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# Insertion of Difluorovinylidene into Hydrogen and Methane

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# Insertion of Difluorovinylidene into Hydrogen and Methane

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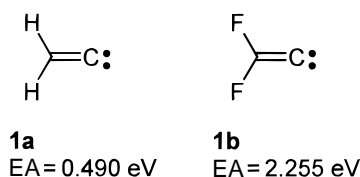
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**Abstract:** Insertion reactions of difluorovinylidene **1b** into H<sub>2</sub>, CH<sub>4</sub>, and CD<sub>4</sub> have been observed in argon matrixes at 20–40 K. These reactions are controlled by diffusion of trapped species rather than by activation barriers, indicating that the activation barriers are very small (<1 kcal/mol) or absent. In contrast, no insertion was observed into CF<sub>4</sub> or C<sub>2</sub>H<sub>4</sub>. With C<sub>2</sub>H<sub>4</sub>, addition to the double bond to give (difluoromethylene)cyclopropane (**5**) is the only pathway. This was rationalized by ab initio (MP2/6-31G(d,p)) and DFT (B3LYP/6-311++G-(d,p)) calculations, which predict activation barriers of essentially zero for the H<sub>2</sub> and CH<sub>4</sub> insertion, but 40 and 3 kcal/mol for the insertion into CF<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, respectively.

## Introduction

The insertion into XH bonds (X = C, Si, O, etc.) is highly characteristic of carbenes and widely used in synthetic chemistry. Both singlet and triplet carbenes show insertion reactions, although the mechanisms are different. Intermolecular CH insertions were systematically studied in low-temperature organic glasses by Tomioka et al.<sup>1–7</sup> and Platz et al.<sup>8–11</sup> The conclusion of these and many other studies is that triplet carbenes at low temperature react via an abstraction recombination mechanism with radical pairs as intermediates. Typical activation barriers for CH insertions of triplet carbenes are several kcal/mol (for example, for the reaction of diphenylcarbene with toluene in the solid state a barrier of 6.9 kcal/mol was determined).<sup>11</sup> Since in several cases the insertions were still observed at 77 K and curved Arrhenius plots were found, quantum chemical tunneling was suggested to be important under these conditions.<sup>11</sup> A problem of the investigation of thermal carbene reactions in organic glasses is secondary photolysis of the long-lived carbenes during photolysis of the precursor, which leads to the photochemical rather than the thermal products (e.g., CH insertion instead of OH insertion in polycrystalline alcohols).<sup>12</sup>

The insertions of singlet carbenes into CH bonds are concerted reactions. The activation energy for the insertion of (singlet) methylene into methane was calculated to be 9.1 kcal/mol at the SCF/6-31G(d) level of theory, but this barrier is reduced to zero if electron correlation is considered at the MP3/6-31G(d) level of theory.<sup>13</sup> For typical singlet ground-state carbenes bearing electronegative substituents (halogen, OR, NR<sub>2</sub>) a reduced electrophilicity and substantial barriers for insertions are expected, and thus these reactions are generally not observed in low-temperature matrixes. One of the few examples is the rearrangement of *tert*-butylchlorocarbene to 2,2-dimethyl-1-chlorocyclopropane in argon at 11 K, an intramolecular CH insertion.<sup>14</sup> High-level ab initio calculations (CCSD(T)) predict activation barriers of 8 and 33 kcal/mol for the insertion of HFC: and F<sub>2</sub>C: into H<sub>2</sub>, respectively.<sup>15</sup> Substitution of the hydrogen atoms in H<sub>2</sub>C: by fluorine leads to an increase of the nucleophilicity of these carbenes, and since the primary step in the carbene insertion is an electrophilic attack of the carbene center on the XH bond, the reactivity is drastically reduced. This also explains why the highly stable nucleophilic carbenes of Arduengo type<sup>16</sup> are completely unreactive toward CH bonds.



Vinylidenes **1** are another class of ground-state singlet carbenes, and for the parent vinylidene **1a** the activation energy for the insertion into H<sub>2</sub> was calculated to be almost 13 kcal/mol using high-level ab initio calculations, again predicting a low reactivity.<sup>17</sup> Substitution of the hydrogen atoms in **1a** by fluorine atoms drastically increases the electron affinity EA, in

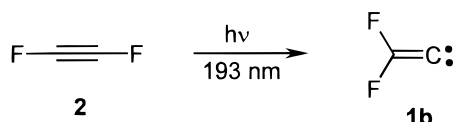
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contrast to fluorine substitution in  $\text{H}_2\text{C}$ , which decreases EA.<sup>18</sup> Thus, difluorovinylidene (**1b**) is one of the most electron deficient and electrophilic carbenes known, and its high reactivity toward CH bonds was demonstrated by Brahms and Dailey in gas-phase experiments.<sup>19</sup> Recently we reported on the synthesis of **1b** in low-temperature matrices in high yields, which allows the study of the chemistry of this unusual species using direct spectroscopic methods.<sup>20–22</sup> Here we describe a matrix isolation and computational study of the insertion of difluorovinylidene (**1b**) into  $\text{H}_2$  and  $\text{CH}_4$ , again demonstrating the extreme reactivity of **1b**, unprecedented for other singlet ground-state carbenes.<sup>23</sup>

