Molecular and electronic structures of germylene and stannylene complexes $(CO)_5MECl_2 \cdot n$THF (M = Cr, W; E = Ge, Sn; n = 1, 2) as studied by IR and Raman spectroscopy, X-ray analysis, and quantum chemistry

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The Raman and IR spectra of the complexes $(CO)_5CrSnCl_2 \cdot$THF (**1**), $(CO)_5WSnCl_2 \cdot$THF (**2**), $(CO)_5CrGeCl_2 \cdot$THF (**3**), $(CO)_5WGeCl_2 \cdot$THF (**4**), $(CO)_5CrSnCl_2 \cdot$2THF (**5**), and $(CO)_5WSnCl_2 \cdot$2THF (**6**) were measured and interpreted using quantum chemical calculations. Complexes **3** and **5** were characterized by X-ray analysis. The stretching vibrations of the CO groups in the spectra of solutions of complexes **1—6** obey the selection rules for C_{4v} local symmetry. For the complexes containing 0 (type A), 1 (type B), and 2 (type C) THF molecules, a comparison was made of the calculated and experimental $M{\overset{...}{-}}E^{II}$ bond lengths and energies, as well as the ν(CO) vibrational frequencies. The contribution of the π-component to the $M{\overset{...}{-}}E^{II}$ bond decreases in the order A→B→C and leads to enhancement of the donor ability of the carbene-like ligand and to a slight elongation and weakening of this bond. An attempt to grow crystals of complex **6** in air unexpectedly resulted in a polynuclear complex $[(CO)_5WSn(Cl)(\mu\text{-}OH)_2SnCl_2(\mu\text{-}OH)]_2 \cdot$6THF, which was characterized by X-ray analysis and Raman spectroscopy.

Key words: germylenes, stannylenes, complexes with metal carbonyls and Lewis bases, X-ray analysis, vibrational spectra, quantum chemical calculations, density functional theory, "Atoms in molecule" theory.

Heavy carbene analogs $E^{II}XY$ (E = Si, Ge, Sn) offer a great coordination potential.[1] In particular, they form complexes with transition metal carbonyls (see a review[2] and later studies[3—11]). In most cases, the carbene-like ligand possesses acidic properties, as in the Fischer carbene complexes.[12] Moreover, complexes of carbene analogs with transition metal carbonyls can also contain neutral Lewis base molecules (Z) coordinated to the carbenoid* atom;[2] the Z molecules stabilize the complex, thus reducing its reactivity. In such complexes, the carbene-like ligand acts as a donor toward the transition metal and simultaneously acts as an acceptor toward the Lewis base.

The nature of the $M—E^{II}$ bond and the structure of the carbene-like ligand is of the greatest interest. The structures of many germylene and stannylene complexes with transition metal carbonyls were determined by X-ray analysis.[2—4,5b,7a,b,8—10,13a] There is also considerable literature[2,3,7—16] on the IR spectra of the complexes $(CO)_mME^{II}XY$ (E = Ge, Sn) in the region of the stretching vibrations of carbonyl groups, ν(CO), and in the low-frequency region; these are used for assessment of the electronic structures of the complexes.

The $M{\overset{...}{-}}E^{II}$ bond is commonly treated as a partially double bond. Indeed, two types of interaction contribute to the formation of this bond, *viz.*, σ-interaction (electron transfer from the σ-orbital of the carbenoid atom E^{II} to the metal) and π-interaction (back donation of metal d-electrons with suitable energies and symmetry to the vacant p_z-orbital of the E^{II} atom). An interesting feature of the $M—E^{II}$ bond, which is shorter than the ordinary $M—E^{IV}$ bond, is a low barrier to rotation; this can be explained by a small contribution of the π-component and/or the presence of a set of d-orbitals, which "assist" one another as the carbene-like ligand rotates.[2,12] It should be noted that the efficiency of back donation in the "Fischer" carbene and carbene analog complexes noticeably decreas-

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* Here, the term "carbenoid atom" implies the E^{II} atom in the molecules of heavy carbene analogs and their complexes.

