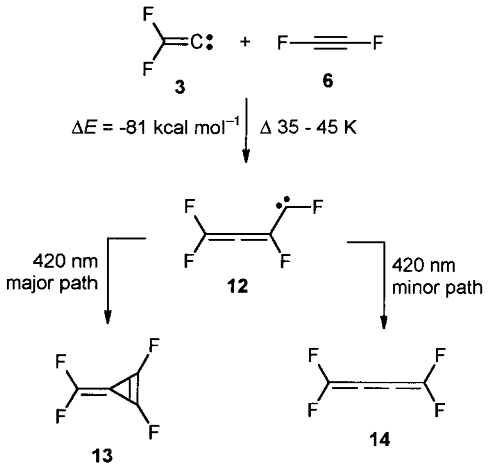
Scheme 4. Oxidation of vinylidene **3** with O_2.

Addition to double and triple bonds: Vinylidene **3** rapidly reacts with ethylene[20] and acetylene[21] to yield difluoromethylenecyclopropane (**10**) and difluoromethylenecyclopropene (**11**), respectively (Scheme 5). These are the expected products of cycloaddition reactions of **3**.

With difluoroacetylene (**6**), however, the only product formed thermally at 35 K is allenylcarbene **12**, which on subsequent visible light irradiation cyclizes to tetrafluorocyclopropene **13** as the major and tetrafluorobutatriene (**14**) as the minor product (Scheme 6). The only example of a direct observation of a stepwise reaction of a carbene with an alkyne is the reaction of fluorenylidene in polycrystalline phenylacetylene.[22] Carbene **12** is stabilized by the fluorine substituent at the carbene center, which makes the cyclization to **13** less favorable. In addition, the low migratory aptitude of the fluorine atom in α-position prevents the 1,2-migration to butatriene **14**. Thus, the formation of (singlet) carbene **12** from $3 + C_2F_2$ is calculated (B3LYP/6-311G(d) + ZPE) to be exothermic by 81.9 kcal mol^{-1}, and the $12 \rightarrow 13$ cyclization releases 16.8 kcal mol^{-1}. In contrast, the corresponding singlet carbene from the $3 + C_2H_2$ reaction is not a minimum, and the triplet carbene is only 46 kcal mol^{-1} below the reactants but 34 kcal mol^{-1} higher in energy than **11**.

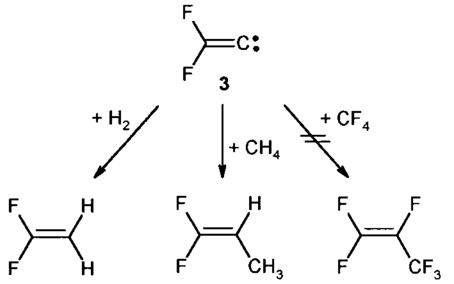


Scheme 5. Reactions of vinylidene **3** with double and triple bonds.



Scheme 6. Reaction of vinylidene **3** with difluoroacetylene (**6**).

Insertion reactions: The extreme electrophilicity of **3** is demonstrated by the insertion reactions into H_2, CH_4, and CD_4 (Scheme 7).[20] These reactions are rapid at temperatures below 30 K which means that the activation barriers must be close to zero. At the MP2/6-31G(d,p) level of theory a very shallow barrier of only 1.7 kcal mol^{-1} was found for the



Scheme 7. Insertion reactions of vinylidene **3**.

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$3 + H_2$ reaction, whereas for the $H_2C{=}C{:} + H_2$ insertion a barrier of 13.7 kcal mol^{-1} was calculated. Since the barrier for the rearrangement of $H_2C{=}C{:}$ to acetylene is much smaller (less than 3 kcal mol^{-1}),[23] the latter reaction will never be observed! The transition state for the H_2 insertion of **3** shows the expected in plane approach of the H_2 molecule with the H–H bond pointing towards the LUMO of **3** (see Figure 2).