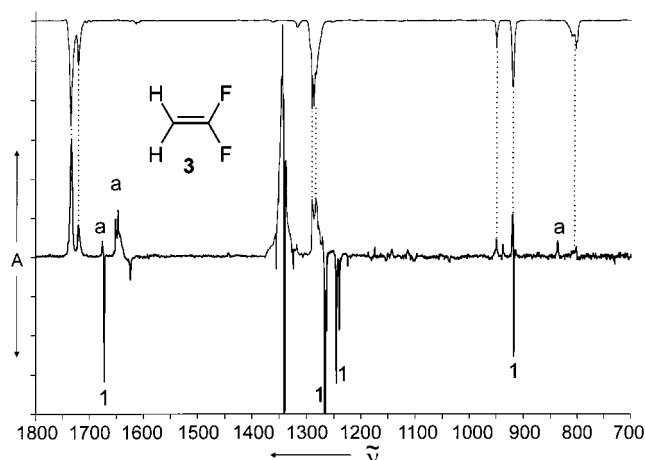
## Results and Discussion

Difluorovinylidene (**1b**) is produced in high yields by photolysis of matrix-isolated (Ar, 8 K) difluoroacetylene (**2**) with the 193 nm light of an ArF excimer laser.<sup>20a</sup> Since the barrier for the thermal rearrangement of **1b** back to acetylene (**2**) is calculated to be higher than 30 kcal/mol,<sup>24</sup> matrix-isolated vinylidene **1b** is kinetically stable at low temperature as long as intermolecular reactions are inhibited. At temperatures above 25–30 K diffusion of small molecules in solid argon becomes rapid, and bimolecular reactions are observed if the activation barriers are small enough. Thus, annealing of argon matrixes containing vinylidene **1b** at 30 K results in the rapid dimerization to tetrafluorobutatriene.<sup>22</sup>



In typical trapping experiments the matrix ratio of **2** is < 1:1000 and the matrixes are doped with ca. 0.5% of a trapping reagent. Under these conditions a large fraction of **2** is isolated in matrix cages that do not contain the trapping reagent, and thus the 193 nm irradiation produces mainly **1b** and only small amounts of secondary in-cage reaction products. Vinylidene **1b** is extremely reactive, and the reactions with  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{F}_2$ , and  $\text{C}_2\text{H}_2$  have been investigated in our laboratory.<sup>20–22</sup>

**Reaction of Vinylidene **1b** with  $\text{H}_2$ .** Although the vapor pressure of  $\text{H}_2$  at 8 K is approximately  $10^{-1}$  mbar, a substantial amount of hydrogen can be trapped in solid argon at this temperature. The mobility of  $\text{H}_2$  in argon is very high, and diffusion becomes rapid at temperatures as low as 20 K. If a 0.5%  $\text{H}_2$ -doped argon matrix containing about 0.05% of **2** is irradiated at 193 nm, vinylidene **1b** is formed as the major product. A minor product exhibits very strong IR absorptions at 1734/1720 and 1290/1283  $\text{cm}^{-1}$ . Annealing of the matrix at 20–30 K rapidly results in a further increase of these bands and simultaneously decrease of all absorptions assigned to **1b** (Figure 1). By comparison with an authentic matrix-isolated sample, the new product was identified as 1,1-difluoroethene (**3**). The rapid insertion of **1b** into a hydrogen molecule at 20



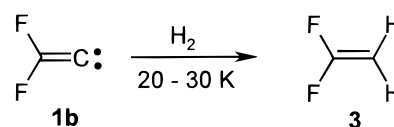
**Figure 1.** Center: Difference IR spectrum (in absorbance) showing changes in the IR spectra during annealing of a 0.5%  $\text{H}_2$ -doped argon matrix containing difluorovinylidene (**1b**) at 40 K. Bands pointing downward are disappearing and bands pointing upward are appearing during the thermal reaction. Top: IR spectrum of 1,1-difluoroethene (**3**), matrix-isolated in argon at 10 K as reference. a:  $\text{F}_2\text{C}=\text{C}=\text{N}_2$  formed from  $\text{N}_2$  contamination of the matrix.

**Table 1.** Computed Activation Energies and Thermochemistry of the Reactions.

	$E_A$			$\Delta H_R$		
	MP2 <sup>a</sup>	MP2 <sup>b</sup>	B3LYP <sup>c</sup>	MP2 <sup>a</sup>	MP2 <sup>b</sup>	B3LYP <sup>d</sup>
<b>1b</b> + $\text{H}_2 \rightarrow \textbf{3}$	0.6	1.7	0	127.8	118.5	113.4
<b>1a</b> + $\text{H}_2 \rightarrow \text{C}_2\text{H}_4$	9.7	13.7	9.7	99.4	88.4	82.8
<b>1b</b> + $\text{CH}_4 \rightarrow \textbf{4}$	0	0	0	114.1	109.1	101.1
<b>1b</b> + $\text{CF}_4 \rightarrow \text{C}_3\text{F}_6$	40.0	40.6	40.9	90.6	87.3	82.4
<b>1b</b> + $\text{C}_2\text{H}_4 \rightarrow \textbf{5}$	0	0	0	104.8	99.7	88.7
<b>1b</b> + $\text{C}_2\text{H}_4 \rightarrow \textbf{6}$	5.2	5.9	3.1	122.9	118.6	110.4

<sup>a</sup> MP2/6-31G(d,p). <sup>b</sup> MP2/6-31G(d,p) + ZPE. <sup>c</sup> B3LYP/6-311++G-(d,p) + ZPE. <sup>d</sup> B3LYP/6-311G(d,p) + ZPE.

K implies that the activation barrier for this process is very small or zero and again demonstrates the enormous reactivity of the vinylidene.