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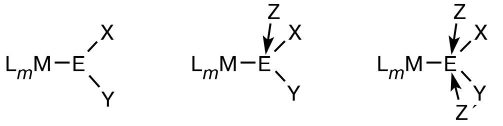
es on going from the carbon to tin atom, whereas the coordination potential of the carbenoid atom becomes even greater. That is why the E^{II} atom in such complexes remains coordinatively unsaturated and can coordinate one or even two Lewis base molecules. There are three types of carbene analog complexes with transition metal carbonyls, *viz.*, those containing no (type A), one (type B), and two (type C) Lewis base molecules.[2]



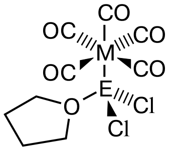
A B C

L = Cp, CO, PPh_3, *etc.*; X, Y = Alk, Ar, Hal, SR´; E^{II} = Si^{II}, Ge^{II}; M is transition metal; Z, Z´ is a neutral Lewis base.

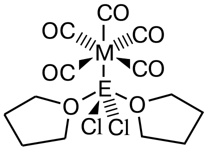
Conversion of the type-A into type-B complexes has been considered earlier[2] based on the X-ray, IR, and NMR data. The contribution of the π-component to the $M\overset{...}{-}E^{II}$ bond was shown to decrease hereby, as indicated by enhancement of the ligand donor ability and by elongation of this bond by about 0.1 Å. However, changes emerging on going from the type-B complexes to type-C complexes due to the addition of the second Lewis base molecule to the E^{II} atom are poorly studied. There is only one study[3] on the synthesis of complexes $(CO)_5WSnCl_2 \cdot n$THF ($n = 1, 2$) and comparison of their properties based on the X-ray and NMR data, which reported a slight elongation of the Sn—O bond at $n = 2$. Most other known (formally, type-C) complexes contain complicated chelating substituents.[1b,2,8]

The aim of the present work was to carry out comprehensive studies of the structure and properties of the type-B and type-C complexes **1—8** of the simplest carbene analogs, namely, $GeCl_2$ and $SnCl_2$, with chromium and tungsten carbonyls by vibrational spectroscopy, X-ray analysis, and quantum chemistry.

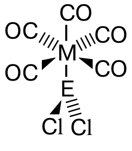
It was interesting to elucidate how does successive addition of one and two molecules of a base (THF) affect the structure of the complexes, the donor-acceptor properties of the carbene-like ligand, the nature of the $M\overset{...}{-}E^{II}$ bond, and to comparatively estimate the energies of the $M-E^{II}$ and $E^{II}\leftarrow O$ bonds.



1—4



5—8



9—12

Compound	M	E
1, **5**, **9**	Cr	Sn
2, **6**, **10**	W	Sn
3, **7**, **11**	Cr	Ge
4, **8**, **12**	W	Ge

Complexes **1—4** and **6** were described earlier.[2,3,5,13,14,17] For complexes **2**, **4**, and **6**, X-ray data are available[3,5b] while compounds **5**, **7**, and **8** were studied for the first time. As for the synthesis and properties of similar type-A complexes, only data on $(CO)_5MGeCl_2$ (M = Cr (**11**)[13,14] and W (**12**)[5c,6,14]) are available. However, the IR data for compound **12** [5c] in the ν(CO) region are doubtful because the reported spectral region (1913 and 1873 cm^{-1}) is not typical of this type of compounds[2,13,14] (probably, complex **12** could decompose in the course of the sample preparation). Our attempts to obtain type-A complexes by eliminating a THF molecule from type-B complexes have failed; the type-B complexes decomposed in accord with Refs 2 and 13. Therefore, for the type-A compounds only the corresponding quantum chemical calculations of isolated molecules $(CO)_5CrSnCl_2$ (**9**), $(CO)_5WSnCl_2$ (**10**), $(CO)_5CrGeCl_2$ (**11**), and $(CO)_5WGeCl_2$ (**12**) were carried out.

