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Reaction of 4-Oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene with Acetylene: A Carbene to Carbene Reaction

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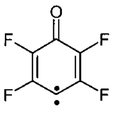
The EPR spectrum of triplet 4-oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene **1** was recorded in solid argon at 15 K. Carbene **1** reacts with acetylene under the conditions of matrix isolation yielding triplet vinylmethylene **4**, which was characterized by its IR, UV−vis, and EPR spectrum. Carbene **4** is photolabile and is converted to spiro compound **5** on irradiation with $\lambda > 515$ nm. The reaction of triplet carbene **1** with acetylene to produce triplet carbene **4** is predicted to be exothermic by 55 kcal mol^{-1} at the B3LYP/6-31G(d,p) level of theory. The cis isomer is calculated to be only 0.4 kcal mol^{-1} less stable than *trans*-**4** at this level of theory. According to our calculations, singlet carbene S-**4** is not a minimum on the $C_8F_4H_2O$ potential energy surface; however, at the T-**4** geometry, the lowest lying singlet state is predicted to be 20.7 kcal mol^{-1} higher in energy. The subsequent photochemical cyclization of T-**4** yielding spiro compound **5** is exothermic by 10.3 kcal mol^{-1} relative to T-**4** and by 31.1 kcal mol^{-1} relative to S-**4**. 4-Ethinyl-2,3,5,6-tetrafluorocyclohexa-2,5-dienone **9**, the C−H insertion product of **1** and acetylene, was not observed experimentally, although it is favored energetically by 4.3 kcal mol^{-1} over **5**.

Introduction

While stable, nucleophilic carbenes have been the focus of many research activities during the last years,[1−8] the chemistry of highly electrophilic carbenes is much less understood. Recently, we reported on reactions of 4-oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene **1** with molecular oxygen, hydrogen, methane, and propane.[9] By comparison of the experimental IR spectrum recorded in argon at 10 K with the calculated spectra of singlet and triplet **1**, we concluded that **1** is a triplet ground-state carbene. According to these calculations, the closed-shell $^1A'$ symmetrical singlet state is 3.9 kcal mol^{-1} higher and the open shell $^1B_1$ symmetrical singlet 7.4 kcal mol^{-1} higher in energy than the $^3B_1$ triplet state.

Carbene **1** exhibits an unusually high reactivity toward hydrocarbons and molecular hydrogen.[9] Thus, it readily inserts into CH bonds even under the conditions of matrix isolation at cryogenic temperatures, in contrast to many other carbenes such as diphenylcarbene or the parent 4-oxocyclohexa-2,5-dienylidene **2**. This is rationalized by the extreme electrophilicity of **1**. The electron affinity of **1**, which can be taken as a measure of its electrophilicity,[10] was predicted at the B3LYP level of theory to 3.6 eV for the lowest singlet state and 3.3 eV for the triplet ground state. This is well above that of difluorovinylidene $F_2C{=}C$: (exptl: 2.26 eV, calcd: 2.16 eV),[11−14] an extremely electrophilic singlet ground-state carbene.



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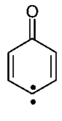

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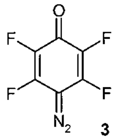

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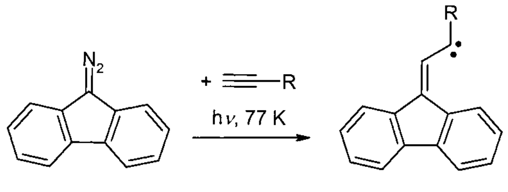
Only a few detailed mechanistic studies on reactions of carbenes with acetylenes have been reported in the literature.[15,16] On irradiation of 9-diazofluorene in polycrystalline phenylacetylene and other terminal acetylenes at 77 K, Lee and Jackson obtained triplet EPR spectra that were different from the EPR spectrum of triplet fluorenylidene.[15] These triplet species were assigned to the corresponding vinylcarbenes.