A comparison of the vibrational spectra of ethene **3** and vinylidene **1b** reveals an amazing similarity. The symmetrical and asymmetrical FCF stretching vibrations are approximately at the same frequency, and the  $\text{C}=\text{C}$  stretching vibration in **1b** is red-shifted by 50  $\text{cm}^{-1}$  only, compared to **3**. This is in accordance with the very similar CF bond distances in **1b** and **3** of 1.327 and 1.331 Å, respectively (MP2/6-31G(d,p)). The  $\text{C}=\text{C}$  distance increases from 1.325 Å in **3** to 1.357 Å in **1b**.

The insertion of **1b** into  $\text{H}_2$  to give **3** is calculated to be exothermic by 113.4 kcal/mol at the B3LYP/6-311G(d,p) and 118.5 kcal/mol at the MP2/6-31G(d,p) level of theory (these values include ZPE, Table 1). According to a systematic theoretical study by Jursic on the **1b**  $\rightarrow$  **2** rearrangement,<sup>24</sup> the B3LYP method is very reliable to calculate thermodynamic properties and activation barriers of reactions of **1b**. The difference of 5.1 kcal/mol obtained for the reaction energy of the **1b** +  $\text{H}_2$  reaction with B3LYP and MP2 calculation is also found for the **1b**  $\rightarrow$  **2** rearrangement, and so far it is not clear whether it reflects problems of the DFT or the ab initio theory to accurately describe **1b**. The exothermicity of the **1b** +  $\text{H}_2$

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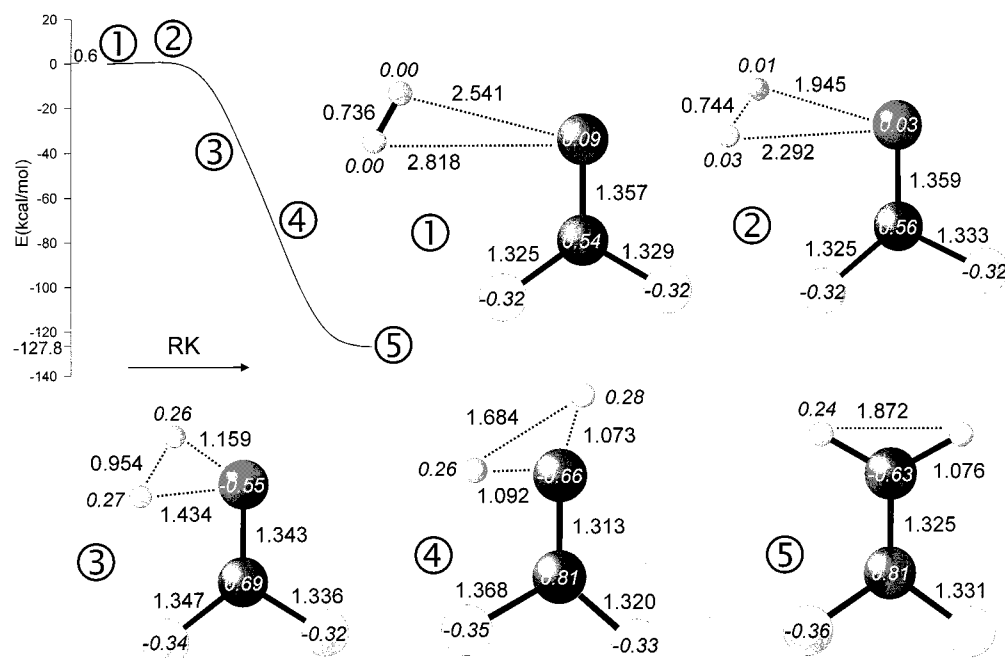
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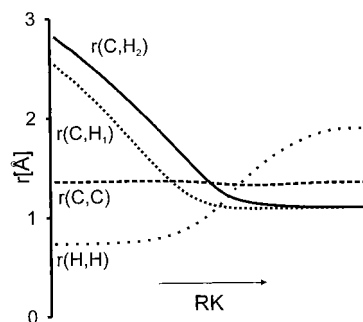


**Figure 2.** Some structures along the reaction pathway (IRC) of the insertion of difluorovinylidene (**1b**) into H<sub>2</sub>, calculated at the MP2/6-31G(d,p) level of theory. Bond distances and NBO charges (in italics) are given in the structure drawings, relative energies in the reaction coordinate diagram.

reaction is considerably larger than that of the insertion of the parent vinylidene **1a** into H<sub>2</sub>. For the latter reaction Jensen et al. found a reaction energy of -81.0 kcal/mol using MP4/6-311+G(d,p)//MP2/6-31G(d,p) theory,<sup>17</sup> while the DFT value is -82.8 kcal/mol. Here, the ab initio and DFT results are in very good agreement.

While semiempirical or RHF theory predicts a substantial activation barrier for the insertion reaction, the barrier becomes very small if electron correlation is taken into account (0.6 kcal/mol predicted by MP2/6-31G(d,p) and zero by B3LYP/6-311++G(d,p) + ZPE calculations, Table 1). Starting from the transition state, the reaction pathway was calculated using the IRC method<sup>25</sup> and MP2 theory (Figure 2). During the reaction the hydrogen atoms are located in the molecular plane of **1b**. As predicted by the Hammond postulate,<sup>26</sup> a very early transition state is observed for this exothermic reaction. The hydrogen molecule is located at about 2 Å distance from the carbene center C(1) with the H-H bond pointing toward the LUMO of **1b**, clearly indicating the electrophilic nature of the attack of **1b** on H<sub>2</sub>. In this transition state the H-H distance is elongated by 1.1% only, and the H<sub>2</sub> molecule is still almost neutral. With decreasing C(1)H distance a considerable amount of charge is transferred from H<sub>2</sub> to the carbene carbon atom C(1), and simultaneously the HH bond becomes weaker and the HH distance larger. In the last step the two hydrogen atoms move in the molecular plane toward their final positions at almost constant C(1)H distance (Figure 3).

