Study of complexation between difluorostannylene and aromatics by matrix IR spectroscopy

S. E. Boganov, M. P. Egorov, and O. M. Nefedov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: mpe@cacr.ioc.ac.ru

Complexes (1 : 1) between difluorostannylene and benzene, chlorobenzene, and toluene as well as the $(PhH)_2 \cdot SnF_2$ complex were obtained and characterized by matrix IR spectroscopy. The capability of carbene analogs to form labile complexes with aromatics was demonstrated for the first time taking SnF_2 as an example.

Key words: difluorostannylene, benzene, chlorobenzene, toluene, donor-acceptor complex; matrix isolation, IR spectroscopy.

The singlet state is the ground electron state of all known carbene analogs (CAs), *viz.*, silylenes, germylenes, and stannylenes,[1–3] which allows them to behave as Lewis acids due to the presence of a low-lying vacant p-orbital. The well known capability of carbene analogs to form complexes with relatively strong Lewis bases[4–12] allows one, in particular, to control their reactions.[12] In addition, the existence of complexes between CAs and weaker Lewis bases (haloalkanes,[13–16] alkenes,[17] alkynes,[18,19] and nitrogen[20–22]) has been experimentally demonstrated.

Since aromatic compounds (ACs) are weak Lewis bases, one can expect that they will form complexes with CAs. In fact, recently[23] experimental and calculated data indicating the existence of carbene complexes with ACs were reported. The formation of complexes between Me_2Ge and ACs was suggested in a study of the effect of the precursor nature on the position of the absorption band maximum in the UV spectrum of Me_2Ge generated in hydrocarbon glasses.[24] However, no conclusive evidence of the existence of labile complexes between CAs and ACs has been reported. At the same time, similar complexes can play an important role in generating CAs from precursors whose decomposition is accompanied by the formation of an AC as the second, stable, product.

The aim of this work, carried out in continuation of our investigations of SnF_2 complexation reactions,[16,18–20] was to detect experimentally complexes between this CA and several simplest ACs: benzene (PhH), toluene (PhMe), and chlorobenzene (PhCl).

Experimental

Monomeric SnF_2 was obtained by evaporating a sample of tin difluoride (Aldrich, 99% purity) from a graphite Knudsen cell with an outlet of diameter 1 mm fixed inside a quartz pyrolyzer attached to a vacuum optical helium cryostat. The evaporation temperature was varied in the range 500—700 °C. To reduce the interaction between SnF_2 vapors and the surface of the quartz pyrolyzer resulting in the formation of SiF_4, argon was passed through the pyrolyzer.

Efficient mixing of the components of argon mixtures with substrates (benzene, toluene, or chlorobenzene) was achieved by storing the mixtures in a glass vessel for ~24 h. The amount of each component was determined from its partial pressure using a mercury pressure gauge. The molar ratios of the components were varied from 1 : 30 to 1 : 400 for the PhH—Ar and PhCl—Ar mixtures and from 1 : 200 to 1 : 400 for the PhMe—Ar mixture. The mixtures were introduced into the cryostat *via* an independent unheated pipeline.

The products of SnF_2 evaporation and the substrate—Ar mixtures were codeposited on the mirror surface of a copper plate cooled to 12 K and located inside the cryostat 80 mm from the outlet of the Knudsen cell and at a distance of 50 mm from the outlet of the mixture introduction pipeline. The duration of deposition of the matrix layer whose thickness was sufficient for the recording of the spectrum was varied from 30 to 90 min at the mixture consumptions of ~15 mmol h^{-1}. The amount of deposited SnF_2 was evaluated from the weight loss of the Knudsen cell after the experiment taking into account the geometric factor of the pyrolyzer (0.5). The SnF_2 : Ar molar ratio in the matrices was varied from 1 : 100 to 1 : 600.

The copper plate was cooled using a Displex CSW-208R closed cycle cryogenic system. The working pressure in the cryostat was ~10^{-5} Torr. IR spectra were recorded on an IKS-24-LOMO spectrophotometer using the reflection scheme in the region 4000—400 cm^{-1} with a resolution of 1 cm^{-1}.

If a sample of tin difluoride was evaporated from the surface of the quartz pyrolyzer (without using the Knudsen cell) at 250—300 °C in an Ar stream, no bands of monomeric SnF_2 were observed in the IR spectra of the matrices obtained; at the same time, judging from the intensities of the bands of associated compounds (SnF_2 dimer and HF), the concentrations of these compounds corresponded to their typical concentrations in the experiments on tin difluoride evaporation from the Knudsen cell, while the concentration of SiF_4 was appreciably higher. To prove that no complexation between benzene and $(SnF_2)_2$ or SiF_4 occurs, the experiments on

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 97—102, January, 1999.

codeposition of tin difluoride and benzene were carried out under conditions of tin difluoride evaporation such that the matrix was totally free from the monomeric SnF_2.