CF_4 is one of the few molecules that did not react with **3**. This is also in agreement with theory, since the activation barrier for the CF insertion is calculated to be 40.6 kcal mol^{-1} and thus thermally inaccessible even at room temperature.

And finally—xenon as nucleophile: The highly electrophilic pentafluorophenyl cation forms the stable cation $[C_6F_5Xe]^+$ with a Xe–C bond length of 2.092 Å.[24] It was thus tempting to look for the reaction of **3** with Xe. Initial experiments with difluoroacetylene (**6**) in a xenon matrix were disappointing, since under these conditions 193 nm irradiation did not lead to any photochemistry. However, in a 0.5 % Xe-doped argon matrix at 7 K high yields of **3** were formed, which could now be reacted with Xe by annealing the matrix at 40 K.[25] Indeed, within several minutes the formation of a novel compound with a characteristic set of IR absorptions could be directly monitored. This compound was identified as a complex of **3** with Xe by comparison with the calculated IR spectrum. According to the ab initio calculations (MP2/RCEP,TZ2Pf) it is described best as a charge-transfer complex with a considerable positive charge at the Xe atom and a negatively charged carbon atom (Figure 2). As a consequence, the dipole moment increases from 1.1 to 3.3 D. Irradiation of the complex with 193 nm yields acetylene **6** and xenon, which explains that the complex could not be formed under these conditions in a neat xenon matrix.

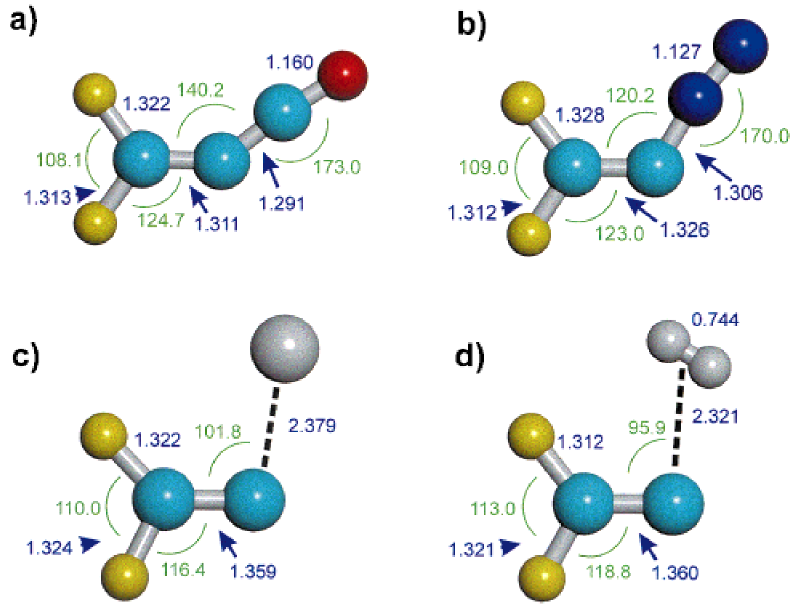


Figure 2. Some calculated structures of adducts of difluorovinylidene (**3**). a) Difluoropropadienone **4** (B3LYP/6–311G(d)); b) difluorodiazoethene (**5**) (B3LYP/6–311G(d)); c) charge-transfer complex of **3** and xenon (MP2/RCEP,TZ2Pf); d) transition state of the insertion of **3** into H_2 (MP2/6–31G(d,p)).

Recently Maier and Lautz described a similar complex between C_2 and Xe.[26] Since the electron affinity of C_2 (3.27 eV) even exceeds that of **3**, this finding is in perfect agreement with our observation.