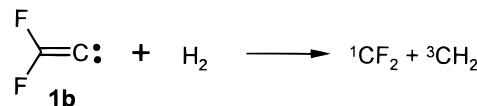
This mechanism is very similar to the insertion of the parent vinylidene **1a** into H<sub>2</sub>, as it was described by Jensen et al.<sup>17</sup> The major difference is a nonzero activation barrier for the latter reaction at all levels of theory. MP4/6-311+G(d,p) calculations predict a barrier of 12.8 kcal/mol,<sup>17</sup> and at the B3LYP/6-311++G(d,p) level a barrier of still 10 kcal/mol is found (Table 1). The transition state shows C(1)H distances of 1.395 and 1.764 Å for the two hydrogen atoms and a considerable charge transfer from the H<sub>2</sub> molecule to the carbene center



**Figure 3.** Calculated (IRC, MP2/6-31G(d,p)) atomic distances during the insertion of **1b** into H<sub>2</sub>.

(Figure 4). Obviously, the less electrophilic character of **1a** compared to **1b** results in a significantly reduced reactivity toward weak nucleophiles such as a hydrogen molecule. Since the activation barrier for the [1,2]-H migration in **1a** is estimated to be less than 3 kcal/mol,<sup>27</sup> the **1a** + H<sub>2</sub> reaction cannot compete with this rearrangement.

In other bimolecular reactions of **1b** (e.g., the reaction with O<sub>2</sub>)<sup>21</sup> the formation of the thermodynamically stable CF<sub>2</sub> is an important reaction channel; we therefore calculated the overall reaction energy for the formation of <sup>1</sup>CF<sub>2</sub> and <sup>3</sup>CH<sub>2</sub>.



This reaction is endothermic by 13.9 kcal/mol (B3LYP/6-311G(d,p) + ZPE), and thus CF<sub>2</sub> is not formed in these experiments.

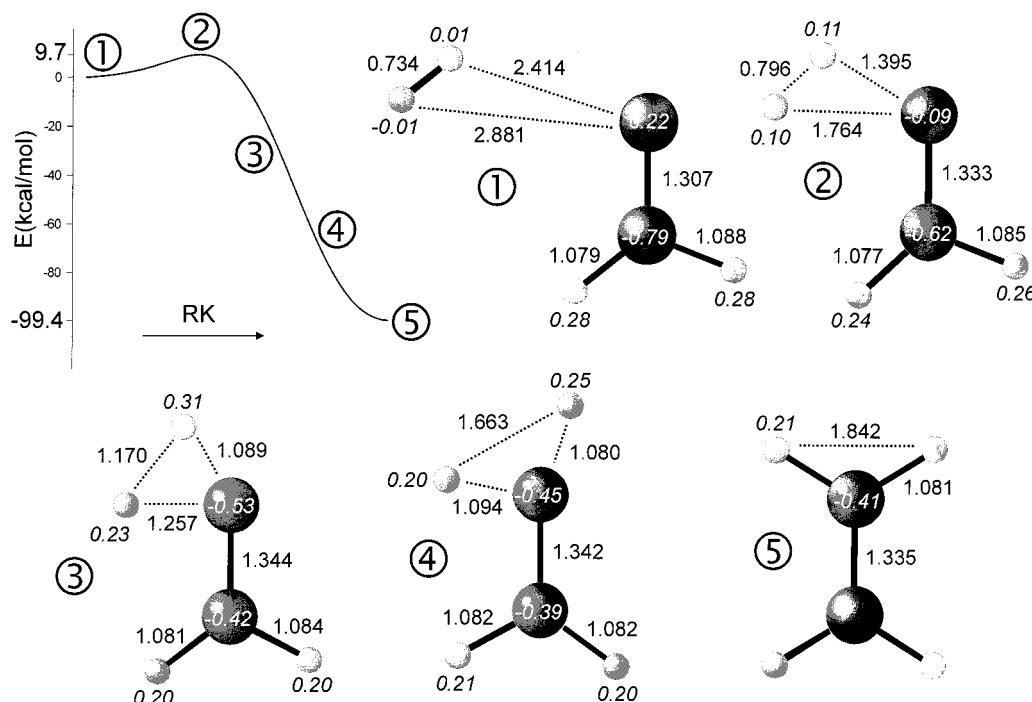
**Reaction of Vinylidene **1b** with Methane.** Annealing of a 0.5% CH<sub>4</sub>-doped argon matrix containing **1b** at 40 K results in the disappearance of **1b** and formation of a new compound with strong absorptions at 1759 and 1226 cm<sup>-1</sup> (Figure 5, Table 2)