Complexes of ACs with HF were obtained by codeposition of ACs and a H_2O—HF mixture formed upon passing water vapors over tin difluoride at 300 °C. In these experiments, the matrices were free from SnF_2 and its dimer, the SiF_4 concentration was lower than in the experiments described above, while Ar consumptions and AC, and HF concentrations were the same as in the case of codeposition of ACs and SnF_2.

Results and Discussion

Matrix IR spectra of initial compounds

Prior to performing the experiments on codeposition of substrates and SnF_2, the IR spectra of the substrates and products of tin difluoride evaporation isolated in an argon matrix were recorded (Table 1).

The spectra of the substrates were in good agreement with the known IR spectra of benzene in the argon matrix,[25–27] chlorobenzene both in the gas phase[28] and in the argon matrix,[29] and toluene both in the gas phase[30] and in the crystalline phase at 77 K.[31]

In addition to the absorption bands of the substrates, bands corresponding to trace amounts of water[32–34] desorbed in the course of the experiment from the cryostat walls were observed in the IR spectra. In some instances several weak bands in the region of stretching vibrations of the H_2O molecule assigned to a benzene complex with water[26] and, by analogy with benzene, to chlorobenzene and toluene complexes with water were also observed in the IR spectra (see Table 1). The impurity absorption bands had low intensities and did not hamper the identification of the labile adducts of ACs with SnF_2.

In addition to the absorption bands of monomeric SnF_2, its dimer, $(SnF_2)_2$, and oligomer, $(SnF_2)_x$,[17,35] a rather intense band of SiF_4, the product of the interaction of SnF_2 vapors with the surface of the quartz pyrolyzer,[36] with a characteristic isotope splitting was observed in the matrix IR spectrum of the products of tin difluoride evaporation. Unfortunately, the design of the cryostat used did not prevent the formation of SiF_4.

In addition to the compounds listed above, trace amounts of water,[32–34] HF[37] (a product of the SnF_2 hydrolysis), and $N_2 \cdot HF$[37] (dinitrogen appears in the matrix as a result of desorption from the cryostat walls) and $H_2O \cdot HF$[37] complexes were observed in several experiments in the matrices containing the products of tin difluoride evaporation (see Table 1). The above products were characterized by weak absorption bands in the frequency region higher than 3500 cm^{-1}. The same impurities, whose concentrations varied randomly, were also observed in the experiments on codeposition of SnF_2 and the substrates. The simultaneous presence

Table 1. Absorption bands observed in the matrix IR spectra

Compound	ν/cm^{-1}
PhH	608 w, 677 v.s, 850 w, 971 w, 995 w, 1014 w, 1041 s, 1149 v.w, 1180 m, 1250 v.w, 1391 m, 1480 s, 1522 m, 1618 w, 1670 w, 1757 w, 1811 s, 1958 s, 2600 v.w, 2619 v.w, 2822 v.w, 2891 v.w, 2911 sh, 3044 s, 3047 s, 3078 s, 3098 s
PhCl	406 w, 413 w, 466 s, 617 w, 687 s, 706 s, 743 v.s, 825 v.w, 833 v.w, 886 v.w, 905 m, 940 w, 947 sh, 967 v.w, 985 v.w, 1006 m, 1017 w, 1028 s, 1072 m, 1091 s, 1100 m, 1122 sh, 1127 m, 1158 v.w, 1176 w, 1214 v.w, 1238 w, 1277 v.w, 1300 w, 1327 v.w, 1372 v.w, 1388 v.w, 1447 s, 1479 s, 1500 m, 1519 v.w, 1539 v.w, 1566 m, 1584 s, 1726 m, 1786 m, 1860 m, 1862 sh, 1880 w, 1939 m, 1944 w, 1959 m, 3008 v.w, 3021 v.w, 3030 v.w, 3060 sh, 3067 m, 3091 sh, 3168 v.w
PhMe	455 sh, 461 s, 518 w, 697 s, 731 v.s, 790 w, 845 v.w, 898 w, 986 v.w, 1007 v.w, 1035 sh, 1041 m, 1085 m, 1110 w, 1159 v.w, 1184 w, 1197 v.w, 1216 v.w, 1315 v.w, 1336 v.w, 1383 m, 1450 m, 1471 s, 1500 s, 1523 v.w, 1570 v.w, 1608 m, 1731 m, 1798 m, 1815 v.w, 1854 m, 1857 sh, 1871 w, 1939 m, 1955 w, 1958 sh, 2738 w, 2860 sh, 2875 m, 2923 s, 2934 s, 2962 s, 2985 m, 3035 sh, 3044 s, 3066 m, 3095 m, 3109 sh, 3119 sh
H_2O	1609 w, 1623 w, 3638 v.w, 3711 w, 3754 w, 3775 w
$(H_2O)_x$	3572 w, 3519 v.w
$PhH \cdot H_2O$	1597 w, 1600 w, 3604 w, 3614 w, 3704 w, 3713 w
$PhCl \cdot H_2O$	3658 w, 3711 w
$PhMe \cdot H_2O$	3587 sh, 3608 v.w, 3727 w
SnF_2	571 s, 593 s
$(SnF_2)_2$	580 m
$(SnF_2)_x$	521 w
SiF_4	1007 w, 1016 w, 1026 s
$SiF_4 \cdot H_2O$	988 w
HF	3918 w, 3954 sh, 3963 w
$(HF)_2$	3822 v.w
$N_2 \cdot HF$	3881 v.w
$H_2O \cdot HF$	3554 v.w
$PhH \cdot HF$	3796 w, 688 sh
$PhCl \cdot HF$	3793 w, 753 sh
$PhMe \cdot HF$	3762 w, 740 sh
$PhH \cdot SnF_2$	542 m, 564 sh, 688 sh, 696 sh
$(PhH)_2 \cdot SnF_2$	538 sh, 562 sh
$PhCl \cdot SnF_2$	549 m, 566 sh, 753 sh, 764 sh
$PhMe \cdot SnF_2$	536 m, 563 sh, 740 sh
Products of vacuum oil pyrolysis	1084 w, 1180 w, 1295 w, 2859 w, 2928 m, 2960 w

