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Singlet Halophenylcarbenes as Strong Hydrogen Bond Acceptors

Geneviève Richter, Enrique Mendez-Vega, and Wolfram Sander*

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Abstract

Chlorophenylcarbene and fluorophenylcarbene were generated in water-doped argon matrices at cryogenic temperatures by photolysis of the corresponding matrix-isolated diazirines. When diffusion of H₂O in solid argon was induced by annealing of the matrices at temperatures above 20 K, hydrogen-bonded complexes between the carbenes and water were formed. UV photolysis of these complexes resulted in the formation of benzaldehyde and hydrogen halides HX. The same products were obtained after photolysis of the diazirines in amorphous water ice. Obviously, the primary insertion product of the carbenes into H-OH is unstable under these conditions, and benzaldehyde is formed via secondary photolysis. The stable primary photochemical insertion product of chlorophenylcarbene into an O-H bond was observed in the reaction of the carbene with methanol.

Introduction

The properties of closed-shell singlet carbenes are governed by the presence of a lone pair in the σ -plane and an empty π orbital, rendering them both nucleophilic and electrophilic. Substituents strongly influence the philicity of singlet carbenes, and the spectrum of carbene reactivity ranges from the extremely electrophilic difluorovinylidene^{1, 2} that even with CO₂ reacts as electrophile by abstracting an oxygen atom,³ to the highly nucleophilic N-heterocyclic carbenes (NHCs)⁴ that

are more or less stable under ambient conditions. Typical electrophilic reactions of singlet carbenes are the formation of complexes and ylides with N and O containing aprotic compounds such as ethers.⁵ Singlet carbenes are strong neutral bases,⁶ and for the parent singlet CH₂ a proton affinity (PA) of 207 kcal/mol, similar to that of NH₃ (204 kcal/mol) was determined. Typical NHCs are even more basic and show PAs between 250 and 260 kcal/mol.⁷ The lowest-lying (closed-shell) singlet states of fluorenylidene (**FL**) and diphenylcarbene (**DPC**, Chart 1) are among the most basic neutral compounds with PAs of 272 and 275 kcal/mol, respectively.^{8, 9} Reaction heats and rate constants of the protonation of carbenes to yield carbocations have been determined by time-resolved photoacoustic calorimetry^{10, 11} and by stopped-flow laser-flash photolysis.¹² Therefore, singlet carbenes should be able to act as powerful hydrogen bond acceptors. An interesting example for a hydrogen-bonded carbene complex is the complex between two NHCs bridged by a single proton resulting in a strong C⋯H⋯C hydrogen bond.¹³ In contrast to the (closed-shell) singlet states of carbenes, the triplet states do not form hydrogen bonds, and therefore hydrogen bonding stabilizes the singlet state of a carbene with respect to the triplet state. This results in a decrease of the singlet-triplet splitting or even in a reversal of the ground state of triplet carbenes. This has been recently used by us to switch the spin state of diphenylcarbene and fluorenylidene, respectively, from triplet to singlet.¹⁴⁻¹⁶

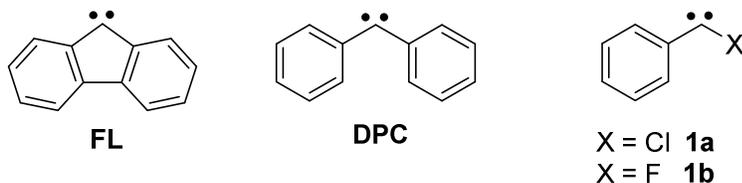
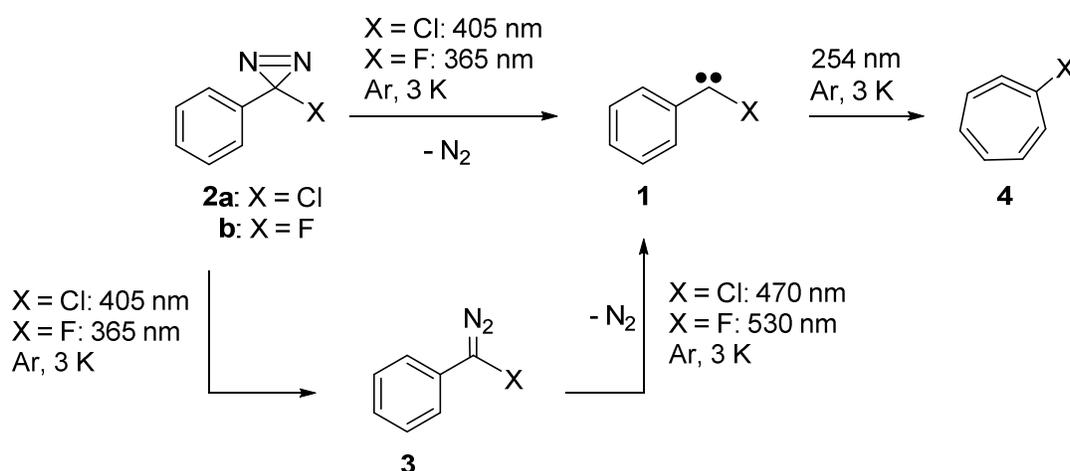


Chart 1. Structures of arylcarbenes.

Chlorophenylcarbene **1a** and fluorophenylcarbene **1b** are prototypical reactive singlet ground state carbenes of low nucleophilicity. The chemistry of **1a** in solution was studied in great detail

by trapping experiments,^{17, 18} matrix isolation spectroscopy,¹⁹⁻²¹ and by time-resolved spectroscopy (Scheme 1).²²⁻²⁵ As a singlet carbene, **1a** reacts only very slowly (compared to triplet carbenes) with molecular oxygen to form the corresponding carbonyl *O*-oxide.¹⁹ UV-photolysis of matrix-isolated **1a** results in ring opening to form cycloheptatetraene **4** in high yields.²⁰ The chemistry of fluorophenylcarbene **1b** has also been studied by time resolved spectroscopy²⁶⁻²⁸ and low temperature spectroscopy,²⁹⁻³¹ and, as expected, is rather similar to that of **1a**.



Scheme 1. Photochemistry of diazirines **2a** and **b** under the conditions of matrix isolation.

Here, we describe the formation of hydrogen-bonded complexes between carbenes **1a** and **b** as hydrogen bond acceptor and water and methanol, respectively, as hydrogen bond donors. An interesting aspect is that hydrogen bonding changes the photochemistry of the carbenes, which has to be considered when generating these carbenes by photolysis of precursors in solution.

Results and Discussion

Chlorophenylcarbene Water Complex. Chlorophenylcarbene **1a** was generated in solid argon doped with 0.1–1% water by visible light photolysis (405 nm) of chlorophenyldiazirine **2a** at 3 K. Under these conditions, matrices are very rigid and diffusion, even of small molecules such as

H₂O, is efficiently inhibited. After the photolysis the IR spectra show the presence of carbene **1a**, isolated water molecules, and water clusters (dimers and higher, depending on the water concentration). Annealing of these matrices at temperatures between 25 and 35 K allows water molecules to diffuse and to undergo aggregation and bimolecular reactions with **1a**. Several new IR bands that appear during warming the matrices are assigned to a complex **1a**···H-OH between the carbene and water (Chart 2, Figure 1a-d, Table 1). These bands are observed only if both **1a** and water are present in the matrix.

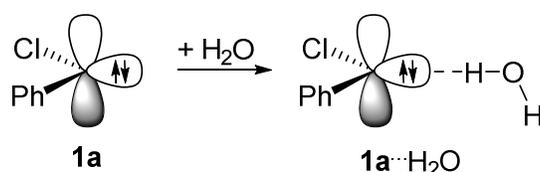


Chart 2. Interaction of carbene **1a** with water to form the hydrogen-bonded complex **1a**···H₂O

As expected, the formation of the complex **1a**···H-OH results in only moderate or small shifts of IR bands compared to the constituents **1a** and H₂O. The strongest band of **1a** at 1226.4 cm⁻¹ assigned to the C-C stretching vibration at the carbene center is blue-shifted to 1237.0 cm⁻¹ (Table 1). The bands at 847.1 and 739.5 cm⁻¹ assigned to the antisymmetric and symmetric C-C-Cl stretching vibrations, respectively, are blue-shifted to 855.6 and 766.7 cm⁻¹, and the band at 568.4 cm⁻¹, assigned to an in-plane C-H deformation mode, is shifted to 575.5 cm⁻¹. The large shifts of the stretching vibrations involving the carbene center indicates a C···H-OH hydrogen bond between the central carbon atom of **1a** and H₂O. The dependency of the intensity of the bands of **1a**···H-OH from the concentration of H₂O in argon suggests that a 1:1 complex between H₂O and **1a** is formed. With 1% H₂O, about 55% yield of the complex was obtained after 10 min annealing at 35 K, and prolonged annealing did not result in a further increase of the yield. With D₂O and H₂¹⁸O, the corresponding isotopologues **1a**···D-OD and **1a**···H-¹⁸OH with very similar IR absorptions in the mid-IR region are observed (see SI).