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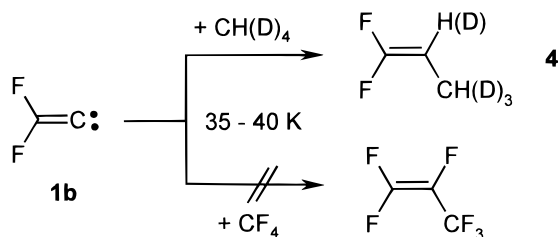
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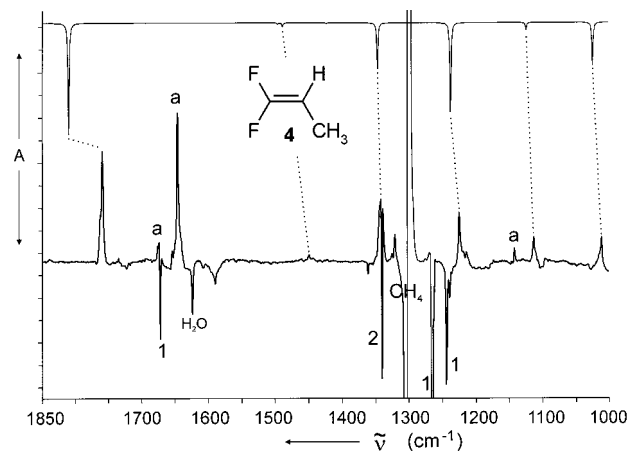


**Figure 4.** Some structures along the reaction pathway (IRC) of the insertion of vinylidene **1a** into  $\text{H}_2$ , calculated at the MP2/6-31G(d,p) level of theory. Bond distances and NBO charges (in italics) are given in the structure drawings, relative energies in the reaction coordinate diagram.

characteristic of  $\text{C}=\text{C}$  and  $\text{FCF}$  stretching vibrations of the difluorovinylidene moiety. With  $\text{CD}_4$  as trapping reagent, these absorptions are shifted to 1749 and  $1188\text{ cm}^{-1}$ , respectively. By comparison with a gas-phase spectrum<sup>28</sup> and with DFT calculations the trapping product was identified as 1,1-difluoropropene (**4**). Since  $\text{CH}_4$  is larger than  $\text{H}_2$ , the matrix has to be annealed at a higher temperature (30 K instead of 20 K) to induce the diffusion. This does not indicate a higher activation barrier for the insertion of **1b** into  $\text{CH}_4$  or  $\text{CD}_4$  compared to  $\text{H}_2$ .



The insertion again is calculated to be very exothermic (101 kcal/mol, B3LYP/6-311G(d,p) + ZPE), and the activation energy is now zero, both at the B3LYP and MP2 level of theory. The reaction pathway (Figure 6) is similar to that of the  $\text{H}_2$  insertion, with the reacting  $\text{C}-\text{H}$  bond approaching the carbene center in the molecular plane of **1b** to allow for a large overlap of the LUMO of **1b** and the  $\text{C}-\text{H}$  bond. The stretching of the methane  $\text{C}-\text{H}$  bond, formation of the new  $\text{C}-\text{H}$  bond with C(1) of the carbene, and transfer of charge from the methane molecule to C(1) are closely linked together. The formation of the new bonds between C(1) and the H and  $\text{CH}_3$  fragments of  $\text{CH}_4$  is asynchronous. In the first step the hydrogen atom is almost completely transferred to C(1), and in the second step the new  $\text{C}-\text{C}$  bond is formed while the H atom moves to its final position.



**Figure 5.** Center: Difference IR spectrum (in absorbance) showing changes in the IR spectra during annealing of a 0.5%  $\text{CH}_4$ -doped argon matrix containing difluorovinylidene (**1b**) at 40 K. Bands pointing downward are disappearing and bands pointing upward are appearing during the thermal reaction. Top: IR spectrum of **4**, calculated at the B3LYP/6-311G(d,p) level of theory. a:  $\text{F}_2\text{C}=\text{C}=\text{N}_2$  formed from  $\text{N}_2$  contamination of the matrix.

In contrast to the insertion reactions described above, vinylidene **1b** does not react with  $\text{CF}_4$  under similar conditions (0.5%  $\text{CF}_4$ -doped argon matrix, 40 K). Dimerization to tetrafluorobutatriene and reactions with trace contaminations in the matrix (mainly  $\text{N}_2$ ) are the only reactions observed under these conditions. This lack of reactivity is in agreement with an activation barrier of 41 and 40 kcal/mol calculated at the B3LYP/6-311++G(d,p) + ZPE and MP2/6-31G(d,p) level of theory, respectively. Comparison of the transition states of the insertion of **1b** into  $\text{CH}_4$  (Figure 6) and  $\text{CF}_4$  (Figure 7) reveals large differences. The transition state for the **1b** +  $\text{CF}_4$  reaction is later and much less charge is transferred to the carbene center, since the fluorine atoms are very weak electron donors. A transition state similar to that of the **1b** +  $\text{CH}_4$  reaction could not be located. The calculated reaction energies are 86 and 90