Conclusion

Difluorovinylidene (**3**) exhibits a unique reactivity towards a large variety of reagents and allows the direct observation of several prototypic singlet carbene reactions (Figure 3). Other singlet carbenes, for example, phenylchlorocarbene,[27, 28] that have been matrix isolated are more nucleophilic and less reactive. In all cases **3** acts as an electrophile with the other reactant approaching in the plane of the molecule to allow for a strong interaction with the LUMO of **3**. The reactivity of **3** is in many respects comparable to a carbenium ion, although the charge at the carbene center is only +0.11. Thus, **3** can be regarded as a neutral cation, which picks up a considerable negative charge during the reaction. Figure 2 visualizes the importance of the LUMO of **3** to describe the structure of products, complexes, and transition states. The C-C-X angle decreases the weaker the C–X interaction is, and approaches almost 90° in the transition state for the insertion of **3** into H_2 (Figure 2 d).

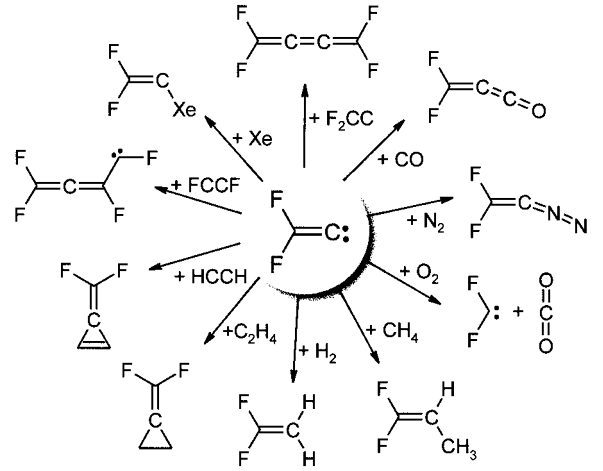
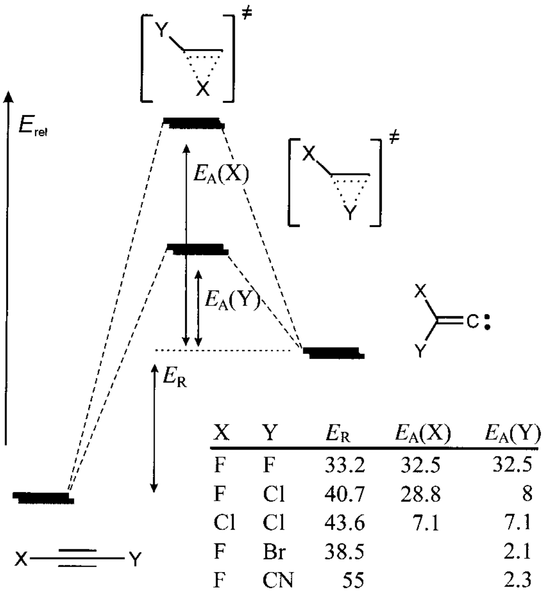


Figure 3. Reactions of difluorovinylidene **3** investigated using the matrix isolation technique.

Is UV photolysis a general approach to the matrix isolation of vinylidenes? Unfortunately all attempts to generate other vinylidenes, such as dichlorovinylidene or cyanofluorovinylidene, failed, so far.[20] While the migration of fluorine is prevented by a high activation barrier, the barriers for the migration of Cl, Br, and CN are calculated to only 7–8, 2, and 2 kcal mol^{-1}, respectively (Figure 4). Since the 193 nm photons deposit the tremendous energy of 148 kcal mol^{-1}, and the dissipation of energy in rare gas matrices is comparatively slow, there is more than enough excess energy available for the vinylidenes to cross these small barriers. Thus, alternative routes have to be developed to isolate vinylidenes with nonfluorine substituents.



X	Y	E_R	$E_A(X)$	$E_A(Y)$
F	F	33.2	32.5	32.5
F	Cl	40.7	28.8	8
Cl	Cl	43.6	7.1	7.1
F	Br	38.5		2.1
F	CN	55		2.3

Figure 4. Calculated (B3LYP/6–311G(d)) activation barriers and energies of reaction for the rearrangement of alkynes to vinylidenes.

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