Difluorovinylidene reacts with difluoroacetylene to give an allenylcarbene, which can be photochemically rearranged to the corresponding methylenecyclopropene.[16]

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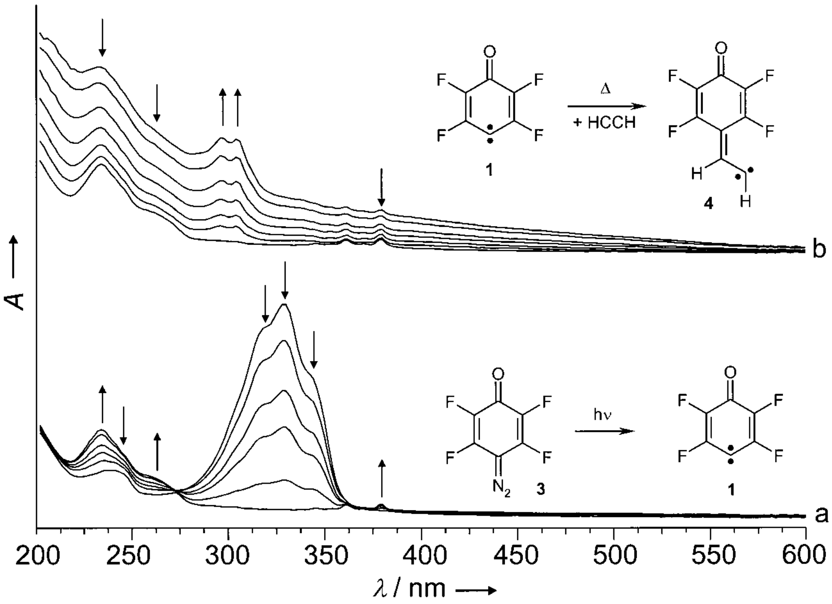


Figure 1. (a) UV spectra displaying the photochemistry (λ > 420 nm) of quinone diazide **3**, matrix-isolated in argon doped with 1% acetylene. (b) UV spectra recorded during annealing (35 K) of an argon matrix containing carbene T-**1** and acetylene.

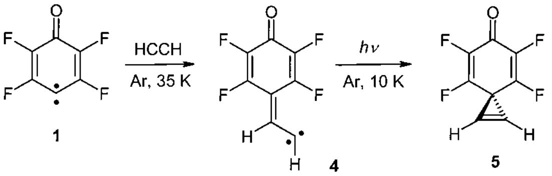
The reverse reaction for the parent system (C_4H_4 surface) was also reported.[17]

Here, we describe a study of the reactions of carbene **1** with acetylene which is aimed toward the following questions: (i) Are addition reactions or insertions the preferred pathways? (ii) Which intermediates are involved in the reaction sequence? (iii) The reaction of the triplet ground-state carbene **1** with acetylene to give singlet products is formally spin forbidden. At which point does the intersystem crossing (ISC) occur?

Results and Discussion

UV photolysis (λ = 260−320 nm) of 2,3,5,6-tetrafluoro-4-diazocyclohexa-2,4-dien-1-one **3** in solid argon doped with 1% acetylene at 15 K results in complete conversion of the diazo compound to carbene **1**. The IR spectrum of **1** obtained under these conditions was identical to the spectrum obtained in pure argon reported previously.[9] In the UV−vis spectrum, **1** was characterized by absorptions at 234, 263, and 379 nm and a very weak, broad band between 600 and 650 nm (Figure 1a). The triplet ground state of **1** had previously been inferred from the good agreement of the experimental IR spectrum with that calculated for the triplet state, while there was less agreement with the two lowest singlet states. This is now confirmed by EPR spectroscopy in argon at 15 K, which produces a spectrum characteristic of a triplet carbene with the zero field parameters $|D/hc| = 0.3300\ \mathrm{cm}^{-1}$ and $|E/hc| = 0.0063\ \mathrm{cm}^{-1}$ (Figure 2). The D value is in the range found for other oxocyclohexadienylidenes (Table 1). Due to hyperfine coupling with the adjacent fluorine atoms, the z_1, y_2, and z_2 transitions are split into triplets by 16, 36, and 16 G, respectively.

Annealing of a 0.5−1% acetylene-doped argon matrix containing carbene **1** at 35 K results in rapid changes in the IR, UV−vis, and EPR spectra, indicating the thermal reaction of the carbene with acetylene. This thermal reaction depends very much on the conditions of the matrix deposition. If the matrix is deposited at 30 K to obtain an optically transparent matrix most of the acetylene forms the well-known T-shaped van der Waals dimer.[18] This dimer is of lower mobility than the monomeric acetylene, and thus the thermal reaction of the dimer with carbene **1** is less efficient (only very low yields of products) than that of the monomer. The highest yields of thermal reaction products are observed if the matrix is deposited directly at 10 K or below, since under these conditions most of the acetylene is isolated as monomer. After the deposition the matrix is irradiated at 10 K to produce carbene **1**, annealed at 35 K for several minutes to induce thermal reactions, and finally cooled back to 10 K to record the spectra.



