# Matrix IR spectra and quantum chemical studies of the reaction between difluorostannylene and hept-1-yne. The first direct observation of a carbene analog π-complex with alkyne

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IR studies of $SnF_2$ and hept-1-yne codeposited in an argon matrix at 12 K has revealed new bands at 540, 565, 1011, 2088 and 3256 cm$^{-1}$, assigned to the formation of a complex between $SnF_2$ and the alkyne. Quantum chemical AM1 and PM3 calculations confirm this assignment to the π-complex of $SnF_2$ and the triple bond of hept-1-yne, and show that the complex forms without an activation barrier. The energy of the formation of the complex according to AM1 and PM3 calculations is 7.4 and 9.1 kcal/mol, respectively. The calculations indicate that the product of the cycloaddition of $SnF_2$ to a triple bond, stannyrene, is significantly less stable than the π-complex.

**Key words:** π-complex, difluorostannylene, hept-1-yne, matrix IR spectra, AM1, PM3

Cycloaddition to multiple carbon-carbon bonds is a characteristic reaction of carbenes and silylenes.[1] However attempts to carry out this reaction with other carbene analogs of group IVB elements (germylenes and stannylenes) have succeeded in only a few cases.[2]

The reaction centers of singlet carbenes and their analogs have a low laying vacant *p*-MO enabling them to form complexes with electron donors, *e.g.*, π-bonds. Many cycloadditions of carbenes to alkenes and alkynes are known to date, but no intermediate complexes have been detected in these reactions. One can explain this fact by both the high reactivity of carbenes and the high exothermicity of additions, which make the formation of any intermediates very unlikely. The only exception are dihalocarbenes. There are indirect experimental data indicating the formation of complexes of dihalocarbenes with alkenes.[3] Unfortunately, the quantum chemical calculations[3] did not provide unequivocal evidence of their existence. The experimental facts related to the complexation of carbene analogs with π-systems are limited to a single work[4] on a matrix IR-spectroscopy study of the products of $SnF_2$ interaction with ethylene. Unfortunately, the assignments of bands in Ref. 4 were based on spectral correlations only and do not reveal the structure of the complex.

Our previous[5] semi-empirical AM1[6] calculations of the potential energy surfaces (PES) for the reactions of carbenes and their analogs with ethylene and acetylene have shown the possibility of the formation of intermediate π-complexes in the course of additions of silylenes, dihalogermylenes and dihalostannylenes to multiple carbon-carbon bonds.

The problems of the existence of intermediate complexes, and their stabilities and structures are of fundamental interest from the point of view of the mechanisms of reactions of carbenes and their analogs with unsaturated substrates.

Here we report the isolation in Ar matrices at 12 K of the first representative of carbene analog complexes with alkynes — the π-complex hept-1-yne (**1**) — $SnF_2$. The IR bands of the complex were assigned with the help of semi-empirical AM1 and PM3[7] calculations.

## Experimental

In matrix isolation experiments a sample of difluorostannylene was evaporated from a graphite Knudsen cell with orifice diameter 1 mm positioned inside a quartz pyrolyzer, coupled to an optical helium cryostat. The evaporation temperature varied between 800 and 900 K. The evaporation products and excess Ar or mixture of **1**:Ar (1:30—1:150), introduced through a separate jet, were frozen at 12 K on a mirror copper plate, located ~50 mm from the quartz pyrolyzer orifice inside the cryostat. A closed-cycle refrigerator "Displex-CSW-208R" (Air Products Co.) cooled the plate. The pressure in the cryostat during deposition was $10^{-5}$—$10^{-6}$ Torr. A solid matrix sufficient for recording the IR spectrum was obtained after 30—60 min at a flow rate of argon of ~10 mmol/h. IR spectra were recorded on an IKS-24-LOMO spectrophotometer in the range 4000—400 cm$^{-1}$ by reflection of the IR beam from the mirror plate.

Quantum chemical AM1 and PM3 calculations were carried out with full optimization using the MOPAC package of programs adapted for an AT 486, using the parameters for fluorine[6,7] and tin,[8,9] respectively.

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## Results and Discussion

Five new bands, differing from those found in experiments on the deposition of only $SnF_2$ or only alkyne **1**, appear in the matrix IR spectrum upon codeposition of $SnF_2$ and alkyne **1**. The intensities of these bands vary simultaneously with changes in the dilution of the starting materials. We assign these bands to the complex of $SnF_2$ with hept-1-yne.

In all experiments carried out with $SnF_2$, along with the IR bands of monomer $SnF_2$, those of dimer[4] $(SnF_2)_2$ and of $SiF_4$ — the product of the reaction between $SnF_2$(g) and a quartz pyrolyzer surface, were recorded. The possibility of $(SnF_2)_2$ and $SiF_4$ participation in the formation of the observed complex was excluded by special experiments on the codeposition of **1** with $(SnF_2)_2$ and $SiF_4$.

Except those at 1011 $cm^{-1}$, the observed bands of the complex are similar to the characteristic vibrations of Sn-F, C≡C and H-C≡C in the individual reagents, but are shifted by several tenths of $cm^{-1}$. Therefore one can expect only minor changes in the geometry of difluorostannylene and hept-1-yne upon complexation.

Annealing of the matrix below 40—45 K resulted in the decrease and finally the complete disappearance of the complex bands, as well as those of $SnF_2$ and it dimer, which indicated decomposition of the complex with the formation of difluorostannylene oligomers that do not have well pronounced bands in the spectral region studied.[4]

Quantum chemical calculations show that the PES of the $SnF_2$ + **1** system has a minimum for complex **2**, the structure of which is presented in a Fig. 1.