Note. The following notations of bands were used: v.s is very strong, s is strong, m is medium, w is weak, v.w is very weak, and sh is shoulder.

of these compounds in the matrix did not hamper recording the absorption bands of the complexes and, as will be shown below, did not affect the SnF_2 complexation with the substrates.

Identification of absorption bands of SnF_2 complexes with substrates

Complexes of SnF_2 with benzene. The absorption bands at 3796, 696, 688, 564, and 542 cm^{-1} (Fig. 1, *b*) differing from the bands recorded upon the deposition of the initial reagents were observed in the IR spectrum upon codeposition of benzene and SnF_2 (at an Ar : PhH ratio not less than 100 : 1). The band at 3796 cm^{-1}, as well as the band at 688 cm^{-1} whose intensity must be close[25] to that of the former band, corresponds to a benzene complex with HF.[25] In our experiments, the band at 688 cm^{-1} was much more intense than that at 3796 cm^{-1}, which is most likely due to the contribution of the absorption of another product of the codeposition of the reagents. In fact, in the control experiments on codeposition of a HF—H_2O mixture and PhH the bands at 3796 and 688 cm^{-1} had equal intensities (Fig. 1, *c*), and no bands at 696, 564, and 542 cm^{-1} were observed.

Since SiF_4 and $(SnF_2)_2$ were present in the matrices, the absorption bands at 696, 688 (minus the contribution from the absorption of the PhH · HF complex), 564, and 542 cm^{-1} could be due to the products of their interaction with benzene. To exclude such a possibility, experiments on codeposition of benzene and SiF_4 and $(SnF_2)_2$ were carried out. No bands at 696, 688, 564, and 542 cm^{-1} were observed in the IR spectra obtained (Fig. 1, *d*), which makes it possible to assign them to a product of interaction between the monomeric SnF_2 and benzene.

At different molar ratios between the monomeric SnF_2 and benzene in the matrices, the intensities of the above bands (minus the contribution from the absorption of the PhH · HF complex to the band at 688 cm^{-1}) changed synchronously, which indicates that they correspond to the same product or to several equally stable products of the interaction between SnF_2 and benzene. The fact that the frequencies listed above are close to those of SnF_2 and benzene indicates that the geometry of the initial molecules changes insignificantly upon the interaction. This makes it possible to identify the observed product as a SnF_2 complex with benzene. Even at a maximum dilution of both reagents (1 : 400) at which, on the one hand, the absorption bands of the complex still can be observed, and, on the other hand, the interaction between one molecule of any of the reagents and more than one molecule of the second reagent seems to be unlikely, no other absorption bands were observed. This fact makes it possible to assign the absorption bands at 696, 688, 564, and 542 cm^{-1} to the PhH · SnF_2 complex of the simplest composition 1 : 1.