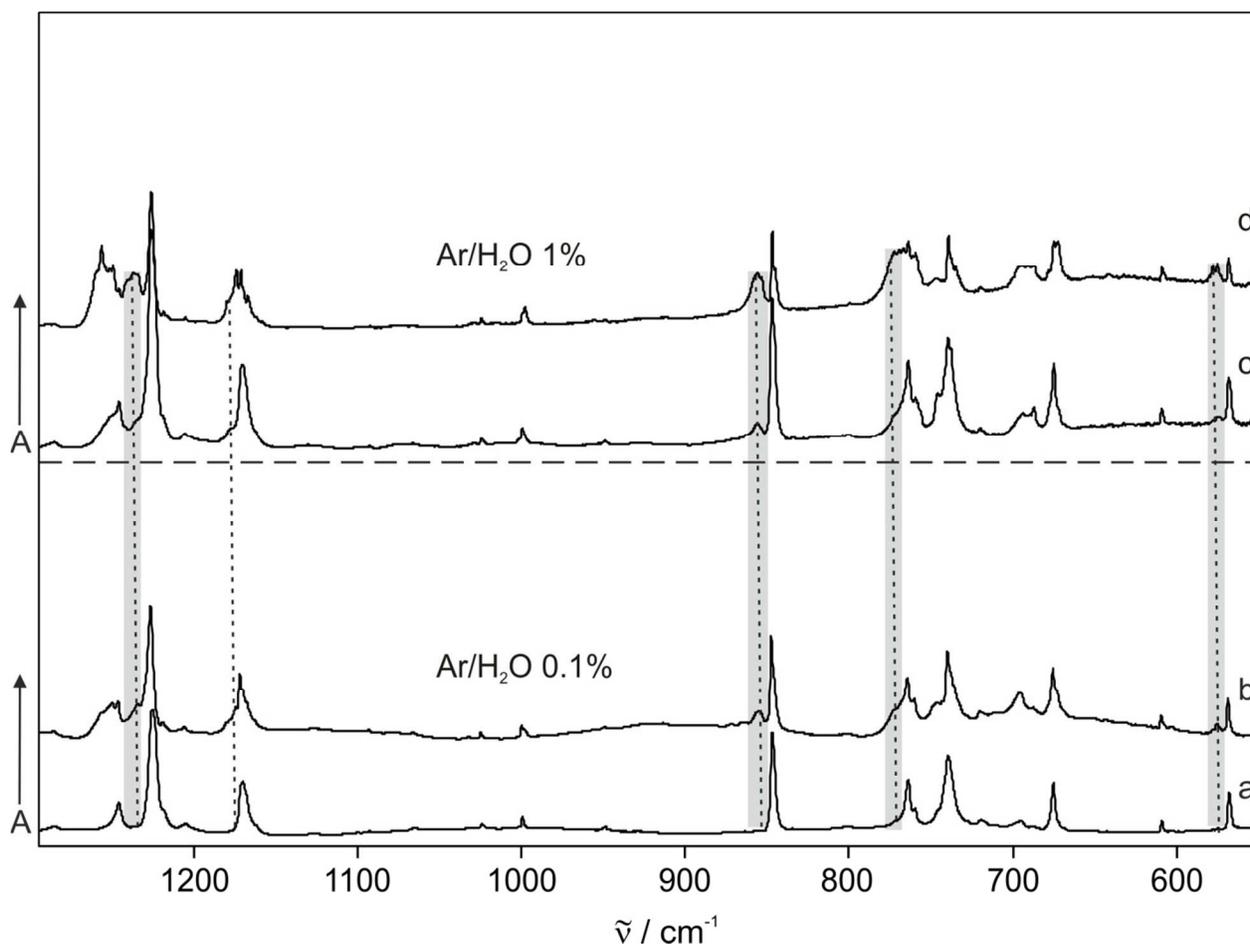


Figure 1. IR spectra showing the formation of the complex between carbene **1a** and H₂O. a) **1a** in argon doped with 0.1% H₂O at 3 K. b) After annealing the matrix to 35 K for 10 min. c) **1a** in argon doped with 1% H₂O at 3 K. d) After annealing the matrix to 35 K for 10 min. The vibrational absorption bands of the **1a**···H₂O complex are highlighted in grey.

Since annealing of water-doped argon matrices results in the formation of the water dimer,³²⁻³⁴ trimer,³⁵ and higher oligomers³⁶ that all exhibit strong absorptions in the OH stretching region, it is difficult to identify IR bands of **1a**···H-OH in this region. A new band at 3199.6 cm^{-1} is formed only during annealing of matrices containing both **1a** and H₂O, and is thus tentatively assigned to an OH stretching vibration of the complex. This band is red-shifted from the symmetric O-H

stretching vibration of H₂O at 3638.0 cm⁻¹ by 438.4 cm⁻¹ (Figure 2, Table 2). With D₂O, the corresponding O-D stretching vibration is found at 2286.4 cm⁻¹, red-shifted by 371.4 cm⁻¹ from the symmetrical D₂O stretching vibration at 2657.8 cm⁻¹. The large red shift of the OH stretching vibration provides strong evidence for a hydrogen bonded complex, where water acts as hydrogen bond donor and carbene **1a** as hydrogen bond acceptor.

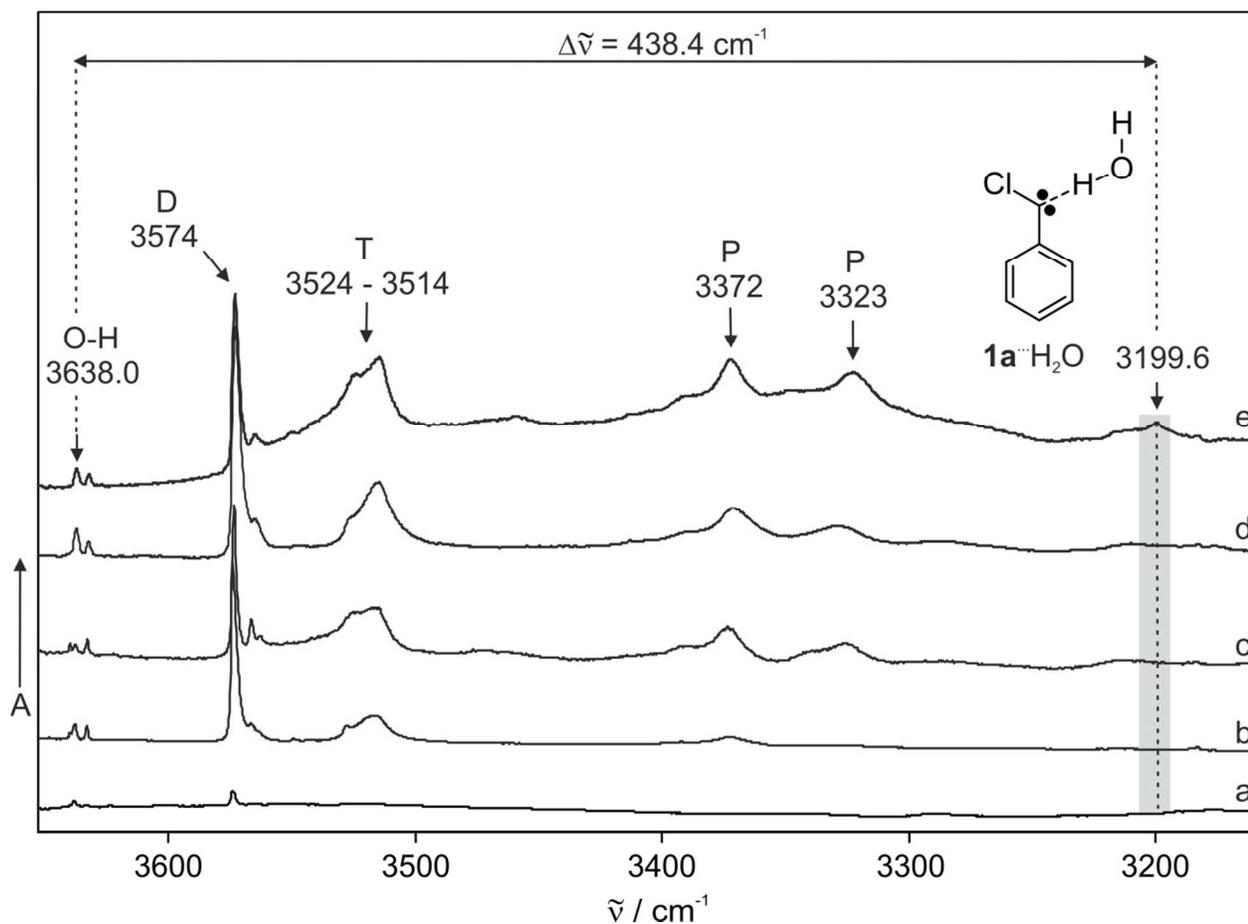


Figure 2. IR spectra showing the formation of the complex between **1a** and H₂O. a) **1a** in argon at 3 K. b) 1% H₂O in argon at 3 K. c) After annealing the matrix to 35 K for 10 min and cooling down to 3 K. d) **1** in argon doped with 1% H₂O at 3 K. e) After annealing the matrix to 35 K for 10 min and cooling down to 3 K. D: water dimer, T: water trimer, P: water oligomer. The O-H stretching vibration of the **1a**···H₂O complex is highlighted in grey.