In the IR spectrum, the thermal reaction of **1** with acetylene results in the decrease of all absorptions assigned to carbene **1** and formation of a new compound A with intense IR bands at 1583, 1555, 1341, 1020, and 975 cm^{-1} (Table 2). The color of the matrix changes from blue to red during the thermal reaction. The red color results from a very broad, weak absorption in the visible region extending from 400 to 550 nm. Intense absorptions of A are observed in the UV at 297 and 305 nm (Figure 1b). IR bands between 1550 and 1600 cm^{-1} and long-

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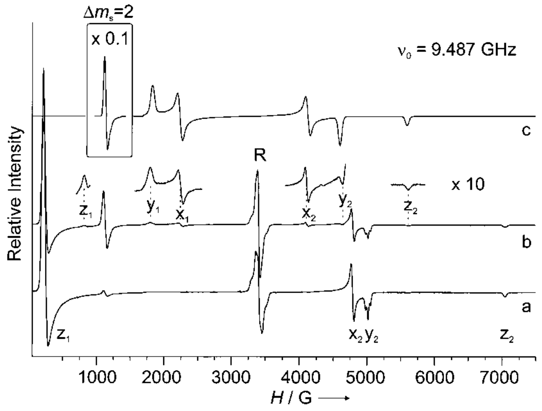
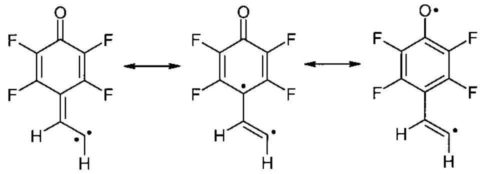


Figure 2. EPR spectra of triplet carbenes **1** and **4**. (a) Spectrum of T-**1**, photolytically generated in an argon matrix doped with 1% acetylene. (b) The same matrix after annealing at 35 K for 15 min. (c) Simulated EPR spectrum of T-**4** (parameters see text).

wavelength absorptions in the visible region indicate an extended conjugated system in A.

Most characteristic are the changes in the EPR spectrum during warming of the matrix (Figure 2). The EPR transitions assigned to carbene **1** decline, while simultaneously a new triplet species with a zero-field splitting significantly smaller than that of **1** is formed. These changes in the EPR spectrum are concurrent with changes in the IR and UV–vis spectra. On the basis of its IR spectrum (vide infra), compound A was assigned the structure of the vinylmethylene **4**.

The EPR spectrum of carbene **4** exhibits all features of a randomly oriented triplet species, including the $\Delta m_s = 2$ transition. By simulation of the experimental spectrum, the zero field splitting parameters were determined to be $|D/hc| = 0.2047$ cm^{-1} and $|E/hc| = 0.0133$ cm^{-1}. All EPR spectra recorded after irradiation of the matrix isolated samples exhibited signals in the $g = 2$ region due to radical impurities generated by the irradiation of the matrix. The D value of **4** is significantly smaller than that of the parent vinylmethylene (cis: $|D/hc| = 0.4578$ cm^{-1} and $|E/hc| = 0.0193$ cm^{-1}, trans: $|D/hc| = 0.4093$ cm^{-1} and $|E/hc| = 0.0224$ cm^{-1}),[19] indicating a significant contribution of the diradicaloid mesomeric structure.