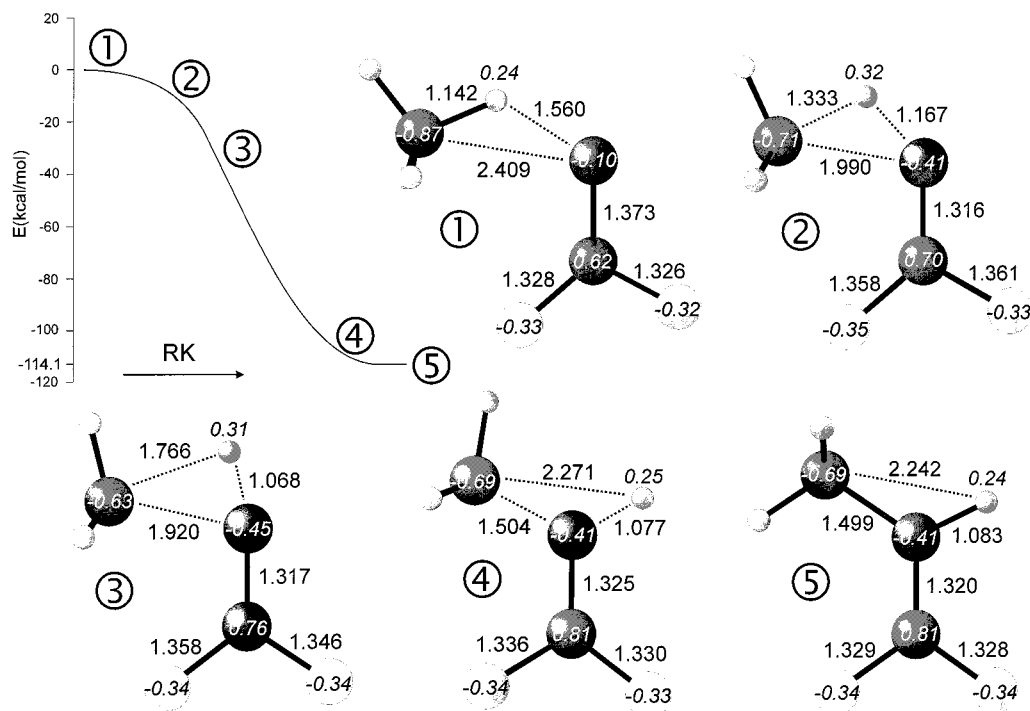
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**Table 2.** Experimental and Calculated IR Data of **4** and **4-d<sub>4</sub>**: Computed Harmonic and Experimental Vibrational Wavenumbers (cm<sup>-1</sup>) of **4**

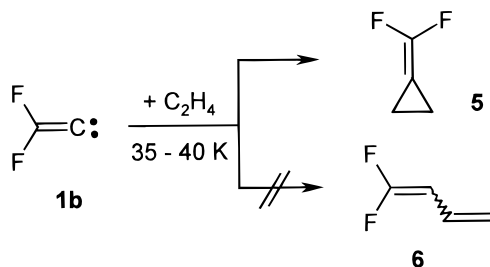
mode <sup>a</sup>	sym	assignment	$\tilde{\nu}_{\text{exp}}^b$	$I_{\text{exp}}^{b,c}$	$\tilde{\nu}_i/\tilde{\nu}^d$	$\tilde{\nu}_{\text{Lit}}^e$	$\tilde{\nu}_{\text{calc}}^f$	$I_{\text{calc}}^{c,f}$	$\tilde{\nu}_i/\tilde{\nu}^d$
7	A''	CH <sub>wag</sub>	808	10	0.769		821	16	0.790
8	A'	$\nu_s(\text{CF}_2)+\text{CH}_3\text{--rock}$	840	15	0.865	838(w)	849	8	0.865
9	A'	CH <sub>3</sub> –rock	1012	35	0.827	1011(m)	1024	39	0.829
11	A'		1114	20	0.841		1124	7	0.854
12	A'	$\nu_{\text{as}}(\text{CF}_2)$	1226	65	1.033	1228(s)	1239	80	1.035
13	A'	CH <sub>rock</sub>	1321	55	0.794	1323(m)	1348	42	0.792
14	A'						1425	1	0.842
15	A''	CH <sub>3</sub> –as–bend	1450	5	0.724		1490	4	0.720
17	A'	$\nu(\text{C}=\text{C})$	1759	100	0.994	1760(s)	1810	100	0.990

<sup>a</sup> Number of calculated vibrations. The assignment is based on band positions and relative intensities and is only tentative. <sup>b</sup> Argon at 10 K. <sup>c</sup> Relative intensities, based on the strongest absorption. <sup>d</sup> Ratio of D/H isotopic frequencies. <sup>e</sup> Gas phase.<sup>28</sup> <sup>f</sup> B3LYP/6-311G(d,p). Other vibrations of **4**, not observed in the experimental spectrum:  $\nu_{\text{calc}}(I_{\text{rel}})$ : 139(0), 235(1), 248(0), 498(3), 585(0), 614(1), 1065(0), 1497(1), 3024(13), 3067(10), 3116(6), 3194(3).

**Figure 6.** Some structures along the reaction pathway (IRC) of the insertion of difluorovinylidene (**1b**) into CH<sub>4</sub>, calculated at the MP2/6-31G(d,p) level of theory. Bond distances and NBO charges (in italics) are given in the structure drawings, relative energies in the reaction coordinate diagram.

kcal/mol, respectively, at the B3LYP and MP2 level of theory, only about 25 kcal/mol less than in the CH<sub>4</sub> insertion. In contrast to the other insertion reactions discussed above, a weakly bound complex between CF<sub>4</sub> and **1** is observed in the initial stage of the reaction (Figure 7, structure 1).

**Reaction of Vinylidene **1b** with Ethene.** Two reaction channels have to be considered for the reaction of **1b** with ethene: (i) the insertion into a vinylic CH bond to give 1,1-difluorobutadiene (**6**), and (ii) the addition to the double bond to give (difluoromethylene)cyclopropane (**5**). Both reactions are expected to proceed with very small activation barriers.