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6 Several possible structures for complexes between carbene **1a** and H₂O were considered, and their
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8 geometries, energies, and IR spectra were calculated at the B3LYP-D3/6-311++G(2d,2p) level of
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10 theory (Figure 3). Only complex A shows the strong C···H-O hydrogen bond expected from the
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12 spectroscopic data. This complex is computed to be stabilized by 7.53 kcal/mol (including BSSE
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14 and ZPE corrections), whereas the other complexes are only weakly stabilized by Cl···HO
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16 (complex B), CH···OH (complex C), and π ···HO (complex D) interactions. For complex A, a
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18 very large red shift of the OH stretching vibration of water is predicted (-447 cm^{-1}), in excellent
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20 agreement with the experiment (-438.4 cm^{-1}). Complexes B–D are described best as weakly
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22 bound van der Waals complexes with predicted red shifts of the OH stretching vibrations of less
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24 than 35 cm^{-1} . The small shifts of the IR bands of carbene **1a** observed after annealing of water-
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26 doped argon matrices are in good agreement with predictions from DFT calculations, further
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28 providing evidence for the formation of complex A (Table 1).
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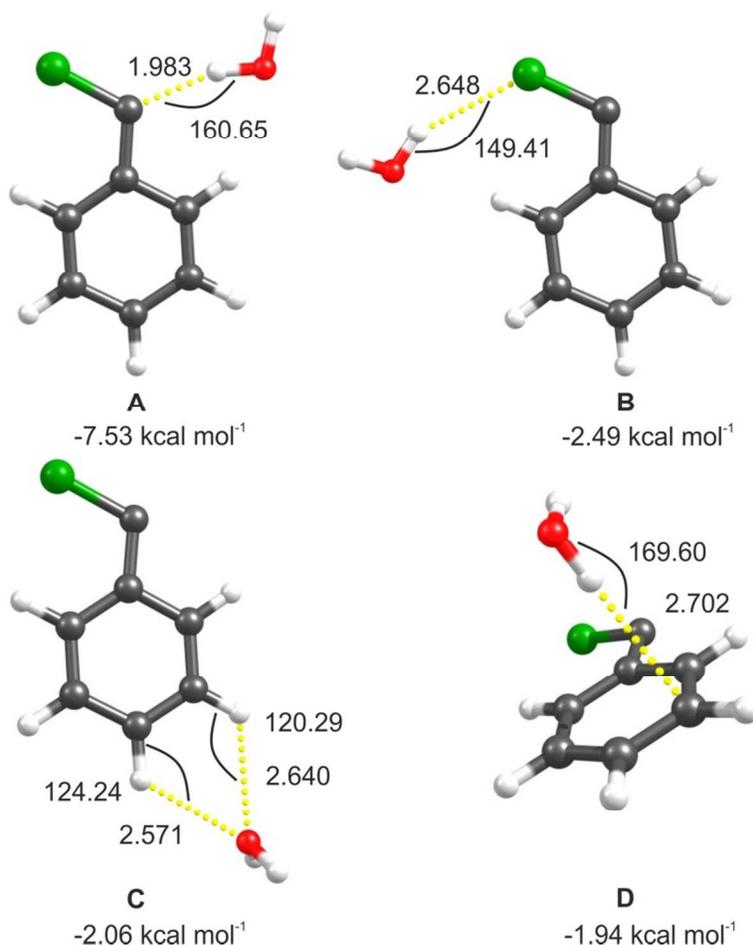


Figure 3. Four weakly bound complexes A - C between **1a** and water calculated at the B3LYP-D3/6-311++G(2d,2p) level of theory are shown, including selected bond lengths (in Å) and bond angles (in degree); the complex energies are relative to non-interacting monomers.

Fluorophenylcarbene Water Complex. The interaction of **1b** with water is analogous to that of **1a**, and therefore only briefly described here (see SI for details). The carbene is formed in high yields by 365 nm photolysis of matrix-isolated fluorophenyldiazirine **2b** at 3 K. If the matrix is doped with 1% H₂O, annealing at 35 K results in the formation of complex **1b**⋯H-OH in up to 40% yield. The complex shows some characteristic shifts in the IR spectrum, similar to that of **1a**⋯H-OH (Table 3). Most notably is the strong red shift of 455.6 cm⁻¹ of the OH stretching

vibration of the water molecule in the complex **1b**···H-OH, which is slightly larger than in **1a**···H-OH. The assignment of the IR spectra of **1b**···H-OH was confirmed by isotopic labelling (D_2O , $H_2^{18}O$) and by comparison with results from DFT calculations at the B3LYP-D3/6-311++G(2d,2p) level of theory. The large red shift of the OH stretching vibration is only compatible with a C···O-H hydrogen bond involving the carbene center (Figure 3, complex A). The other calculated structures are of lower energy (Figure 4) and predicted to show much smaller red shifts of the OH stretching modes.

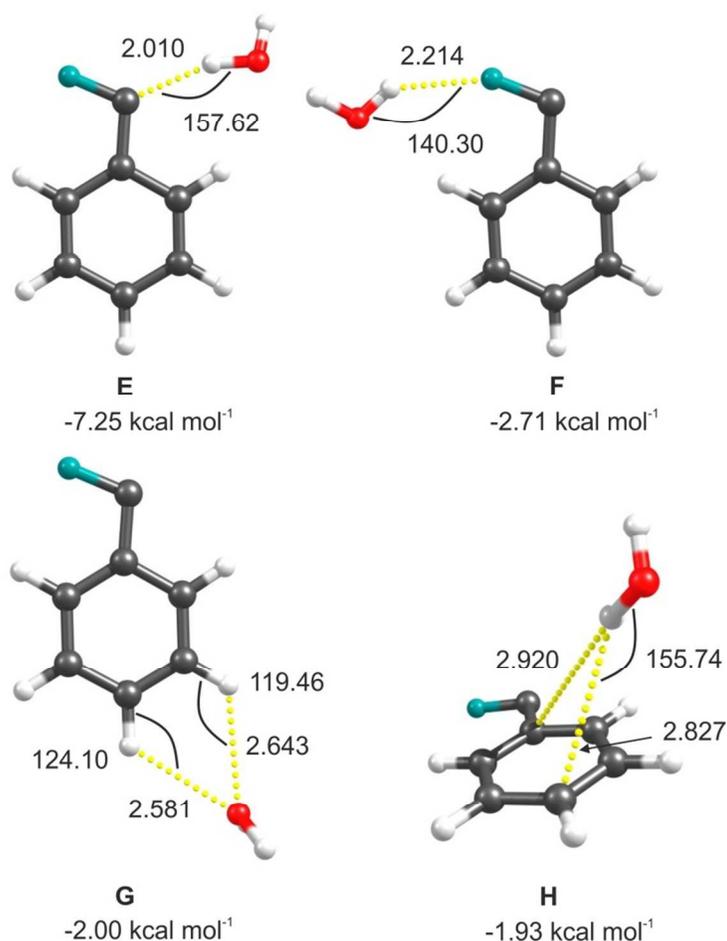
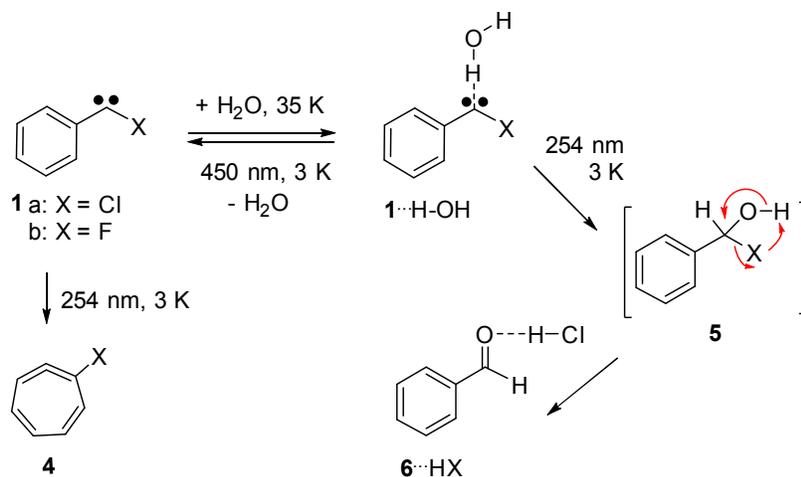


Figure 4. Four weakly bound complexes between **1b** and water calculated at the B3LYP-D3/6-311++G(2d,2p) level of theory are shown, including selected bond lengths (in Å) and bond angles (in degree); the complex energies are relative to non-interacting monomers.