Structure elucidation of complexes **1—8** based on vibrational spectra was done using a traditional approach.[18,19] The region of the ν(CO) stretching modes (1800—2300 cm^{-1}) is well known[18,19] to be very sensitive to the local symmetry of the $L-M(CO)_n$ fragment and to the substituent effect; the ν(CO) frequencies characterize the σ-donor and π-acceptor properties of the ligand L.[2,14,15,18,19] If the $L-M(CO)_5$ fragment has octahedral geometry and the ligand freely rotates about the L—M bond, the local symmetry of the $L-M(CO)_5$ fragment is C_{4v}. In this case, four vibrations of the following symmetry species $2A_1 + B_1 + E$ should be observed in the ν(CO) region, all modes being Raman active and only the A_1 and E modes being IR active. The local symmetry lowering of the $M(CO)_5$ fragment should lead to a splitting of the doubly degenerate E-type mode. In the spectrum of a solid sample, this can be due to the crystal field effect. If deviations from the C_{4v} local symmetry are observed in solution as well, this is a consequence of hindered rotation of the asymmetric ligand about the $M-E^{II}$ bond. However, for correct application of this approach we had to refine the assignment of the ν(CO) modes with respect to their eigenvectors and symmetry types. Earlier, the assignment was often incorrect or not done at all due to the lack of Raman spectra (except for those reported in Ref. 16) and relevant computational methods.

Experimental

Synthesis of complexes $(CO)_5MECl_2 \cdot THF$ (M = Cr, W; E = Sn, Ge) (1—4).[17] In a quartz tube, complex $GeCl_2 \cdot diox$ (250 mg) or $SnCl_2$ (205 mg, 1.08 mmol) and 1.1 mmol of $M(CO)_6$ (255 mg and 475 mg for M = Cr and W, respectively) were dissolved in 20 mL of anhydrous THF. The solution was irradiated with a high-pressure UV lamp DRSh-1000 in an argon atmosphere for 3—4 h. The reaction mixture was concentrated to dryness *in vacuo* at 70 °C, the product was extracted with hot hexane (40 mL), the solution was concentrated to 1—2 mL and cooled to −20 °C. The residual solution was decanted, and products were dried *in vacuo*. Complexes $(CO)_5MECl_2 \cdot THF$ were isolated as yellow crystalline residues. The yield was 60—70%. M.ps: **1**, 96 °C (*cf.* 95—96 °C, Ref. 17c); **2**, 105 °C (*cf.* 104—106 °C, Ref. 17c); **3**, 75 °C (*cf.* 70—72 °C, Ref. 13e); and **4**, 105 °C (*cf.* 104—108 °C, Ref. 13e).

Growing of the crystal of $(CO)_5CrSnCl_2 \cdot 2THF$ (5) and $(CO)_5WSnCl_2 \cdot 2THF$ (6). Crystals of compounds **5** and **6** were grown in an argon atmosphere using a modified procedure.[3] To about 30 mg of complex **1** or **2**, 0.5 mL of a THF—hexane mixture (1 : 4) was added and the solution was slowly cooled to −20 °C. Crystalline precipitate was decanted and dried in an argon stream. The structures of compounds **5** and **6** were established by X-ray analysis. Complexes **5** and **6** can be stored under argon only at −20 °C or lower temperatures, because at room temperature the second THF molecule is slowly eliminated over a period of a few days.

Synthesis of the complex $[(CO)_5WSn(Cl)(\mu\text{-}OH)_2SnCl_2(\mu\text{-}OH)]_2 \cdot 6THF$ (13). Complex **2** (20—30 mg) was dissolved in a mixture of hexane (1 mL) and THF (0.5 mL) and the solvent was allowed to spontaneously evaporate in air over a period of 3—4 days until the formation of light-yellow crystals. The structure of complex **13** was established by X-ray analysis.

Measurements of vibrational spectra. The Raman spectra were measured for saturated solutions of the compounds under study in hexane or THF. Compounds (10—20 mg) were placed in NMR tubes, the tubes were closed with rubber septa in an argon atmosphere and the necessary volume of a solvent (about 1 mL) was injected with a syringe. The Raman spectra of solid compounds were measured for samples placed in argon-filled tubes that were then sealed.

The Raman spectra in the region 50—3500 cm^{-1} were recorded with a last-generation Horiba Jobin-Yvon LabRAM laser Raman spectrometer equipped with a microscope, video camera, and a coolable CCD detector. The 632.8 nm line of a He-Ne laser (power at most 6 mW) was used as the excitation line.