The thermal reaction of matrix-isolated **1b** with C<sub>2</sub>H<sub>4</sub> leads to an IR spectrum that is dominated by a strong absorption at

1861 cm<sup>-1</sup>. By comparison with the gas-phase spectrum of **5** published by Dolbier et al.,<sup>29</sup> this absorption is assigned to the C=C stretching vibration of **5**. The high frequency of this vibration is characteristic of methylenecyclopropanes.<sup>30</sup> Other characteristic vibrations of **5** are the FCF stretching vibrations found at 1226 and 1237 cm<sup>-1</sup>, again in good agreement with the gas-phase spectrum and with the spectrum calculated at the B3LYP/6-311G(d,p) level of theory (Figure 8, Table 3).

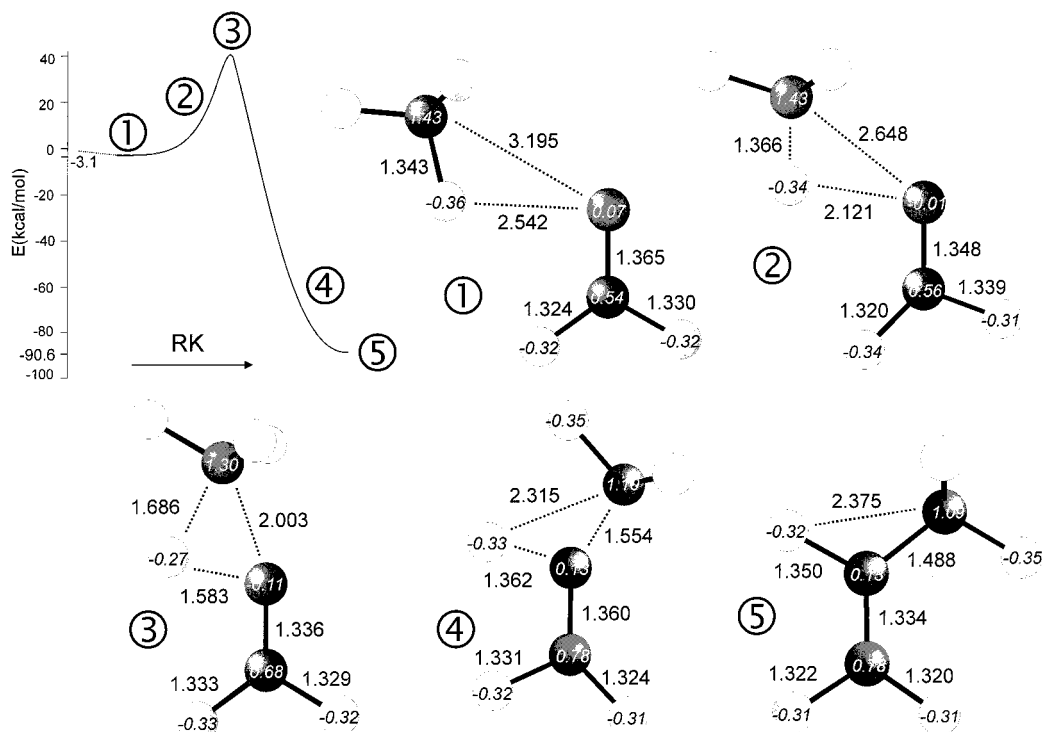
A byproduct observed in the matrix is difluoroethylene (**3**), the insertion product of **1b** into H<sub>2</sub>. This indicates that the intense 193 nm irradiation (corresponding to 148 kcal/mol) leads to cleavage of ethylene and formation of H<sub>2</sub>,<sup>31</sup> which is efficiently trapped by **1b**. Since the diffusion of H<sub>2</sub> in solid argon is more rapid than that of ethylene, even low yields of H<sub>2</sub> result in the formation of substantial yields of **3**.

The formation of **5** is exothermic by 89 kcal/mol (B3LYP/6-311G(d,p) + ZPE, Table 1). A transition state for the addition to the double bond could not be located, which indicates the

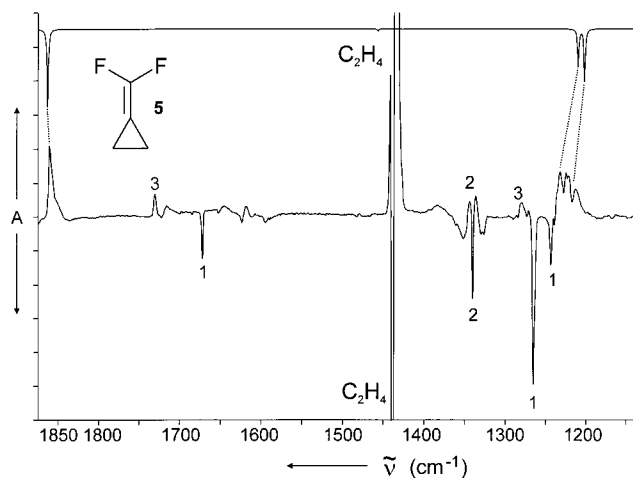
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**Figure 7.** Some structures along the reaction pathway (IRC) of the insertion of difluorovinylidene (**1b**) into  $\text{CF}_4$ , calculated at the MP2/6-31G(d,p) level of theory. Bond distances and NBO charges (in italics) are given in the structure drawings, relative energies in the reaction coordinate diagram.