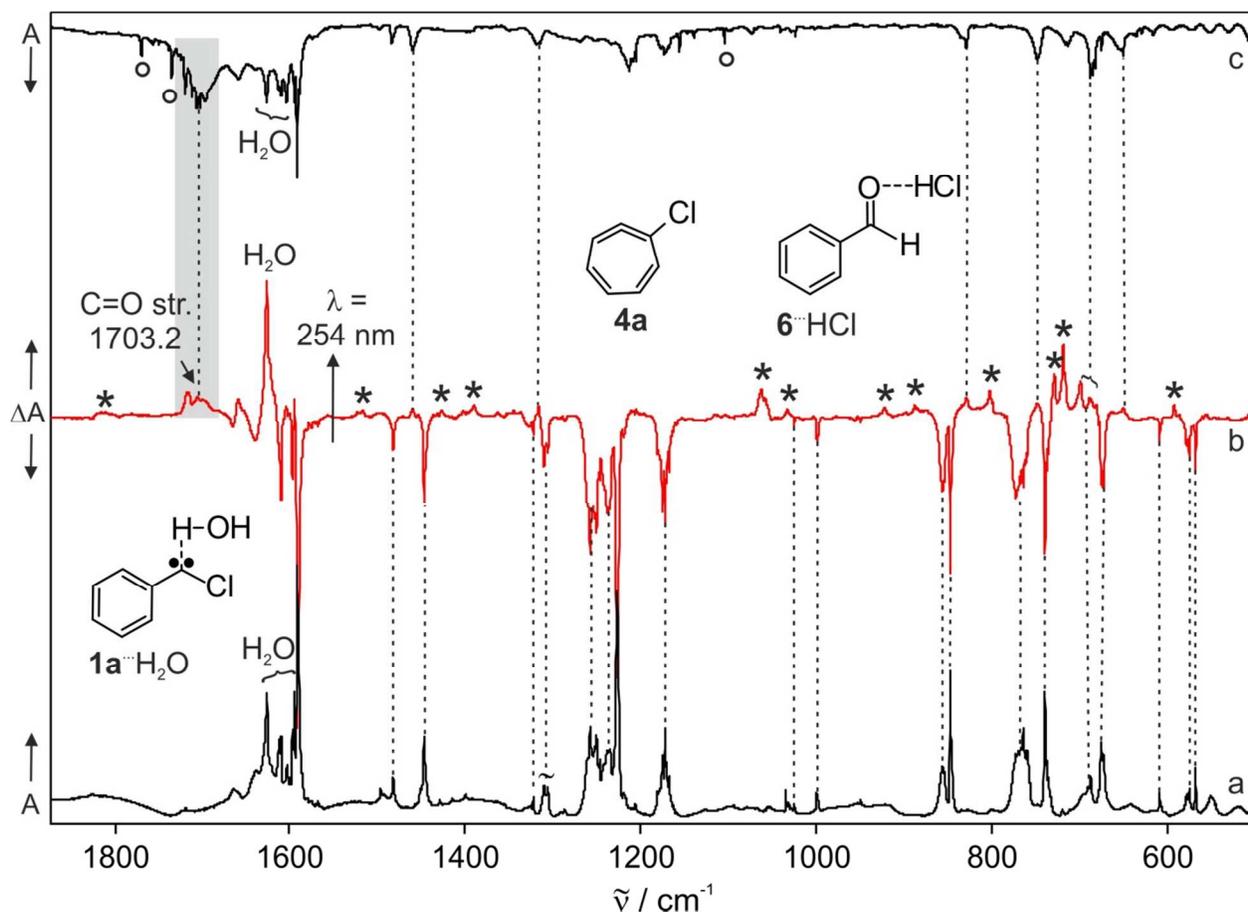
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3 **Photochemistry of the Halophenylcarbene Water Complexes.** The halophenylcarbenes **1a** and
4 **1b** are stable towards visible light irradiation, but upon short wavelength UV irradiation (254 nm)
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6 rearrange to the corresponding cycloheptatetraenes **4a** and **4b**, respectively (Scheme 1). Visible
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8 light irradiation of the complexes (**1a**···H-OH: 630, 450 nm, **1b**···H-OH: 450 nm) at 3 K results
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10 in their dissociation and formation of the “free” carbenes **1**. Annealing of the matrices at 30–35 K
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12 again produces the complexes, and this photolysis/annealing process can be repeated several
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14 times without formation of other products. The UV photochemistry of the complexes **1**···H-OH
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16 is markedly different not only from their visible light photochemistry, but also from that of the
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18 carbenes **1a** and **1b** that are not bound to water. Several hours of 254 nm irradiation of matrices
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20 containing a mixture of the carbenes **1** and their water complexes **1**···H-OH results in the
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22 expected rearrangement of “free” carbenes **1** to cycloheptatetraenes **4a** and **4b**, respectively. In
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24 contrast, photolysis of **1**···H-OH produces hydrogen-bonded complexes between benzaldehyde **6**
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26 and HCl or HF, respectively (Scheme 2, Figure 5). The complex **6**···H-Cl was synthesized
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28 independently by annealing matrices containing both benzaldehyde **6** and HCl. In complex **6**···H-
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30 Cl the C=O stretching vibration of **6** is red-shifted from 1718.0 cm⁻¹ to 1703.2 cm⁻¹.
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39 Photolysis of the complexes of **1a** or **1b** with D₂O results in the formation of the corresponding
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41 deuterated complexes d₁-**6**···D-Cl or d₁-**6**···D-F, respectively, with the aldehyde group of **6**
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43 deuterated. If H₂¹⁸O is used in these experiments, the ¹⁸O isotopologue of **6** is formed, as
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45 expected. The isotopic shifts in the IR spectra of these isotopologues are in excellent agreement
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47 with the shifts predicted from DFT calculations (for details see SI).
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Scheme 2. Reaction of **1a** and **1b** with H_2O and subsequent photochemistry.



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3 **Figure 5.** IR spectra showing the secondary photochemistry of the **1a**···H₂O complex. a) The
4 **1a**···H₂O complex produced in H₂O-doped argon matrix at 3 K. b) Difference IR spectrum
5 obtained after 254 nm irradiation for 15 h. Bands pointing downwards are disappearing during
6 irradiation and belong to the **1a**···H₂O complex and carbene **1a**. Bands pointing upwards are
7 appearing concomitantly and are assigned to **4** (bands marked by asterisks) and the **6**···H₂O
8 complex. c) Benzaldehyde **6** in 1% HCl-doped argon at 9 K. The bands marked by ° are due to
9 HCl and H₂O complexes.
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23 A reasonable mechanism for the formation of benzaldehyde and HX involves the unstable α -
24 halobenzylalcohol **5**, the formal product of the insertion of carbenes **1** into the OH bond of water.
25 This step obviously needs photochemical excitation; however, it is not clear from our
26 experiments if this is a true photochemical or a “hot ground state” reaction. Calculations at the
27 B3LYP-D3/6-311++G(d,p) level of theory predict activation barriers of 11.1 kcal/mol for the
28 insertion of **1a** (Figure 6), and 12.2 kcal/mol for the insertion of **1b** into the OH bond of water to
29 form the corresponding halobenzylalcohols **5**. These barriers are too large to be overcome in
30 thermal reactions at temperatures below 20 K, and therefore photochemical excitation is
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presumably also larger tunneling distances, effectively inhibit tunneling rearrangements of **1a**···H-OH and **1b**···H-OH.

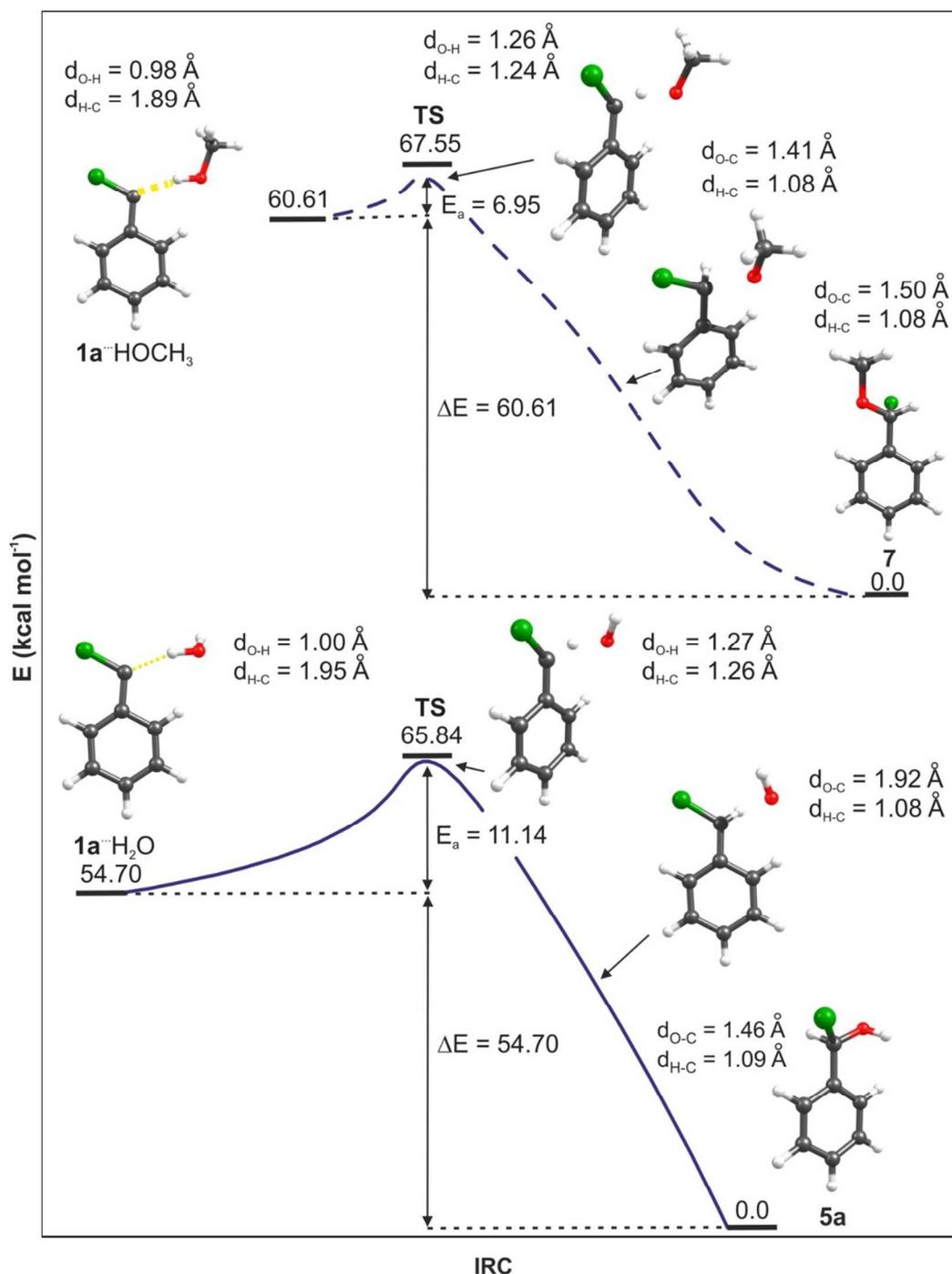


Figure 6. Intrinsic reaction coordinate (IRC) for the O-H insertion of carbene **1a** into H₂O and CH₃OH calculated at the B3LYP-D3/6-311++G(d,p) level of theory. Energies are given in