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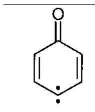
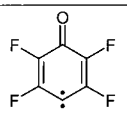
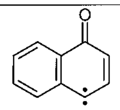
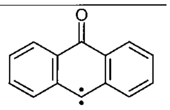
The IR spectrum of **4** shows strong absorptions at 1583, 1555, 1341, 1020, and 975 cm^{-1}, in good agreement with the IR data calculated at the UB3LYP/6-31G(d,p) level of theory (Table 2, Figure 3). The strongest absorption of **4** is an anti-symmetrical combination of the ν(C=C) vibrations observed at 1555 cm^{-1}. The corresponding symmetrical combination is found at 1659 cm^{-1}. The absorption at 1583 cm^{-1} is assigned to the ν(C=O) stretching mode. The ν(C–H) modes 38 and 39, calculated at 3102 and 3263, respectively, were not detected in the experimental spectrum. Reaction with d$_2$-acetylene yields deuterated carbene d$_2$-**4**. In agreement with the calculated spectra the IR absorption which shows the strongest isotopic shift is the δ(C–H) mode at 838 cm^{-1}, which is shifted by 58 to 780 cm^{-1} on deuteration.

Table 1. |*D*/*hc*| Values of Oxocyclohexadienylidenes

 **2**	 **1**		
0.3179 cm^{-1} [24]	0.3300 cm^{-1}	0.3333 cm^{-1} [24]	0.3360 cm^{-1} [25]

In the case of the parent vinylmethylene both the cis and the trans isomer were observed after photolysis of the precursor in frozen solutions, while deposition of the precursor from the gas phase and trapping at 8 K produced the trans carbene as the only isomer.[19] The IR and EPR spectra of matrix isolated **4** do not provide any evidence for the presence of geometric isomers. According to the DFT calculations (B3LYP/6-31G(d,p)) both isomers are nearly degenerate with a slight (probably not significant) preference of 0.4 kcal mol^{-1} for the trans isomer. A comparison of the IR spectra calculated for the cis and trans isomers reveals only small differences which do not allow a definitive assignment of the experimental spectrum (Table 2). The most characteristic differences in the IR spectra of *trans*- and *cis*-**4**—apart from the ν(C–H) modes which are too weak to be definitively assigned—are the relative intensities of the in-plane ring deformation modes 31 and 32 and of modes 25 and 26. While for *cis*-**4** modes 25 and 26 are equally intense, in *trans*-**4** mode 25 is almost twice as intense as mode 26. For *cis*-**4**, the calculation predicts mode 31 to be of much lower intensity than 32; for *trans*-**4** mode 31 is predicted to have a slightly higher intensity than 32. In both cases, the experimental spectrum is reproduced better by the calculated spectrum of *trans*-**4**.

Carbene **4** is labile toward visible light, and irradiation with $\lambda > 515$ nm rapidly converts **4** to a further compound **5**, which does not show any EPR signals. Compound **5** exhibits pronounced absorptions in the carbonyl region of the IR spectrum, and again the experimental spectrum was assigned by comparison with DFT calculations. The spectrum calculated for the product of ring closure, 4,5,7,8-tetrafluoro-spiro[2.5]octa-1,4,7-trien-6-one, nicely fits the experimental spectrum (Figure 3, Table 3). The absorption at 1690 cm^{-1} is attributed to the ν(C=O) mode, absorptions between 1678 and 1666 cm^{-1} to symmetrical and anti-symmetrical combinations of ν(C=C) stretching vibrations. Thus, the photochemical activation of carbene **4** results in ring-closure to cyclopropene **5**, which is an independent proof of the proposed structure of **4**. The rearrangement of vinylcarbenes to cyclopropenes is well documented in the literature.[20]

The thermochemistry of the reaction of carbene **1** with acetylene estimated by DFT calculations is shown in Figure 4. The primary addition step to give **4** in its triplet ground state is exothermic by 55 kcal mol^{-1}. This reaction step converts a triplet carbene to another triplet carbene and is thus a spin-allowed reaction. Since it proceeds rapidly at cryogenic temperatures, the barrier for this

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Table 2. IR Spectroscopic Data of Triplet Carbene 4 Generated via the Reaction of 1 with HCCH