**Figure 8.** Center: Difference IR spectrum (in absorbance) showing changes in the IR spectra during annealing of a 0.5%  $\text{C}_2\text{H}_4$ -doped argon matrix containing difluorovinylidene (**1b**) at 40 K. Bands pointing downward are disappearing and bands pointing upward are appearing during the thermal reaction. Top: IR spectrum of **5**, calculated at the B3LYP/6-311G(d,p) level of theory.

absence of an activation barrier for the addition reaction. The insertion product **6** is more stable than the addition product **5** by 22 kcal/mol, but since for the former reaction an activation energy of 3.1 kcal/mol (B3LYP/6-311G(d,p) + ZPE, 5.2 kcal/mol at the MP2/6-31G(d,p) level of theory) is calculated, only the addition product is formed in a kinetically controlled reaction.

In conclusion, the observed thermal insertions of difluorovinylidene **1b** into  $\text{H}_2$  and  $\text{CH}_4$  at cryogenic temperatures again demonstrates the extreme reactivity and electrophilicity of **1b**. This reactivity is in accordance with ab initio and DFT calculations, which predict no or very small (<1 kcal/mol) barriers for the insertion into  $\text{H}_2$  or CH bonds. Due to its kinetic

**Table 3.** Computed Harmonic and Experimental Vibrational Wavenumbers ( $\text{cm}^{-1}$ ) of **5**

mode	sym	assignment	$\tilde{\nu}_{\text{exp}}^a$	$I_{\text{exp}}^{a,b}$	$\tilde{\nu}_{\text{calc}}^{c,e}$	$I_{\text{rel}}^{b,c}$	$\tilde{\nu}_{\text{lit}}^d$
16	B <sub>2</sub>	$\nu_{\text{as}}(\text{CF}_2)$	1226.1	70	1240.5	67	1238
17	A <sub>1</sub>	$\nu_{\text{s}}(\text{CF}_2) + \text{ring breathing}$	1237.4	40	1249.0	49	1257
20	A <sub>1</sub>	$\nu(\text{C}=\text{C})$	1860.6	100	1921.4	100	1860

<sup>a</sup> Argon at 10 K. <sup>b</sup> Relative intensities, based on the strongest absorption. <sup>c</sup> B3LYP/6-311G(d,p). <sup>d</sup> Gas phase.<sup>29</sup> <sup>e</sup> Other vibrations of **5**, not observed in the experimental spectrum:  $\nu_{\text{calc}}(I_{\text{rel}})$ : 161.1(0), 184.5(0), 213.8(0), 448.9(5), 553.4(0), 598.3(2), 679.4(5), 783.6(0), 938.5(0), 952.2(2), 1049.3(3), 1053.6(0), 1085.8(1), 1103.6(0), 1173.7(0), 1472.0(0), 1502.2(2), 3103.1(6), 3104.0(6), 3174.3(0), 3187.1(6).

instability, the chemistry of the parent vinylidene **1a** is not known experimentally; however, the calculated activation barrier of 10–13 kcal/mol for the insertion into  $\text{H}_2$  reflects the much lower electrophilicity compared to **1b**. The substantial barrier for the insertion of **1b** into the vinylic C–H bond of ethylene results in the exclusive formation of the addition product **5**. Obviously, insertion reactions into  $\text{sp}^2$  CH bonds of alkenes—and as was shown previously also in  $\text{sp}$  CH bonds of alkynes<sup>21</sup>—cannot compete with addition reactions to the multiple bonds or insertions into  $\text{sp}^3$  CH bonds. A consequence of the very high barrier for the insertion into CF bonds is the absence of any reactivity with  $\text{CF}_4$ . Thus, perfluorinated solvents should allow the study of the solution chemistry of **1b**.

## Experimental Procedure

**Matrix isolation experiments** were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrixes were produced by deposition of argon (Messer-Griesheim, 99.9999%) on top of a CsI window at 8 K with a rate of approximately 0.15 mmol/min. Mixtures of argon with gaseous compounds (typically 0.5%) were produced in a vacuum line:  $\text{H}_2$ , 99.999% Messer-Griesheim;  $\text{CH}_4$ , 99.995%, Messer-Griesheim;  $\text{CD}_4$ , 99% deuteration; 1,1-difluoroethylene (**3**), PCR. Infrared spectra were recorded by using

a Bruker IFS66 FTIR spectrometer with a standard resolution of 0.5  $\text{cm}^{-1}$  in the range 400–4000  $\text{cm}^{-1}$ . Irradiations were carried out with use of an ArF excimer laser ( $\lambda = 193 \text{ nm}$ ; Lambda Physik COMPex 100).

**Calculations** were performed with the Gaussian 94 program package.<sup>32</sup> Geometries and vibrations were calculated at the B3LYP/6-311G(d,p) level of theory. Transition states were calculated first at lower levels (RHF and small basis sets), where the curvature next to

the stationary points is higher. The results of these calculations were used as starting geometries for the next higher level. The IRC (intrinsic reaction coordinate) calculations were performed at the MP2/6-31G(d,p) level of theory. In the case of the insertion of **1b** into  $\text{CH}_4$  the reaction channel was found starting from a transition-state geometry of a HF calculation. All stationary points were characterized by a vibrational analysis.

Calculated IR spectrum of **6**: 136.3 (0), 177.3 (0), 234.5 (0), 390.3 (0), 485.9 (2), 598.5(1), 605.9 (0), 679.7 (4), 858.8 (2), 904.7 (14), 918.4 (16), 1009.1 (17), 1028.6 (6), 1197.8 (11), 1229.7(30), 1330.6 (12), 1360.2 (22), 1472.5 (8), 1686.8 (0), 1773.0 (100), 3136.4 (2), 3159.1(1), 3195.7 (1), 3224.7 (4)  $\text{cm}^{-1}$  (rel intensity).

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