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3 kcal/mol. Some structures along the reaction coordinate are shown in the diagram. O-H and C-H
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5 bond distances involving the hydroxyl H atom in Å.
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11 **Halophenylcarbenes 1 in Amorphous Water Matrices.** Visible light ($\lambda = 405$ nm) irradiation
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13 of the diazirines **2a** or **2b** in amorphous water ice at 9 K resulted in the rapid photolysis of the
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15 precursors, similar to the experiments in argon matrices. The photolysis was followed by IR and
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17 UV-vis spectroscopy, which revealed the formation of the corresponding carbenes **1a** and **1b** in
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19 addition to the halophenyldiazomethanes **3a** and **3b** (Scheme 1). A comparison of the IR spectra
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21 shows that, as expected, the water complexes of the carbenes **1** are formed rather than the free
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23 carbenes. In the ice matrix carbene **1a** shows a strong UV-absorption at 308 nm and **1b** at 279
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25 nm. These absorptions are slightly red-shifted compared to the bands in argon at 302 and 269 nm,
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27 respectively. Annealing at temperatures up to 50 K did not result in any reaction of the **1**···H-OH
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29 complexes. This is in contrast to the chemistry of fluorenylidene **FL**¹⁵ and diphenylcarbene **DPC**
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31 in amorphous water,¹⁶ which are readily protonated at cryogenic temperatures under formation of
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33 the corresponding carbenium ions. Prolonged 405 nm irradiation leads to the formation of the
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35 HCl or HF complexes, respectively, of benzaldehyde **6**, again in analogy to the photochemistry of
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37 the **1**···H-OH complexes in solid argon. In amorphous D₂O ice, the DX complexes of d₁-**6** are
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39 formed, as expected (Figure 7).
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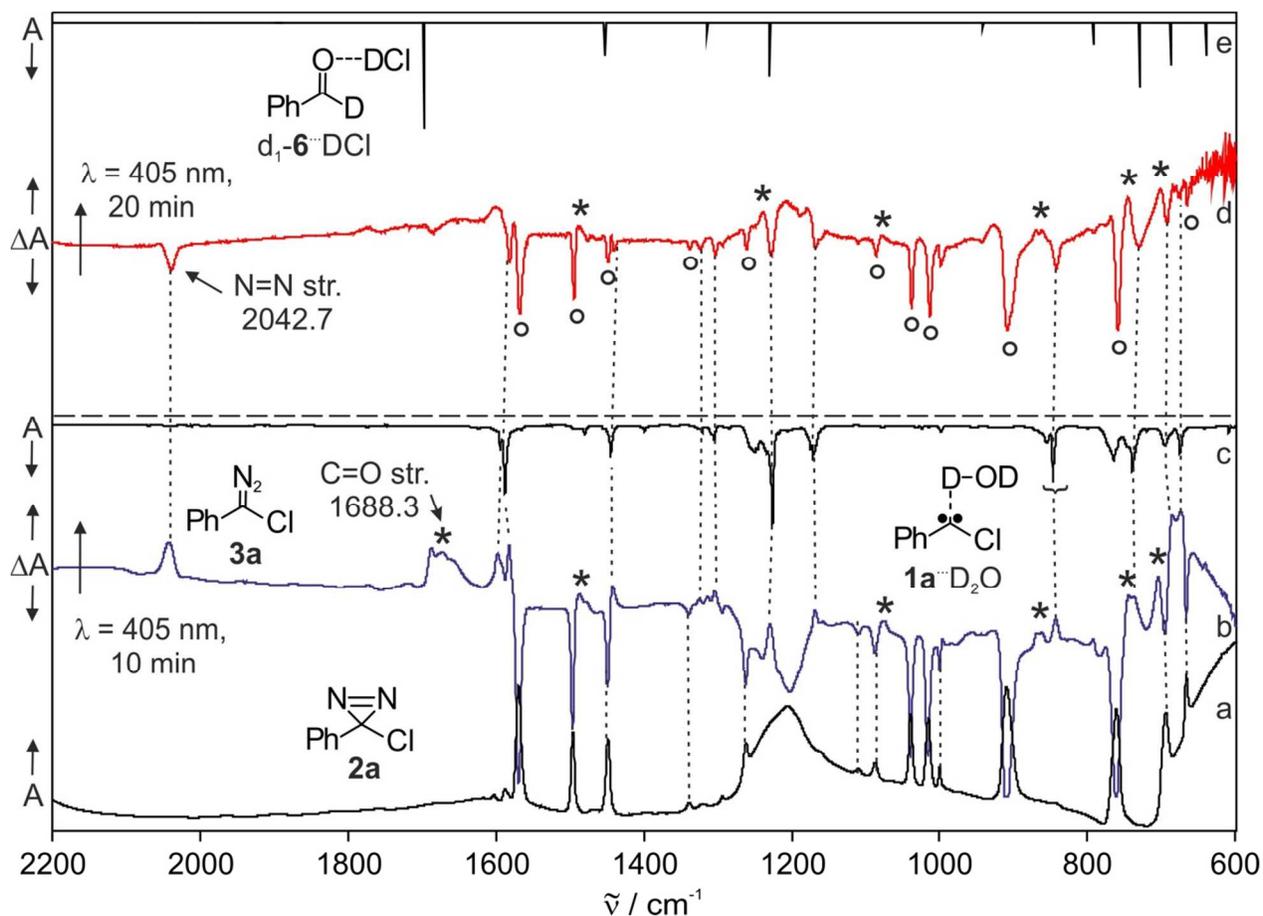
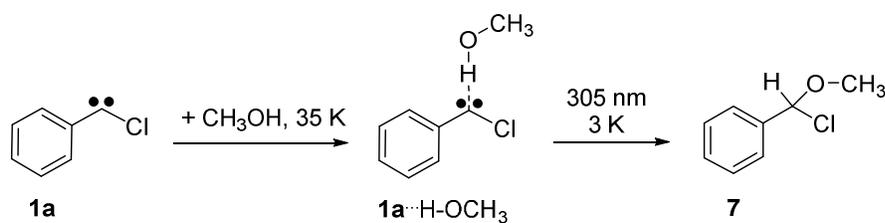


Figure 7. IR spectra in solid D₂O showing the formation of the **1a**···D₂O complex, a small amount of **3a** and the d₁₋₆···DCl complex at 9 K. a) IR-spectrum of **2a** in amorphous D₂O ice at 9 K. b) Difference IR spectrum after 405 nm photolysis of **2a** in D₂O at 9 K for 10 min. Bands pointing downwards are disappearing during irradiation and are assigned to **2a**. Bands pointing upwards are appearing concomitantly and are assigned to the **1a**···D₂O complex, a small amount of **3a** and the d₁₋₆···DCl complex (bands marked by *). c) **1a**···D₂O complex formed in an argon matrix doped with 1% D₂O upon annealing from 9 to 35 K. d) Difference IR spectrum after prolonged irradiation of the matrix a with 405 nm for a total of 20 min in D₂O matrix at 9 K. Bands pointing downwards are disappearing and are assigned to the **1a**···D₂O complex and **2a** (bands marked by °). Bands pointing upwards are appearing and are assigned to the d₁₋₆···DCl complex (bands marked by *). e) IR spectrum of d₁₋₆ simulated with data from ref. ³⁷

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6 **Chlorophenylcarbene 1a Methanol Complex.** Carbene **1a** was also generated in 0.1–2%
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8 methanol-doped argon matrices at 3 K. Annealing of these matrices at 25–35 K resulted in
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10 characteristic shifts of some bands of **1a**, indicating the formation of the hydrogen-bonded
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12 complex **1a**···H-OCH₃ (Scheme 3, Figure 8). The band shifts are very similar than those
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14 observed for the water complex **1a**···H-OH. Complex **1a**···H-OCH₃ proved to be photolabile,
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16 and UV light ($\lambda > 305$ nm) irradiation resulted in the formation of the primary OH insertion
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18 product **7**. In contrast to the water adduct **5**, the methanol adduct **7** is stable and can be identified
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20 by comparison of the IR spectra with that of the authentic matrix-isolated compound. Prolonged
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22 irradiation did not result in the formation of further photoproducts. As expected, with CH₃OD the
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24 corresponding deuterated d₁-**7** is formed.
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39 **Scheme 3.** Reaction of **1a** with CH₃OH and subsequent photochemistry.

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42 The activation barrier for the insertion of carbene **1a** into the OH bond of methanol and the
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44 intrinsic reaction coordinate (IRC) for this reaction was calculated at the B3LYP-D3/6-
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46 311++G(d,p) level of theory (Figure 6). With 7 kcal/mol the barrier is considerably lower than
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48 that of the insertion of **1a** into H-OH (11.1 kcal/mol), and only slightly larger than that of the
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50 insertion of **DPC** into H-OH (6.6 kcal/mol). Nevertheless, a tunneling reaction as in the insertion
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52 reactions of both **DPC** and **FL** into water and methanol was not observed.
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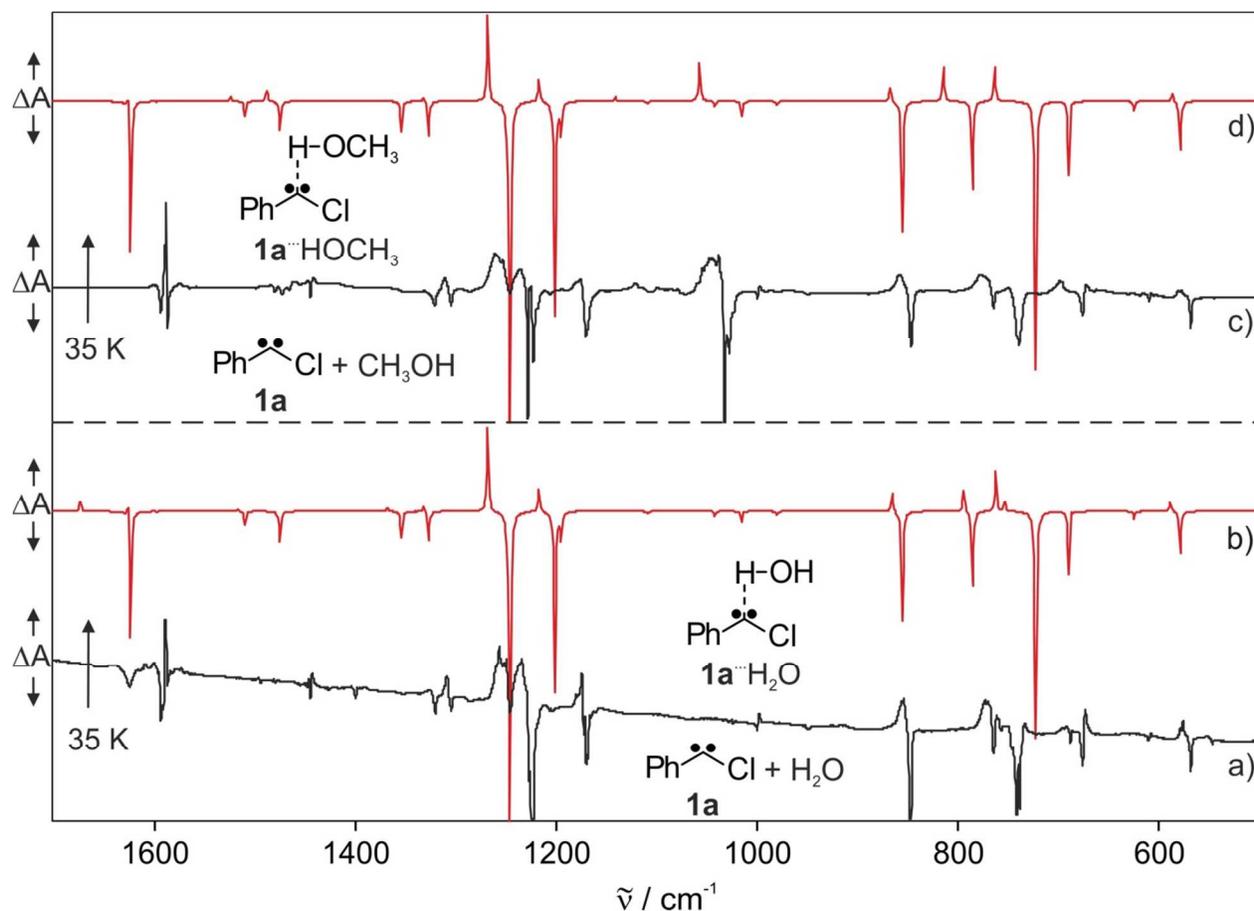