Controlled annealing of the matrix at 30—40 K resulted in weakening of the absorption bands of the monomeric SnF_2, its dimer, and the PhH · SnF_2 complex followed by their successive disappearance and in the formation of difluorostannylene oligomers with no distinct bands in the medium IR region.[35] This indicates that the PhH · SnF_2 complex is labile.

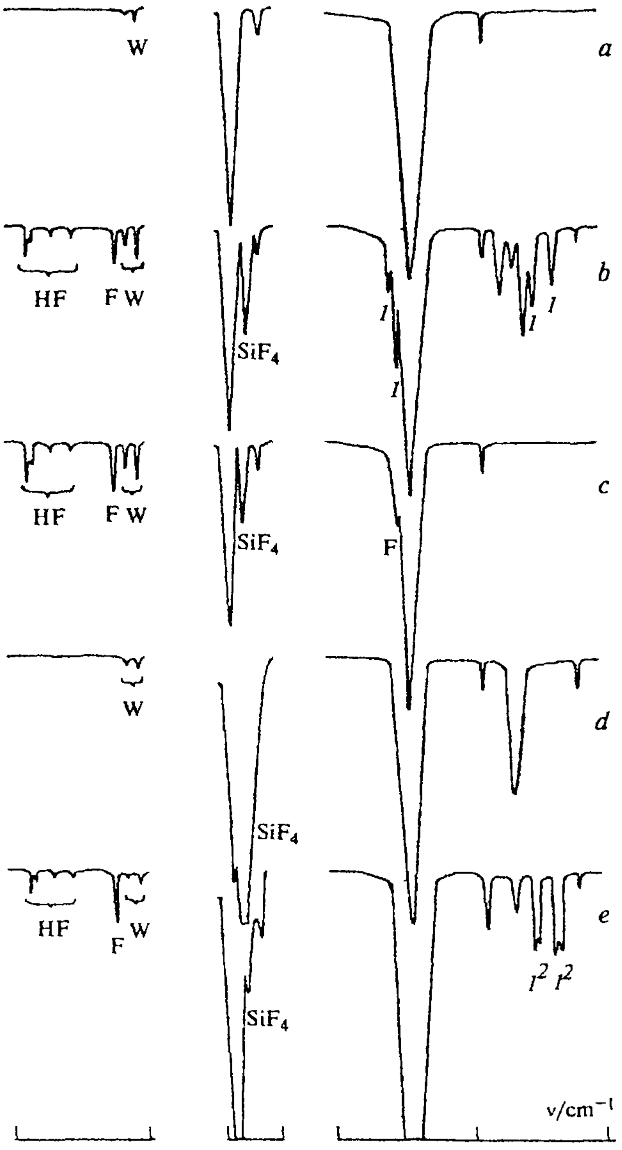

Fig. 1. Fragments of matrix IR spectra of benzene, Ar : PhH = 100 : 1 (*a*); products of codeposition of benzene and SnF_2, Ar : PhH = 200 : 1, Ar : SnF_2 = 250 : 1 (*b*); products of codeposition of benzene and HF, Ar : PhH = 100 : 1 (*c*); products of codeposition of benzene and SiF_4, Ar : PhH = 100 : 1 (*d*); and products of codeposition of benzene and SnF_2, Ar : PhH = 40 : 1, Ar : SnF_2 = 200 : 1 (*e*): *1*, the bands of PhH · SnF_2; *2*, the bands of $(PhH)_2$ · SnF_2; F, the band of PhH · HF; and W, the bands of H_2O.

Two new bands at 562 and 538 cm^{-1} whose frequencies coincided (with a shift of 2—4 cm^{-1}) with those of the absorption bands of the PhH · SnF_2 complex (Fig. 1, *e*), were observed in the matrix IR spectra upon decreasing the PhH : Ar molar ratio down to 1 : 40 (at SnF_2 : Ar molar ratios varied from 1 : 200 to 1 : 250). We assigned these bands to the $(PhH)_2 \cdot SnF_2$ complex. We failed to observe absorption bands of this complex in the region 680—700 cm^{-1} because of the large width of the band at 677 cm^{-1} corresponding to the out-of-plane deformation vibrations of the benzene C—H bonds.

Since at Ar : SnF_2 molar ratios less than 100 : 1 the concentration of the monomeric SnF_2 in the matrix decreased due to the formation of $(SnF_2)_x$ oligomers, we failed to detect complexes of the type $SnF_2 \cdot PhH \cdot SnF_2$.

Previously,[17] stabilization of the $PhH \cdot SnF_2$ complex in an argon matrix and two frequencies of this complex in the region of stretching vibrations of Sn—F bonds, at 564 and 551 cm^{-1}, were reported. However, only the first of them coincides with the frequency we observed for the $PhH \cdot SnF_2$ complex. Unfortunately, the reason for these discrepancies is unclear, since no detailed description of the experiments was reported in Ref. 17.