				trans-**4**		*cis*-**4**		
no.	sym	$\tilde{\nu}_{\mathrm{exp}}/\mathrm{cm}^{-1}$ [a]	$I_{\mathrm{rel,exp}}$ [b]	$\tilde{\nu}_{\mathrm{calcd}}/\mathrm{cm}^{-1}$ [c]	$I_{\mathrm{rel,calcd}}$	$\tilde{\nu}_{\mathrm{calcd}}/\mathrm{cm}^{-1}$ [c]	$I_{\mathrm{rel,calcd}}$	mode
39	*a'*			3263	0.00	3294	0.02	
38	*a'*			3102	0.01	3151	0.01	
37	*a'*	1659	0.24	1674	0.28	1674	0.32	ν_s(C=C)
36	*a'*	1583	0.68	1603	0.70	1598	0.68	ν(C=O)
35	*a'*	1555	1.00	1579	1.00	1578	1.00	ν_{as}(C=C)
34	*a'*	1483	0.14	1520	0.40	1516	0.45	ν(C−C)
33	*a'*	1466	0.12	1466	0.10	1466	0.09	ν(C=C)
32	*a'*	1359	0.40	1396	0.40	1386	0.74	δ(C−C)
31	*a'*	1341	0.72	1373	0.52	1365	0.20	δ(C−C)
30	*a'*			1339	0.02	1342	0.03	
29	*a'*	1259	0.04	1279	0.07	1283	0.02	δ(C−H)
28	*a'*	1163	0.10	1224	0.01	1218	0.01	ν(C−F)
27	*a'*	1033	0.18	1147	0.01	1145	0.00	ν(C−F)
26	*a'*	1020	0.40	1048	0.31	1032	0.50	δ(C−H)
25	*a'*	975	0.72	992	0.55	987	0.48	ν(C−F)
24	*a'*	–	–	876	0.01	911	0.16	
23	*a"*	838	0.08	875	0.17	886	0.27	δ(C−H)
22	*a'*	–	–	782	0.01	779	0.04	
21	*a"*	701	0.10	703	0.09	722	0.03	γ(C−H)
20	*a"*	633	0.14	652	0.01	661	0.02	γ(C−C)
19	*a'*	600	0.12	609	0.02	610	0.01	δ(C−C)
18	*a"*			580	0.00	580	0.00	
17	*a'*			557	0.02	562	0.00	
16	*a"*			549	0.05	557	0.00	
15	*a'*			457	0.02	454	0.00	
14	*a'*			422	0.01	423	0.01	

[a] Argon, 10 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP/6-31G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

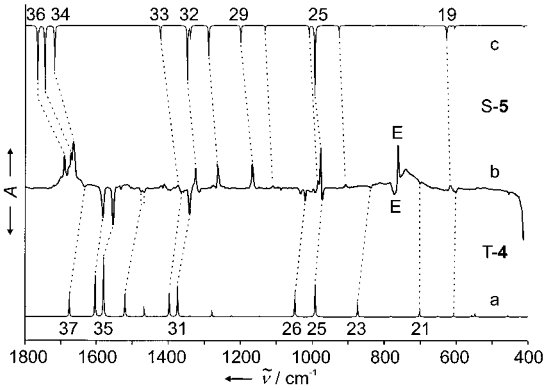

Figure 3. Photochemistry of triplet carbene **4**. (a) Calculated (UB3LYP/6-31G(d,p), unscaled) spectrum of T-**4**. (b) IR difference spectrum. Bands pointing downward disappear, bands pointing upward appear on irradiation of T-**4** with λ > 570 nm. Bands marked with E are due to acetylene. (c) Calculated (B3LYP/6-31G(d,p), unscaled) spectrum of **5**.

reaction must be small or absent. The singlet state of **4** is about 20 kcal mol^{-1} higher in energy (vertical excitation); however, we were unable to locate a minimum for S-**4** using B3LYP/6-31G(d,p) calculations. S-**4** directly converges to the 31 kcal mol^{-1} more stable cyclopropene **5**. The cyclization of the triplet carbene T-**4**, on the other hand, requires a spin inversion which results in a thermal barrier for the T-**4** → **5** ring closure. This reaction is still exothermic by 10 kcal mol^{-1}.

Table 3. IR Spectroscopic Data of 5 Generated by the Photochemical Ring-Closure of Carbene 4