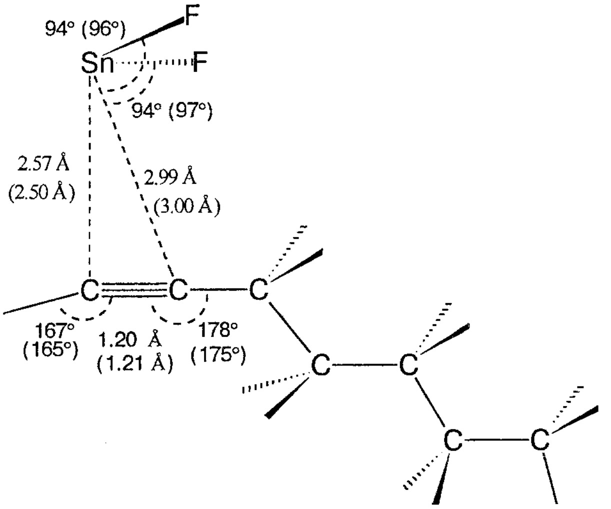

**Figure 1.** Basic structural parameters of π-complex **2** between hept-1-yne and $SnF_2$ calculated by PM3 and (in parentheses) AM1 methods.

AM1 and PM3 methods give very similar geomertic parameters for structure **2**. In both cases the Sn atom is coordinated to a π-bond and the fluorine atoms are extended towards the alkyl group. In fact, complexation does not change the geometry of the reagents, with the exception of the conspicuous bending of the H-C≡C fragment (up to 167° and 166° according AM1 and PM3, respectively) and the slight lengthening of the C≡C bond (0.013 E by both methods). Complexation only slightly affects the linearity of the C-C≡C fragment (177° and 178° by AM1 and PM3). According to AM1 and PM3 calculations the energy of alkyne **1** : $SnF_2$ complexation is 7.4 and, respectively 9.1 kcal/mol.

Let us consider in more detail the vibrations of complex **2** that have pronounced shifts in comparison to the frequiencies of alkyne **1** or $SnF_2$ (Table 1). Both quantum chemical methods reproduce the observed shifts that occur upon complexation, although the PM3 values are closer to the experimental ones than those of AM1. The correlation between the theoretical and experimental shifts is an important argument in support of the calculated structure of π-complex **2**.

The vibration at 1011 $cm^{-1}$ in the matrix IR spectrum of **2** has no analog in the spectra of the isolated reagents and deserves special attention. The calculations assign this band to the vibration of the ≡C-C-C- fragment in **2**. The same vibration in alkyne **1** was calculated to have an almost zero transition dipole moment, so this band should have very low intensity in the IR spectrum. Formation of complex **2** results in an

**Table 1.** Some experimental and calculated IR-frequencies of starting compounds and π-complex **2** ($cm^{-1}$)

| Assignment | Method | Compound | | | Frequency shifts |
|---|---|---|---|---|---|
| | | **1** | $SnF_2$ | **2** | |
| $\nu_{as}$(Sn—F) | Observed | — | 571 | 540 | 31 |
| | AM1 | — | 602 | 585 | 17 |
| | PM3 | — | 741 | 721 | 20 |
| $\nu_s$(Sn—F) | Observed | — | 593 | 565 | 28 |
| | AM1 | — | 615 | 595 | 20 |
| | PM3 | — | 760 | 738 | 22 |
| δ(H—C≡C) | Observed | 626 | — | — | — |
| | AM1 | 836 | — | 800 | 36 |
| | PM3 | 844 | — | 817 | 27 |
| δ(H—C≡C) | Observed | 634 | — | — | — |
| | AM1 | 841 | — | 825 | 16 |
| | PM3 | 859 | — | 839 | 20 |
| δ(≡C—C—C) | Observed | — | — | 1011 | — |
| | AM1 | 1129 | — | 1116 | 13 |
| | PM3 | 1042 | — | 1029 | 13 |
| ν(C≡C) | Observed | 2127 | — | 2088 | 39 |
| | AM1 | 2367 | — | 2308 | 59 |
| | PM3 | 2325 | — | 2267 | 58 |
| ν(≡C—H) | Observed | 3318 | — | 3256 | 62 |
| | AM1 | 3457 | — | 3365 | 92 |
| | PM3 | 3362 | — | 3277 | 85 |

increase in the transition dipole moment by approximately ten times, which should provide an increase of *ca.* two orders of magnitude in the vibration intensity. Therefore this band, invisible in the IR spectrum of **1**, became recognizable in the IR spectrum of its complex.

Quantum chemical calculations indicate there are two more vibrations with frequencies higher than 400 $cm^{-1}$ that should have noticeable shifts after complexation. These are the deformation vibrations of the H-C≡C fragment in the region of 800—870 $cm^{-1}$. The corresponding experimental bands of **1** are at 626 and 634 $cm^{-1}$. We have not detected these bands in IR spectrum of complex **2**. This is probably due to small shifts of these bands and their overlapping with the very intense bands of parent **1**.

No bands we can assign to difluorostannacyclopropene (difluorostannirene), the product of conceivable $SnF_2$ cycloaddition to the C≡C bond of alkyne **1**, have been detected in the matrix IR spectra. Quantum chemical AM1 and PM3 calculations demonstrate that the cycloaddition of $SnF_2$ to the C≡C bond of alkyne **1** is extremely unfavorable energetically (heats of this reaction calculated by AM1 and PM3 are, 42.2 kcal/mol and 31.9 kcal/mol). Recent *ab initio* calculations of the PES for the reaction of $SnF_2$ with acetylene[10] also indicate the high endothermicity of cycloaddition (16.5 kcal/mol).

Thus, the study has demonstrated that the reaction of $SnF_2$ with alkyne stops at the stage of a type **2** π-complex and does not produce a 3-membered cycle.

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