Complex of SnF_2 with chlorobenzene. Five new absorption bands at 3793, 764, 753, 566, and 549 cm^{-1} (Fig. 2, *b*) were observed upon codeposition of PhCl and products of tin difluoride evaporation in the obtained Ar matrices. As in the experiments on codeposition of products of tin difluoride evaporation and benzene, the high-frequency band at 3793 cm^{-1} corresponds to the $PhCl \cdot HF$ complex.[29] According to the reported data,[29] this complex also makes a contribution to the band at 753 cm^{-1}, which was proved by control experiments on codeposition of PhCl and a HF—H_2O mixture (Fig. 2, *c*).

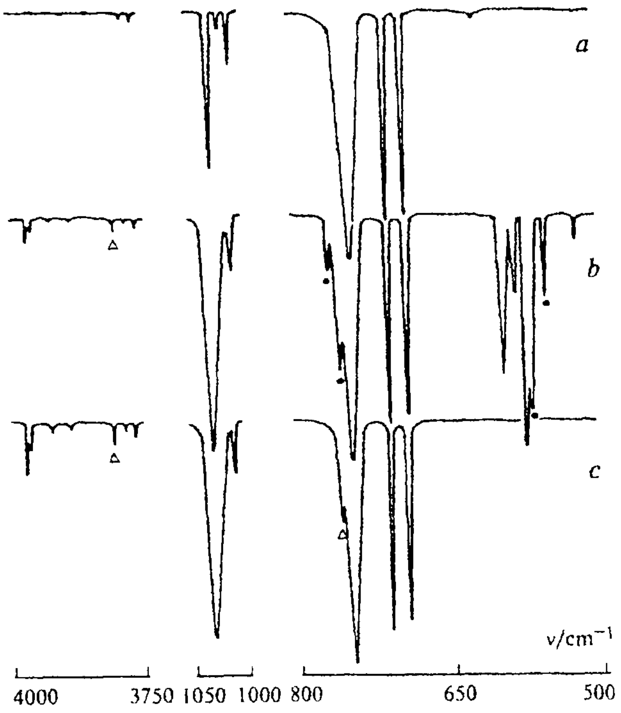

Fig. 2. Fragments of matrix IR spectra of chlorobenzene, Ar : PhCl = 150 : 1 (*a*); products of codeposition of chlorobenzene and SnF_2, Ar : PhCl = 400 : 1, Ar : SnF_2 = 200 : 1 (*b*); and products of codeposition of chlorobenzene and HF, Ar : PhCl = 400 : 1 (*c*): •, the bands of $PhCl \cdot SnF_2$; and Δ, the bands of $PhCl \cdot HF$.

The intensities of the absorption bands at 764, 753 (minus the contribution from the $PhCl \cdot HF$ complex), 566, and 549 cm^{-1} changed simultaneously at different ratios of the monomeric SnF_2 and PhCl in the matrix and were independent of the amount of SiF_4 that varied randomly in each experiment. Moreover, if the reagents were diluted with argon in a ratio of ~1 : 400, these bands were the only bands differing from those of the initial reagents, which made it possible to assign them to a complex between SnF_2 and PhCl of the simplest composition 1 : 1.

Controlled annealing of the matrices at 30—40 K resulted in successive disappearance of the bands of the monomeric SnF_2, its dimer, and, finally, the $PhCl \cdot SnF_2$ complex. Even at a minimum dilution of the reagents (PhCl : Ar = 1 : 60, SnF_2 : Ar = 1 : 100), no formation of complexes of the composition different from 1 : 1 was observed.

Complex of SnF_2 with toluene. Four new absorption bands at 3762, 740, 563, and 536 cm^{-1} (Fig. 3, *b*) were found upon codeposition of PhMe and products of tin difluoride evaporation. As in the case of other substrates (PhH, PhCl), one could expect that the absorption from the complexes between PhMe and HF (H_2O) makes contributions to some of the bands. Since no frequencies of $PhMe \cdot HF$ complex have been reported, the experiments on codeposition of PhMe and a HF—H_2O mixture were carried out (Fig. 3, *c*). The bands at 3762 and 740 cm^{-1} were recorded in the obtained matrix IR spectra. The latter band appeared to be much weaker than in the experiments on codeposition of toluene and SnF_2. Thus, the band at 3762 cm^{-1} observed upon codeposition of toluene and SnF_2 corresponds to the $PhMe \cdot HF$ complex, which makes also contribution to the band at 740 cm^{-1}.