no.	sym	$\tilde{\nu}_{\mathrm{exp}}/\mathrm{cm}^{-1}$ [a]	$I_{\mathrm{rel,exp}}$ [b]	$\tilde{\nu}_{\mathrm{calcd}}/\mathrm{cm}^{-1}$ [c]	$I_{\mathrm{rel,calcd}}$	mode
39	a_1			3329	0.02	
38	b_1			3279	0.04	
37	a_1			1777	0.00	
36	a_1	1690	0.88	1764	0.78	ν(C=O)
35	a_1	1678	0.48	1744	0.92	ν_s(C=C)
		1671	0.94			
34	b_2	1666	1.00	1718	0.65	ν_{as}(C=C)
33	b_2	1412	0.11	1423	0.16	ν(C−C)
32	a_1	1324	0.64	1347	0.78	δ(C−C)
31	b_2	1322	0.53	1340	0.19	ν(C−C)
30	a_1	1263	0.14	1289	0.44	ν(C−F)
29	a_1	1166	0.55	1200	0.25	ν(C−C)
28	b_2	1110	0.05	1132	0.06	ν(C−F)
27	a_1	1049	0.03	1023	0.00	δ(C−H)
26	b_1	985	0.16	1009	0.10	δ(C−H)
25	b_2	977	0.99	993	1.00	ν(C−F)
24	a_1	961	0.07	927	0.09	δ(C−H)
23	a_2	908	0.07	835	0.00	γ(C−H)
22	b_1	811	0.02	832	0.01	δ(C−C)
21	b_2			795	0.00	
20	b_1	658	0.02	689	0.02	δ(C−F)
19	b_2	614	0.19	627	0.22	γ(C−C)
18	a_2			625	0.00	
17	b_1			614	0.01	
16	a_1			605	0.04	
15	a_1			510	0.00	
14	b_2			415	0.00	
13	a_2			415	0.00	
12	a_1			411	0.02	

[a] Argon, 10 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP/6-31G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

The product of the CH insertion **6** is not observed in our experiments, although it is calculated to be 4 kcal mol^{-1} more stable than the addition product **5**. The insertion of a carbene into the CH bond of an acetylene has been described recently by Arduengo et al.[21] The dihydroimidazol-2-ylidene **7**, a stable nucleophilic singlet carbene, reacts with acetylene in THF at room temperature to the insertion product **8**, while the addition to the triple bond is not observed in this case. This unusual reactivity of **7** is rationalized by its high basicity which results in the deprotonation of the acidic acetylene followed by ion recombination. The highly electrophilic carbene **1** is expected to be much less basic than nucleophilic carbenes such as **7** which rules out this type of reactivity.

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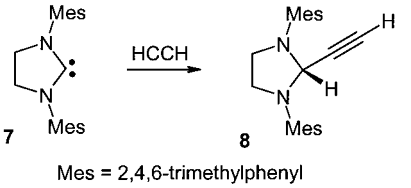


It is interesting to compare the reactivity of the highly electrophilic triplet carbene **1** toward acetylene with that of difluorovinylidene **9**, a highly electrophilic singlet carbene. Both carbenes add to the acetylene triple bond at temperatures below 40 K, which indicates that these reactions are controlled by the diffusion of acetylene in the solid matrix rather than by intrinsic activation barriers. While the reaction of **1** is stepwise, as shown above, vinylidene **9** produces directly the methylenecyclopropene **11**, and allenylcarbene **10** is not observed as an intermediate (Scheme 1).[16] The reaction of **9** with difluoroacetylene, on the other hand, proceeds via singlet allenylcarbene **12** that could be matrix-isolated and spectroscopically characterized. Photochemical activation of **12** results in the cyclization to methylenecyclopropene **13**. Thus, the latter reaction is stepwise, although spin allowed and although both steps are highly exothermic. A detailed computational analysis of the reactions of **9** with acetylene and difluoroacetylene reveals that the major difference in the reaction paths is the stability of the intermediate allenylcarbenes **10** and **12**, respectively. While **12** is a singlet ground state carbene with a fairly large singlet triplet splitting (stabilized by the fluorine atom attached to the carbene center), carbene **10** is a triplet carbene, and the corresponding singlet state is not a minimum on the potential energy surface. Although **10** is not a real intermediate, structures which resemble **10** are passed along the reaction coordinate,[22] and thus the mechanisms for the addition of **9** to HCCH and FCCF are basically identical. For the addition of **1** to HCCH now the spin restriction comes into play leading to the spin-allowed formation of **4**. The ring-closure of **4** to **5** is a photochemical step. It is reasonable to assume that the excited triplet state of **4** crosses to singlet **4**, which then forms **5** without a thermal barrier.