Figure 8. Difference IR spectra showing the formation of the $\mathbf{1a} \cdots \text{H-OH}$ and $\mathbf{1a} \cdots \text{H-OCH}_3$ complexes. a) Difference spectrum after annealing an argon matrix containing $\mathbf{1a}$ and 1% H_2O . b) Difference spectrum calculated at the B3LYP-D3/6-311++G(2d,2p) level of theory. c) Difference spectrum after annealing an argon matrix containing $\mathbf{1a}$ and 1% CH_3OH . d) Difference spectrum calculated at the B3LYP-D3/6-311++G(2d,2p) level of theory.

Conclusion

The halophenylcarbenes $\mathbf{1a}$ and $\mathbf{1b}$ are very strong bases and excellent hydrogen bond acceptors, and thus form strongly hydrogen-bonded complexes $\mathbf{1} \cdots \text{H-OH}$ with water. For $\mathbf{1a}$ the complex with methanol $\mathbf{1a} \cdots \text{H-OCH}_3$ was also investigated. All hydrogen-bonded complexes of $\mathbf{1}$ are

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3 stable under the conditions of matrix isolation, OH insertions via quantum mechanical tunneling
4 (QMT) are not observed. This is in contrast to the hydrogen-bonded complexes of (singlet)
5 diphenylcarbene **DPC**^{14, 16} and fluorenylidene **FL**,¹⁵ which undergo OH insertions via tunneling
6 even at temperatures as low as 3 K. **DPC** and **FL** are even stronger basic and form stronger
7 hydrogen bonds than halophenylcarbenes **1**, which results in lower activation barriers for the OH
8 insertions. DFT calculations predict a considerably larger activation barrier for the insertion of **1a**
9 and **1b** into water than for **DPC** and **FL** (Chart 3), in agreement with the experimental findings.
10 Photochemical excitation of **1**···H-OR results in OH insertion, however, our experiments do not
11 allow to discriminate between true photochemical and “hot ground state” reactions.
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25 The behavior of **1a** and **1b** in amorphous water ice also differs from that of **DPC** and **FL**. While
26 the latter two carbenes are rapidly protonated to form the corresponding carbenium ions, **1a** and
27 **1b** only form water complexes, and proton transfer does not occur.
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32 It is noticeable that none of these carbenes formed ylides with HOR via interaction of the lone
33 pairs at oxygen with the vacant p-orbital at the carbene center. Obviously, hydrogen bonding is
34 preferred, at least under the conditions of matrix isolation.
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43 **Experimental section**

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46 Matrix isolation experiments at 3-50 K were performed by standard techniques using a closed-
47 cycle helium cryostat. Matrix infrared spectra were recorded with a FTIR spectrometer using a
48 standard resolution of 0.5 cm⁻¹ in the range of 400-4000 cm⁻¹. Matrix UV-vis spectra were
49 recorded with a UV-vis NIR spectrophotometer in the range of 200-800 nm with a resolution of
50 0.1 nm. Water, D₂O, H₂¹⁸O, methanol and methanol-D were degassed several times prior to use
51 in the matrix isolation experiments. The matrices were generated by co-deposition of the
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3 substance of interest (**2a**, **2b** or **6**,) and water, D₂O, H₂¹⁸O, methanol or methanol-D with a large
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5 excess of argon on top of different substrates (CsI and sapphire windows for IR and UV-vis
6
7 spectroscopy, respectively) at 3-50 K. A flow rate of approximately 1 mbar/min was used for the
8
9 deposition of the matrix. Matrix-isolated chlorophenylcarbene **1a** or fluorophenylcarbene **1b**
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11 were generated by photolysis of chlorophenyldiazirine **2a** or fluorophenyldiazirine **2b** in argon
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13 matrices at 3 K using 405 nm or 365 nm LED source. After annealing at 35 K for several minutes
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15 the matrices were cooled back to 3 K to record spectra. The experiments in low density
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17 amorphous ice (LDA ice, H₂O or D₂O) were performed in a similar manner by replacing argon
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19 with H₂O or D₂O. For the preparation of LDA ice, purified H₂O or D₂O was degassed in several
20
21 freeze-thaw cycles. The deposition rate of the water or D₂O vapors was controlled by a fine
22
23 metering valve. Water or D₂O was co-deposited with the substance of interest (**2a**, **2b** or **6**) in a
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25 high vacuum system on top of different spectral windows (CsI (for IR spectroscopy) or sapphire
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27 window (for UV-vis spectroscopy)) at 50 K. After deposition the matrices were cooled back to 3-
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29 10 K. For irradiations of matrix-isolated species, LEDs (530, 470, 450, 405 and 365 nm), a low-
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31 pressure mercury lamp (254 nm) and a 500 W high-pressure mercury lamp and cut-off filter with
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33 50% transmission at 305 nm were used. Solvents (D₂O (99% D), H₂¹⁸O (97% isotopic purity),
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35 Methanol (99.9% anhydrous) and methanol-D (99.5% isotopic purity)) were purchased and used
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37 as received without further purification. Benzaldehyde **6** was purified by distillation prior to use.
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39 HCl gas (99.8%) was also used without further purification.
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48 Chlorophenyldiazirine **2a** was synthesized according to a published procedure.³⁸ For additional
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50 purification, **3a** was chromatographed (silica gel 60, 230-400 mesh) using pentane as eluent. (Ar,
51
52 3 K): $\tilde{\nu}$ (cm⁻¹) (%) = 3075.1 (5), 1573.7 (53), 1498.0 (17), 1450.9 (13), 1260.3 (7), 1109.0 (1),
53
54 1040.2 (14), 1015.0 (27) 912.7 (100), 757.1 (31), 692.3 (40), 666.7 (22), 544.5 (10) cm⁻¹.
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3 Fluorophenyldiazirine **2b** was synthesized by a Cl-to-F exchange reaction with the use of tetra-
4
5 butylammonium fluoride according to a published procedure.³⁹ **2a** was further purified by HPLC
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7 (pentane). IR (Ar, 3 K): $\tilde{\nu}$ (cm⁻¹) (%) = 3075 (4), 1559 (8), 1451 (13), 1306 (83), 1077 (34), 1010
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9 (58), 759 (96), 693 (93), 559.6 (56), 553 (50) cm⁻¹.

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13 1-chloro-1-methoxytoluene **7** was synthesized according to a literature procedure.⁴⁰ IR (Ar, 3 K):
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15 $\tilde{\nu}$ (cm⁻¹) (%) = 1369.3 (24), 1251.6 (71), 1195.1 (67), 1121.7 (92), 987.0 (25), 851.0 (24), 695.5
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17 (100), 628.4 (12), 616.3 (8).

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24 **Computational Methods.** The geometries and vibrational frequencies of all species were
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26 calculated using the B3LYP-D3⁴¹ density functional with the 6-311++G(2d,2p) basis set. **7** and
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28 d₁-**7** were calculated at the MP2/6-311++G(2d,2p)⁴² level of theory. All calculations were
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30 performed using the Gaussian 09⁴³ suite of programs. The multiple minima hypersurface
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32 (MMH)⁴⁴ approach was used to localize the minima of the **1a**-water and methanol, **1b**-water, **6**-
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34 HCl and **6**-HF systems. 100 randomly arranged complexes of each of those systems described
35
36 above were generated as starting points and preoptimized at the B3LYP/6-31G(d,p) level of
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38 theory. The most stable structures were taken for further optimizations at different methods
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40 (M06-2X⁴⁵, B3LYP⁴⁶ and B3LYP-D3⁴¹) with the 6-311++G(2d,2p) basis set. All interaction
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42 energies were corrected by the Boys and Bernardi counterpoise correction.⁴⁷ The stabilization
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44 energies were calculated by subtracting the energies of the monomers from those of the dimeric
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46 complexes including ZPE corrections.
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Associated Content

Supporting Information. Additional IR and UV/vis spectroscopic data of the experiments in LDA ice, H₂O- and CH₃OH-doped argon matrices, isotopic labelling IR spectra, experimental and calculated vibrational frequencies, calculated energies and geometries of H-bonded complexes and Cartesian coordinates of all optimized structures. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