The intensities of the absorption bands at 740 (minus the contribution from the $PhMe \cdot HF$ complex), 563, and 536 cm^{-1} changed simultaneously at different ratios of the monomeric SnF_2 and PhMe in the matrix and at a dilution of ~1 : 400 only these bands (among all observed bands) were different from those of the initial reagents, which made it possible to assign them to a complex between SnF_2 and toluene of the simplest composition 1 : 1.

As previously, successive disappearance of the absorption bands of the monomeric SnF_2, its dimer, and the complex was observed upon controlled annealing of the matrices at 30—40 K. No search for the complexes of composition $(PhMe)_2 \cdot SnF_2$ was performed.

Assignment of bands in the IR spectra of the complexes

The observed frequencies of the bands of the complexes and their assignment to the normal vibrations are

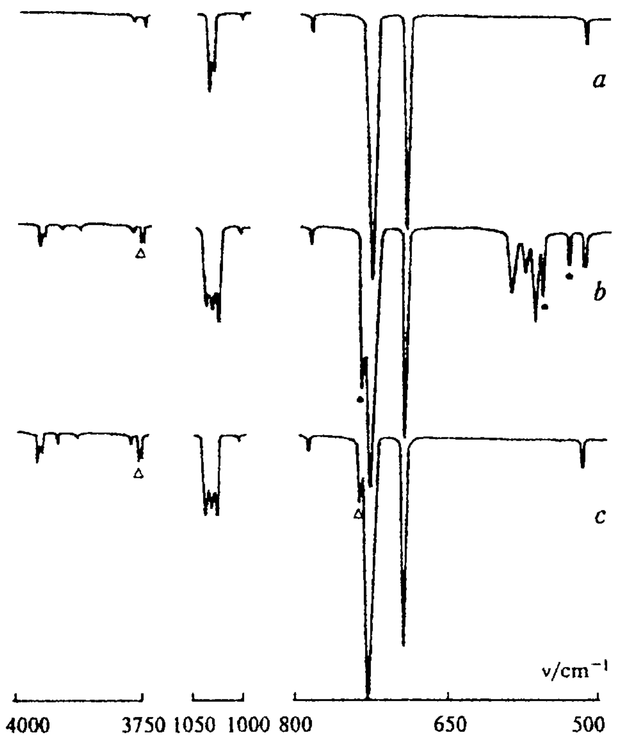

Fig. 3. Fragments of matrix IR spectra of toluene, Ar : PhMe = 200 : 1 (*a*); products of codeposition of toluene and SnF_2, Ar : PhMe = 200 : 1, Ar : SnF_2 = 200 : 1 (*b*); and products of codeposition of toluene and HF, Ar : PhMe = 200 : 1 (*c*): •, the bands of PhMe · SnF_2; and Δ, the bands of PhMe · HF.

listed in Table 2. All complexes of SnF_2 with ACs are characterized by two frequencies in the region of stretching vibrations of Sn—F bonds and by one or two frequencies in the region of deformation vibrations of the C—H bonds of AC (at 677 (PhH), 743 (PhCl), and 731 cm^{-1} (PhMe)).

The relatively small shift of vibrational frequencies upon complexation shows that this interaction is rather weak and does not result in appreciable change in the geometry of the reagents. The fact that only the frequency of the out-of-plane deformation vibration of C—H bonds of the aromatic fragment is shifted indicates an out-of-plane type of the difluorostannylene approach to the aromatic ring. It should be noted that in the case of SnF_2 complexes with PhCl and PhH two shifted frequencies of this vibration are observed. Since the vibration in question is not symmetry-degenerate, the appearance of two new frequencies indicates the formation of two complexes with different mutual arrangement of the SnF_2 fragment and the benzene ring. It is likely that these complexes differ in the orientation of the difluorostannylene F atoms relative to the C—H bonds of the aromatic fragment. Previously,[26] a similar splitting of the band of the benzene out-of-plane deformation vibration observed for PhH · H_2O complex was explained by the presence of several minima with close energies corresponding to different orientations of the O—H bond relative to the aromatic ring on the potential energy surface of the benzene—water system. It is noteworthy that in the case of the complex with toluene only one shifted frequency of the out-of-plane deformation vibration is observed. Apparently, the methyl group in the toluene molecule produces steric hindrances to the formation of the second complex.