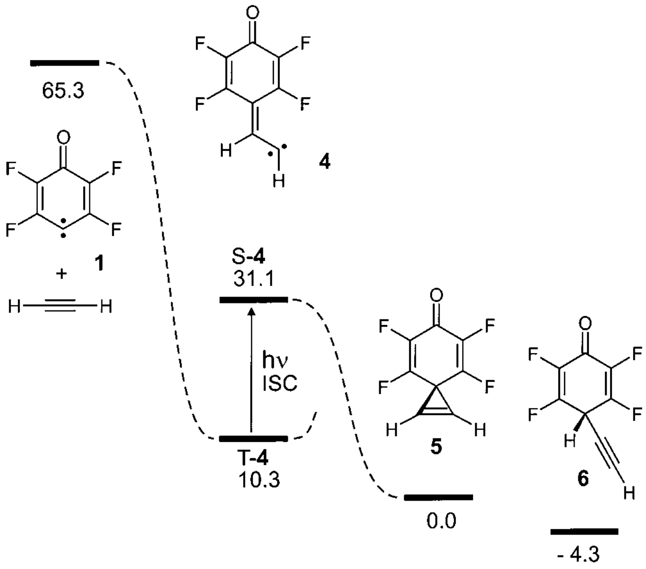
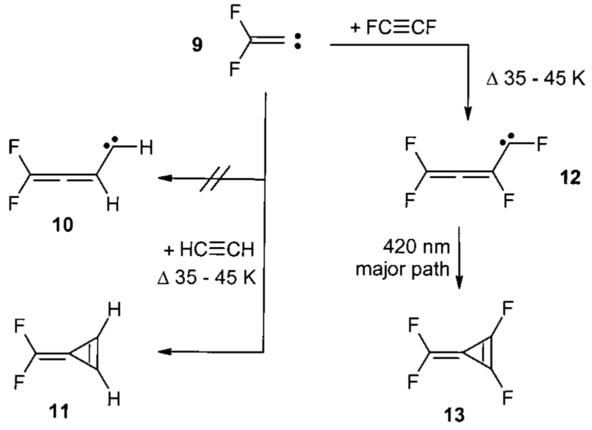


Figure 4. Energy profile of the **1** + HCCH → **5** reaction estimated at the B3LYP/6-31G(d,p) level of theory including the zero-point energy (zpe).

Scheme 1



Conclusion

Carbene **1** is an extremely electrophilic carbene which readily reacts with acetylene via an addition reaction. No transition state could be located for the initial step of the reaction, which indicates that the **1** + HCCH → **4** reaction proceeds without an activation barrier. The CH insertion, although thermodynamically preferred, is not observed. This fits into the reaction pattern observed for highly electrophlic singlet carbenes. Independent of the spin state of the carbene, the first step is the electrophilic addition of the carbene to one of the acetylene carbon atoms forming a second carbene in a spin allowed reaction. This carbene can be trapped as an intermediate if it is a stable singlet on the singlet path or triplet on the triplet path. In this case, the ring-closure requires an additional thermal or photochemical activation.

Experimental Section

Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed cycle cryostat. Matrixes were produced by co-deposition of a large excess of argon (Messer-Griesheim, 99.9999%), doped with 1% acetylene, and the trapped species on a cold CsI window. Deviating from standard protocol, the cold window was kept at minimum temperature (10 K) during deposition in order to avoid the formation of acetylene dimer. Argon matrixes for EPR spectroscopy were deposited on a copper or sapphire rod at 15 K. Infrared spectra were recorded with a Bruker Equinox 55 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range of 400–4000 cm^{-1}. EPR spectra were measured with a Bruker Elexsys E500 spectrometer. Irradiations were carried

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out with an Osram HBO 500 W/2 high-pressure mercury arc lamp in an Oriel housing with quartz optics, a dichroic mirror and cutoff filters (Schott). Calculations were performed with the GAUSSIAN98 suite of programs.[23] Geometries, energies and vibrational spectra were obtained using the B3LYP method with the 6-31G(d,p) basis set. Energies are zero point corrected, band positions are unscaled. Frequency calculations were performed in order to obtain the vibrational spectra and the zero point energies and to determine the nature of the stationary points. The EPR spectrum of **4** was simulated with Bruker's XSophe simulation suite.

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Supporting Information Available: Calculated geometries (Cartesian coordinates), energies and vibrational spectra of *trans*-**4**, *cis*-**4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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