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References

1. Sander, W.; Kötting, C., Reactions of Difluorovinylidene - a Super-Electrophilic Carbene. *Chem. Eur. J.* **1999**, *5*, 24-28.
2. Breidung, J.; Bürger, H.; Kötting, C.; Kopitzky, R.; Sander, W.; Senzlober, M.; Thiel, W.; Willner, H., Difluorovinylidene. *Angew. Chem. Int. Ed.* **1997**, *36*, 1983-1985.
3. Kötting, C.; Sander, W.; Senzlober, M.; Bürger, H., Oxidation of Difluorovinylidene. *Chem-Eur J* **1998**, *4*, 1611-1615.
4. Arduengo, A. J., Looking for Stable Carbenes: The Difficulty in Starting Anew. *Acc. Chem. Res.* **1999**, *32*, 913-921.
5. Moss, R. A., Solvation and Complexation of Carbenes - a Perspective. *J. Phys. Org. Chem.* **2011**, *24*, 866-875.
6. Kirmse, W., Carbene Protonation. In *Advances in Carbene Chemistry*, Brinker, U. H., Ed. Elsevier Science B.V.: 2001; Vol. 3, pp 1-51.
7. Chen, H.; Justes, D. R.; Cooks, R. G., Proton Affinities of N-Heterocyclic Carbene Super Bases. *Org. Lett.* **2005**, *7*, 3949-3952.
8. Pliego, J. R.; DeAlmeida, W. B., Absolute Proton Affinity and Basicity of the Carbenes CH_2 , CF_2 , Ccl_2 , $\text{C}(\text{OH})(2)$, FcoH , Cph_2 and Fluorenylidene. *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 1881-1883.
9. Keeffe, J. R.; O'Ferrall, R. A. M., The Protonation of Carbenes and Structural Effects on the A-Proton Acidity of Carbocations. *ARKIVOC (Gainesville, FL, U. S.)* **2008**, 183-204.
10. Lavilla, J. A.; Goodman, J. L., The Experimental Heats of Formation and Reaction of Singlet Carbenes Via Time-Resolved Photoacoustic Calorimetry. *J. Am. Chem. Soc.* **1989**, *111*, 712-714.
11. Du, X. M.; Fan, H.; Goodman, J. L.; Kesselmayr, M. A.; Krogh-Jespersen, K.; LaVilla, J. A.; Moss, R. A.; Shen, S.; Sheridan, R. S., Reactions of Dimethoxycarbene and Fluoromethoxycarbene with Hydroxyl Compounds. Absolute Rate Constants and the Heat of Formation of Dimethoxycarbene. *J. Am. Chem. Soc.* **1990**, *112*, 1920-1926.
12. Belt, S. T.; Bohne, C.; Charette, G.; Sugamori, S. E.; Scaiano, J. C., Carbocation Formation Via Carbene Protonation Studied by the Technique of Stopped-Flow Laser-Flash Photolysis. *J. Am. Chem. Soc.* **1993**, *115*, 2200-2205.
13. Arduengo, A. J., III; Gamper, S. F.; Tamm, M.; Calabrese, J. C.; Davidson, F.; Craig, H. A., A Bis(Carbene)-Proton Complex: Structure of a C-H-C Hydrogen Bond. *J. Am. Chem. Soc.* **1995**, *117*, 572-573.
14. Costa, P.; Sander, W., Hydrogen Bonding Switches the Spin State of Diphenylcarbene from Triplet to Singlet. *Angew. Chem., Int. Ed.* **2014**, *53*, 5122-5125.
15. Costa, P.; Trosien, I.; Fernandez-Oliva, M.; Sanchez-Garcia, E.; Sander, W., The Fluorenyl Cation. *Angew. Chem. Int. Ed.* **2015**, *54*, 2656-2660.
16. Costa, P.; Fernandez-Oliva, M.; Sanchez-Garcia, E.; Sander, W., The Highly Reactive Benzhydryl Cation Isolated and Stabilized in Water Ice. *J. Am. Chem. Soc.* **2014**, *136*, 15625-15630.
17. Moss, R. A., Improved Production of Phenylchlorocarbene. *J. Org. Chem.* **1962**, *27*, 2683-&.
18. Moss, R. A.; Whittle, J. R.; Freidenreich, P., Stereoselectivity of Carbene Intermediates. Vi. Selectivity of Phenylchlorocarbene. *J. Org. Chem.* **1969**, *34*, 2220-2224.
19. Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H., Reaction of Phenylchlorocarbene in Oxygen-Doped Matrices. *J. Am. Chem. Soc.* **1986**, *108*, 1517-1520.

- 1
2
3 20. Sander, W. W., Chemiluminescence from Arylcarbene Oxidation: Phenylchlorocarbene
4 and (2-Chlorophenyl)Carbene. *Spectrochim. Acta A* **1987**, *43A*, 637-646.
- 5 21. Pliego, J. R., Jr.; De, A. W. B.; Celebi, S.; Zhu, Z.; Platz, M. S., Singlet-Triplet Gap, and
6 the Electronic and Vibrational Spectra of Chlorophenylcarbene: A Combined Theoretical and
7 Experimental Study. *J. Phys. Chem. A* **1999**, *103*, 7481-7486.
- 8 22. Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M.,
9 Absolute Rate Constants for Additions of Phenylchlorocarbene to Alkenes. *J. Am. Chem. Soc.*
10 **1980**, *102*, 7576-7578.
- 11 23. Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H., Pyridine Ylide Formation
12 by Capture of Phenylchlorocarbene and Tert-Butylchlorocarbene - Reaction-Rates of an
13 Alkylchlorocarbene by Laser Flash-Photolysis. *J. Am. Chem. Soc.* **1988**, *110*, 5595-5596.
- 14 24. Bonneau, R.; Liu, M. T. H., Insertion of Phenylchlorocarbenes in the Carbon-Hydrogen
15 Bonds of Alkanes: Measurement of the Rate Constants by Laser Flash Photolysis. *J. Photochem.*
16 *Photobiol., A* **1992**, *68*, 97-106.
- 17 25. Moss, R. A.; Yan, S. Q., Absolute Kinetics of Phenylchlorocarbene C-H Insertion
18 Reactions. *Tetrahedron Lett.* **1998**, *39*, 9381-9384.
- 19 26. Moss, R. A.; Jang, E. G.; Ho, G. J., Absolute Rate Constants for the Reactions of
20 Phenylhalocarbenes with Alkynes. *J. Phys. Org. Chem.* **1990**, *3*, 760-763.
- 21 27. Sun, Y.; Tippmann, E. M.; Platz, M. S., A Search for Carbene-Solvent Interactions Using
22 Time-Resolved Infrared Spectroscopy. *Org. Lett.* **2003**, *5*, 1305-1307.
- 23 28. Wang, J.; Burdzinski, G.; Kubicki, J.; Platz, M. S.; Moss, R. A.; Fu, X.; Piotrowiak, P.;
24 Myahkostupov, M., Ultrafast Spectroscopic Study of the Photochemistry and Photophysics of
25 Arylhalodiazirines: Direct Observation of Carbene and Zwitterion Formation. *J. Am. Chem. Soc.*
26 **2006**, *128*, 16446-16447.
- 27 29. Sander, W.; Bucher, G.; Wierlacher, S., Carbenes in Matrices - Spectroscopy, Structure,
28 and Reactivity. *Chem. Rev.* **1993**, *93*, 1583-1621.
- 29 30. Sheridan, R. S., Exploring Matrix Isolated Carbenes and Bis-Carbenes with Electronic
30 Spectroscopy as a Guide. *J. Phys. Org. Chem.* **2010**, *23*, 326-332.
- 31 31. McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.
32 P.; Mooring, A. M.; West, P. R., 1,2,4,6-Cycloheptatetraene: The Key Intermediate in
33 Arylcarbene Interconversions and Related C7h6 Rearrangements. *J. Am. Chem. Soc.* **1987**, *109*,
34 2456-2469.
- 34 32. Forney, D.; Jacox, M. E.; Thompson, W. E., The Mid- and near-Infrared Spectra of Water
35 and Water Dimer Isolated in Solid Neon. *J. Mol. Spectrosc.* **1993**, *157*, 479-493.
- 36 33. Ayers, G. P.; Pullin, A. D. E., Ir-Spectra of Matrix-Isolated Water Species .4.
37 Configuration of Water Dimer in Argon Matrices. *Spectrochim Acta A* **1976**, *32*, 1695-1704.
- 38 34. Ayers, G. P.; Pullin, A. D. E., Ir-Spectra of Matrix-Isolated Water Species .1. Assignment
39 of Bands to (H2o)2, (D2o)2 and Hdo Dimer Species in Argon Matrices. *Spectrochim Acta A*
40 **1976**, *32*, 1629-1639.
- 41 35. Engdahl, A.; Nelander, B., On the Structure of the Water Trimer. A Matrix Isolation
42 Study. *J. Chem. Phys.* **1987**, *86*, 4831.
- 43 36. Ceponkus, J.; Uvdal, P.; Nelander, B., Water Tetramer, Pentamer, and Hexamer in Inert
44 Matrices. *J. Phys. Chem. A* **2012**, *116*, 4842-4850.
- 45 37. Gerbig, D.; Reisenauer, H. P.; Wu, C.-H.; Ley, D.; Allen, W. D.; Schreiner, P. R.,
46 Phenylhydroxycarbene. *J. Am. Chem. Soc.* **2010**, *132*, 7273-7275.
- 47 38. Graham, W. H., The Halogenation of Amidines. I. Synthesis of 3-Halo- and Other
48 Negatively Substituted Diazirines1. *J. Am. Chem. Soc.* **1965**, *87*, 4396-4397.
- 49
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51
52
53
54
55
56
57
58
59
60