In addition to πv-complexes with stannylene coordination to the aromatic ring, one could expect that the interaction of SnF_2 with chlorobenzene results in the formation of an nv-complex in which SnF_2 is coordinated to the Cl atom. For such a complex, a frequency of the C—Cl bond stretching vibration different from that of the C—Cl bond stretching vibration in PhCl should be observed. However, no corresponding band was detected. At the same time, no shift of the frequency of the C—Cl bond stretching vibration in methyl chloride was also observed when studying the complex MeCl · SnF_2;[16] thus, the absence of the frequency shift of the C—Cl bond vibration in the case of interaction between PhCl and SnF_2 does not rule out the possibility of SnF_2 complexation to the Cl atom. Since the frequencies of stretching vibrations of Sn—F bonds in PhH · SnF_2 (564 and 542 cm^{-1}) and MeCl · SnF_2 (567 and 543 cm^{-1}) complexes[16] are close, one can expect that the frequencies of stretching vibrations of Sn—F bonds for πv- and nv-complexes of composition SnF_2 · PhCl are also close and that the bands observed in this region are due to contributions from corresponding bands of both types of complexes.

On the assumption that complexation is a result of the interaction between the stannylene LUMO and the aromatic ring HOMO, the increase in the shift of frequencies of Sn—F bond stretching vibrations upon complexation in the series PhCl < PhH < PhMe is in agreement with the expected order of the increase in the stability of the complexes due to the effect of substituents in the aromatic ring.

Disappearance of the bands of SnF_2 complexes with ACs upon annealing of the matrix at 30—40 K was observed only after complete disappearance of the bands of the monomeric SnF_2 and its dimer, which indicates that the complexes are more stable towards oligomerization reaction than SnF_2 and its dimer.

Comparison of the frequencies of SnF_2 complexes. Complexation as the first stage of reactions of carbene analogs. The frequencies of all known SnF_2 complexes are listed in Table 2. The shift of frequencies of SnF_2 stretching vibrations must be determined mainly by the change in the electron density distribution in this submolecule upon complexation and, hence, by the complex stability. Based on the values of the shifts of SnF_2 absorption bands upon complexation, one can state that the ethylene double bond is the strongest donor, the nitrogen molecule is the weakest donor, and complexes of other substrates are characterized by intermediate stability.

The formation of complexes between CAs and donor agents was repeatedly postulated to account for the

Table 2. Vibrational frequencies ($\nu, \delta/\mathrm{cm}^{-1}$) of SnF_2 complexes and initial reagents

Complex[a]	ν_{as}(Sn—F)	ν_s(Sn—F)	δ(C—H)
SnF_2	571	593	
$SnF_2 \cdot N_2$[20]	565	588	
$SnF_2 \cdot (N_2)_2$[20]	557	583	
$SnF_2 \cdot ClMe$[16]	543	567	
PhCl			743
$SnF_2 \cdot ClPh$	549	566	753, 764
PhH			677
$SnF_2 \cdot PhH$	542	564	688, 696
$SnF_2 \cdot (PhH)_2$	538	562	
$PhCH_3$			731
$SnF_2 \cdot PhMe$	536	563	740
Hp[18,19]			[b]
$SnF_2 \cdot Hp$[18,19]	540	565	[c]
$SnF_2 \cdot C_2H_4$[17]	537.5	551.5	

[a] Hp is hept-1-yne.

[b] ν(C≡C) is 2127 cm^{-1} and ν(≡C—H) 3318 cm^{-1}.

[c] δ(H—C≡C) is 1011 cm^{-1}, ν(C≡C) is 2088 cm^{-1}, and ν(≡C—H) is 3256 cm^{-1}.

spectral properties, reactivity, and the reaction mechanisms of CAs. Direct spectroscopic evidence of the existence of complexes between a carbene analog (SnF_2) and a number of weak Lewis bases (alkynes, ACs, alkyl halides, and nitrogen) we obtained recently[16,18–20] indicate that complexation is a characteristic property of CAs and that the possibility of complexation between CAs and the molecules of substrate, solvent, precursor, products of precursor decomposition, *etc.*, should be taken into account when considering the reaction mechanisms of CAs.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 98-03-32935 and 96-15-78323) and CRDF (Grant RC1-348).

References

1. P. P. Gaspar, in *Reactive Intermediates*, Eds. M. Jones and R. A. Moss, J. Wiley and Sons, New York, 1978, **1**, 229; 1981, **2**, 335; 1985, **3**, 333.
2. J. M. Jasinski, R. Becerra, and R. Walsh, *Chem. Rev.*, 1995, **95**, 1203.
3. W. P. Neumann, *Chem. Rev.*, 1991, **91**, 311.
4. S. P. Kolesnikov, *Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva*, 1979, **24**, 505 [*Mendeleev Chem. J.*, 1979, **24** (Engl. Transl.)].
5. Y. Inoguchi, S. Okui, K. Mochida, and A. Itai, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 974.
6. S. N. Tandura, S. N. Gurkova, and A. I. Gusev, *Zh. Strukt. Khim.*, 1990, **31**, 154 [*J. Struct. Chem. (USSR)*, 1990, **31** (Engl. Transl.)].
7. V. Ya. Lee, A. A. Basova, I. A. Matchkarovskaya, V. I. Faustov, M. P. Egorov, O. M. Nefedov, R. D. Rakhimov, and K. P. Butin, *J. Organomet. Chem.*, 1995, **499**, 27.
8. S. P. Kolesnikov, I. S. Rogozhin, A. Ya. Shteinshneider, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 799 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29** (Engl. Transl.)].
9. W.-W. Du Mont, B. Neudert, G. Rudolph, and H. Schumann, *Angew. Chem.*, 1976, **88**, 303.
10. T. Ohtaki, Y. Kabe, and W. Ando, *Organometallics*, 1993, **12**, 45 (see also references cited therein).
11. G. R. Gillette, G. H. Noren, and R. West, *Organometallics*, 1989, **8**, 487 (see also references cited therein).
12. M. P. Egorov and O. M. Nefedov, *Metalloorg. Khim.*, 1992, 5, 106 [*Organomet. Chem. USSR*, 1992, **5** (Engl. Transl.)].
13. W. Ando, H. Itoh, and T. Tsumuraya, *Organometallics*, 1989, **8**, 2759.
14. W. Ando, H. Itoh, T. Tsumuraya, and H. Yoshida, *Organometallics*, 1988, **7**, 1880.
15. M. B. Taraban, V. F. Plyusnin, O. S. Volkova, V. P. Grivin, T. V. Leshina, V. Ya. Lee, V. I. Faustov, M. P. Egorov, and O. M. Nefedov, *J. Phys. Chem.*, 1995, **99**, 14719.
16. S. E. Boganov, V. I. Faustov, S. G. Rudyak, M. P. Egorov, and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1121 [*Russ. Chem. Bull.*, 1996, **45**, 1061 (Engl. Transl.)].
17. P. F. Meier, D. L. Perry, R. H. Hauge, and J. L. Margrave, *Inorg. Chem.*, 1979, **18**, 2051.
18. S. E. Boganov, V. I. Faustov, M. P. Egorov, and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 54 [*Russ. Chem. Bull.*, 1994, **43**, 47 (Engl. Transl.)].
19. S. E. Boganov, V. I. Faustov, M. P. Egorov, and O. M. Nefedov, *High Temp. Mater. Sci.*, 1995, **33**, 107.
20. S. E. Boganov, V. I. Faustov, M. P. Egorov, and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1087 [*Russ. Chem. Bull.*, 1998, **47**, 1054 (Engl. Transl.)].
21. D. Tevault and K. Nakamoto, *Inorg. Chem.*, 1976, **15**, 1282.
22. M. Tacke, Ch. Klein, D. J. Stufkens, A. Oskam, P. Jutzi, and E. A. Bunte, *Z. Anorg. Allgem. Chem.*, 1993, **619**, 865.
23. R. A. Moss, S. Yan, and K. Krogh-Jespersen, *J. Am. Chem. Soc.*, 1998, **120**, 1088.
24. K. Mochida, S. Tokura, and S. Murata, *J. Chem. Soc., Chem. Comm.*, 1992, 250.
25. L. Andrews, G. L. Johnson, and R. D. Steven, *J. Phys. Chem.*, 1985, **89**, 1706.
26. A. Engdahl and B. Nelander, *J. Phys. Chem.*, 1985, **89**, 2860.
27. K. G. Brown and W. B. Person, *Spectrochim. Acta, A*, 1978, **34**, 117.
28. D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350.
29. S. R. Davis and L. Andrews, *J. Phys. Chem.*, 1986, **90**, 2600.
30. N. Fuson, C. Garrigou-Lagrange, and M. L. Josien, *Spectrochim. Acta, A*, 1960, **16**, 106.
31. A. L. Schobert, I. C. Hisatsune, and P. S. Skell, *Spectrochim. Acta, A*, 1984, **40**, 609.
32. R. L. Redington and D. E. Milligan, *J. Chem. Phys.*, 1962, **37**, 2162.
33. R. L. Redington and D. E. Milligan, *J. Chem. Phys.*, 1963, **39**, 1276.
34. G. P. Ayers and A. D. E. Pullin, *Spectrochim. Acta, A*, 1976, **32**, 1629.
35. R. H. Hauge, J. W. Hastie, and J. L. Margrave, *J. Mol. Spectrosc.*, 1973, **45**, 420.
36. B. S. Ault, *J. Am. Chem. Soc.*, 1983, **105**, 5742.
37. L. Andrews and G. L. Johnson, *J. Phys. Chem.*, 1984, **88**, 425.

Received October 5, 1998