- 1
2
3 39. Moss, R. A.; Terpinski, J.; Cox, D. P.; Denny, D. Z.; Krogh-Jespersen, K., Azide and
4 Fluoride Exchange Reactions of Halodiazirines. *J. Am. Chem. Soc.* **1985**, *107*, 2743-2748.
5
6 40. Berliner, M. A.; Belecki, K., Simple, Rapid Procedure for the Synthesis of Chloromethyl
7 Methyl Ether and Other Chloro Alkyl Ethers I. *J. Org. Chem.* **2005**, *70*, 9618-9621.
8 41. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A Consistent and Accurate Ab Initio
9 Parametrization of Density Functional Dispersion Correction (Dft-D) for the 94 Elements H-Pu.
10 *J. Chem. Phys.* **2010**, *132*, 154104.
11 42. Head-Gordon, M.; Pople, J. A.; Frisch, M. J., Mp2 Energy Evaluation by Direct Methods.
12 *Chem. Phys. Lett.* **1988**, *153*, 503-506.
13 43. Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani,
14 G.; Barone, V.; Mennucci, B.; Petersson, G., Gaussian 09, Revision A. 02; Gaussian, Inc.
15 *Wallingford, CT* **2009**, *19*, 227-238.
16 44. Montero, L. A.; Esteva, A. M.; Molina, J.; Zapardiel, A.; Hernandez, L.; Marquez, H.;
17 Acosta, A., A Theoretical Approach to Analytical Properties of 2,4-Diamino-5-Phenylthiazole in
18 Water Solution. Tautomerism and Dependence on Ph. *J. Am. Chem. Soc.* **1998**, *120*, 12023-
19 12033.
20 45. Zhao, Y.; Truhlar, D. G., The M06 Suite of Density Functionals for Main Group
21 Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and
22 Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class
23 Functionals and 12 Other Functionals. *Theoret. Chem. Acc.* **2008**, *120*, 215-241.
24 46. Lee, C. T.; Yang, W. T.; Parr, R. G., Development of the Colle-Salvetti Correlation-
25 Energy Formula into a Functional of the Electron-Density. *Phys Rev B* **1988**, *37*, 785-789.
26 47. Boys, S. F.; Bernardi, F., The Calculation of Small Molecular Interactions by the
27 Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**,
28 *19*, 553-566.
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Tables

Table 1. Experimental and calculated vibrational frequencies of **1a** and its complexes with H₂O and CH₃OH.

| Ar ^a , (I _{rel.}) ^f | Ar/H ₂ O ^b , (I _{rel.}) ^f | | LDA ^c , (I _{rel.}) ^f | | Ar/CH ₃ OH ^d , (I _{rel.}) ^f | | DFT ^e , (I _{abs.}) ^h | | |
|---|--|--------------------|--|--------------------|--|--------------------|--|--------------------|-------------------------|
| v (cm ⁻¹) | v (cm ⁻¹) | shift ^g | v (cm ⁻¹) | shift ^g | v (cm ⁻¹) | shift ^g | v (cm ⁻¹) | shift ^g | assignment |
| 568.4 (10) | 575.5 (6) | +7.1 | 567.5 (3) | -0.9 | 578.9 (8) | +10.5 | 588.2 (29) | +8.5 | C-H i.p. def. |
| 675.4 (15) | 673.0 (8) | -2.4 | 676.1 (6) | +0.7 | 672.2 (10) | -3.2 | 687.3 (33) | -4.7 | C-H o.o.p. def. |
| 739.5 (51) | 766.7 (25) | +27.2 | 768.2 (30) | +28.7 | 767.7 (20) | +28.2 | 762.2 (129) | +30.4 | C-C-Cl str. sym. |
| 764.1 (20) | 772.7 (10) | +8.6 | 780.0 (15) | +15.9 | 777.9 (12) | +13.8 | 794.9 (68) | +6.5 | C-H o.o.p. def. |
| 847.1(24) | 855.6 (14) | +8.5 | 860.9 (18) | +13.8 | 857.5 (13) | +10.4 | 865.8 (61) | +3.4 | C-C-Cl str. asym. |
| 1172.2 (40) | 1174.8 (16) | +2.6 | 1171.4 (39) | -0.8 | 1174.4 (16) | +2.2 | 1199.4 (7) | +5.6 | C-H i.p. def. |
| 1226.4 (100) | 1237.0 (28) | +10.6 | 1230.5 (50) | +4.1 | 1236.9 (31) | +10.5 | 1268.5 (266) | +21.4 | C-C str. carbene center |
| 1305.3 (7) | 1309.2 (6) | +3.9 | 1312.0 (5) | +6.7 | 1309.2 (3) | +3.9 | 1332.7 (20) | +4.2 | C=C str. ring |
| 1320.7 (3) | 1326.3 (4) | +5.6 | 1330.4 (2) | +2.7 | 1329.1 (5) | +8.4 | 1368.5 (12) | +13.3 | C-H i.p. def. |

| | | | | | | | | | |
|-------------|--------------|--------|-------------|-------|-------------|------|---------------|--------|----------------|
| 1445.7 (10) | 1443.2 (4) | -2.5 | 1458.3 (12) | +12.6 | 1442.2 (3) | -3.5 | 1475.3 (26) | -0.7 | C=C str. ring |
| 1588.8 (28) | 1588.6 (20) | +0.2 | 1596.5 (35) | +7.7 | 1590.6 (25) | +1.8 | 1626.7 (95) | +1.5 | C=C str. ring |
| / | 3199.6 (100) | -438.4 | / | / | / | / | 3372.8 (1036) | -447.1 | O-H str. sym. |
| / | 3692.7 (15) | -41.6 | / | / | / | / | 3884.5 (57) | -33.1 | O-H str. asym. |

^aIn argon matrix at 3 K. ^bIn argon matrix doped with 1% H₂O at 3 K. ^cIn LDA ice matrix at 9 K. ^dIn argon matrix doped with 1% CH₃OH at 3 K. ^eCalculated at the B3LYP-D3/6-311++G(2d,2p) level of theory. ^fRelative intensities based on the strongest observed absorption band. ^gFrequency shift relative to the monomers (cm⁻¹). ^hAbsolute intensities in km/mol.

Table 2. Comparison of the O-H and O-D shifts of $\mathbf{1a} \cdots \text{H}_2\text{O}$, $\mathbf{1a} \cdots \text{D}_2\text{O}$ and $\mathbf{1a} \cdots \text{H}_2^{18}\text{O}$.

| Mode | H ₂ O | $\mathbf{1a} \cdots \text{H}_2\text{O}$ | D ₂ O | $\mathbf{1a} \cdots \text{D}_2\text{O}$ | H ₂ ¹⁸ O | $\mathbf{1a} \cdots \text{H}_2^{18}\text{O}$ |
|-----------|------------------|---|------------------|---|--------------------------------|--|
| ν_1^a | 3638.0 | 3199.6 (- 438.4) | 2657.8 | 2286.4 (- 371.4) | 3630.8 | 3190.2 (- 440.6) |
| ν_3^b | 3734.3 | 3692.7 (- 41.6) | 2766.0 | 2726.2 (- 39.8) | 3723.5 | 3680.9 (- 42.6) |

^asym. str. O-H, O-D, ¹⁸O-H. ^basym. str. O-H, O-D, ¹⁸O-H. Frequency shifts are given in parenthesis. Frequencies in cm⁻¹.

Table 3. Vibrational frequencies and shifts of the **1b**···H₂O complex.

| Ar ^a | | Ar/H ₂ O ^b | | | LDA ice ^c | | | DFT ^d | | | |
|---------------------------|-------------------------------|----------------------------------|-------------------------------|--------------------|---------------------------|-------------------------------|--------------------|---------------------------|-------------------------------|--------------------|----------------------------|
| ν (cm ⁻¹) | I _{rel} ^e | I _{rel} ^e | I _{rel} ^e | shift ^f | ν (cm ⁻¹) | I _{rel} ^e | shift ^f | ν (cm ⁻¹) | I _{abs} ^g | shift ^f | assignment |
| 626.8 | 21 | 631.4 | 6 | +4.2 | 636.0 | 5 | +9.2 | 644.7 | 15 | +5.8 | skel. vibr. |
| 680.0 | 27 | 678.3 | 10 | -2.5 | 678.4 | 6 | -1.6 | 688.7 | 29 | -3.6 | C-H o.o.p. def. |
| 838.0 | 15 | 847.7 | 2 | +7 | 860.9 | 2 | +22.9 | 863.6 | 3 | +13.5 | C-C-F def. |
| 1064.2 | 47 | 1070.0 | 1 | +5.8 | 1057.9 | 2 | -6.3 | 1097.2 | 144 | +21.8 | C-H i.p. def. |
| 1110.2 | 94 | 1127.1 | 36 | +16.9 | 1122.5 | 10 | +12.3 | 1141.3 | 131 | +20.6 | C-F str. |
| 1168.3 | 10 | 1176.3 | 5 | +8.0 | 1188.5 | 6 | +20.2 | 1215.3 | 45 | +15.4 | C-H bend |
| 1226.8 | 100 | 1243.3 | 13 | +16.5 | 1266.4 | 15 | +39.6 | 1274.2 | 274 | +26.0 | C-C str. carbene center |
| 1314.8 | 17 | 1318.9 | 3 | +4.1 | 1317.5 | 3 | +2.7 | 1346.0 | 11 | +4.7 | C-H i.p. def. |
| / | / | 3182.4 | 100 | -455.6 | / | / | / | 3420.0 | 844 | -399.9 | O-H str. sym. ^h |

^aIn argon at 3 K. ^bIn argon matrix doped with 1% H₂O at 3 K. ^cIn LDA ice matrix at 9 K. ^dCalculated at the B3LYP-D3/6-311++G(2d,2p) level of theory. ^eRelative intensities based on the strongest observed absorption band. ^fFrequency shift relative to the monomers (cm⁻¹). ^gAbsolute intensities

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5 in km/mol. ^hOnly the symmetrical O-H str. could be observed in the H₂O-doped argon matrix. The shift of the O-H str. was difficult to observe in
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7 the LDA ice matrix.
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TOC Graphic