IR spectra were recorded on a Carl Zeiss Specord M82 spectrophotometer; frequency corrections were made using the reference polystyrene spectrum. The spectra of solutions of all carbonyl complexes in the ν(CO) region from 1700 to 2300 cm^{-1} were obtained using cells with fluorite windows (cell thickness 0.03, 0.17, or 1.07 mm), the solution concentrations were chosen experimentally in order to obtain high-quality spectra. To prevent oxidation of the complexes, the cells were preliminarily evacuated to 10^{-2} Torr. IR spectra of solid samples (Nujol mulls) were recorded in the spectral region from 300 to 3600 cm^{-1}.

X-ray studies. All diffraction measurements were carried out with a Bruker APEX2 diffractometer at 100 K. Selected crystal structure parameters are listed in Tables 1 and 2. The structures were solved by the direct method and refined by the full-matrix least squares method with respect to F^2. Hydrogen atoms were located geometrically and refined isotropically with restrictions imposed on their equivalent thermal parameters $U_{eq}(H) = 1.2U_{eq}(C)$, where C and H are the carbon and hydrogen atoms, respectively.

Quantum chemical calculations. Geometry optimization, generation of the electron density function in the wfn format, the normal coordinate analysis (NCA), and calculations of the IR and Raman intensities were carried out using the GAUSSIAN 03 C.01 program[20] in the framework of the density functional theory (DFT) with the PBE and PBE0 functionals.[21] The basis sets used were 6-311G(d,p) for the H, C, O, and Cl atoms,[22] UGBS for the W atom,[23] UGBS and 6-311G(d,p) for the Cr and Ge

Table 1. Selected crystallographic data for compounds **3**, **5**, and **13**

Parameter	3	5	13
Molecular formula	$C_9H_8Cl_2CrGeO_6$	$C_{13}H_{16}Cl_2CrO_7Sn$	$C_{34}H_{54}Cl_6O_{22}Sn_4W_2$
Molecular weight	335.00	473.88	1870.05
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	6.8425(4)	8.1811(5)	15.207(3)
b/Å	20.4918(13)	8.8090(6)	11.3544(19)
c/Å	10.4466(6)	13.5901(9)	16.480(3)
α/deg	90.00	79.286(2)	90.00
β/deg	92.7100(10)	88.234(1)	99.860(4)
γ/deg	90.00	76.687(1)	90.00
V/Å^3	1463.13	936.394	2803.51
Z	4	2	2
T/K	100	100	100
d_{calc}/g cm^{-3}	1.851	1.865	2.215
θ_{max}/deg	27.09	32.03	27.10
Number of measured reflections (R_{int})	15145	15778	28473
Number of independent reflections	3198	6457	8491
Number of reflections $I > 2\sigma(I)$	2211	5626	4769
R_1 ($I > 2\sigma(I)$)	0.033	0.027	0.040
wR_2 (over all reflections)	0.0523	0.0624	0.1099

Table 2. Experimental geometric parameters of compounds **3**, **5**, and **13** (atom numbering scheme is shown in Figs 3, 4, and 9, respectively)

Parameter	**3**	**5**	**13**
Bond		*d*/Å	
E—O(1)	1.948(2)	2.3374(14)	2.000(5)
E—O(2)	—	2.4247(14)	2.000(5)
E—O(3)	—	—	2.085(5)
E—Cl(1)	2.1906(10)	2.3721(5)	2.325(2)
E—Cl(2)	2.1994(10)	2.3714(5)	2.352(2)
E⋯M	2.3880(6)	2.5733(3)	2.6502(7)
Bond angle		ω/deg	
O(1)—E—O(2)	—	157.69(5)	92.2(2)
O—E—M	121.63(7)	102.82(4)	124.7(2)

atoms, and cc-pVTZ-pp for the Ge and Sn atoms.[24] The electron density distribution functions thus obtained were treated in the framework of Bader's theory "Atoms in molecules"[25] using the AIMAll program.[26] The energies of the M⋯E and E←O coordination bonds were calculated using the electron density and the potential energy density values at the (3, −1) critical points thus obtained and the phenomenological correlaton by Epinosa *et al.*[27]

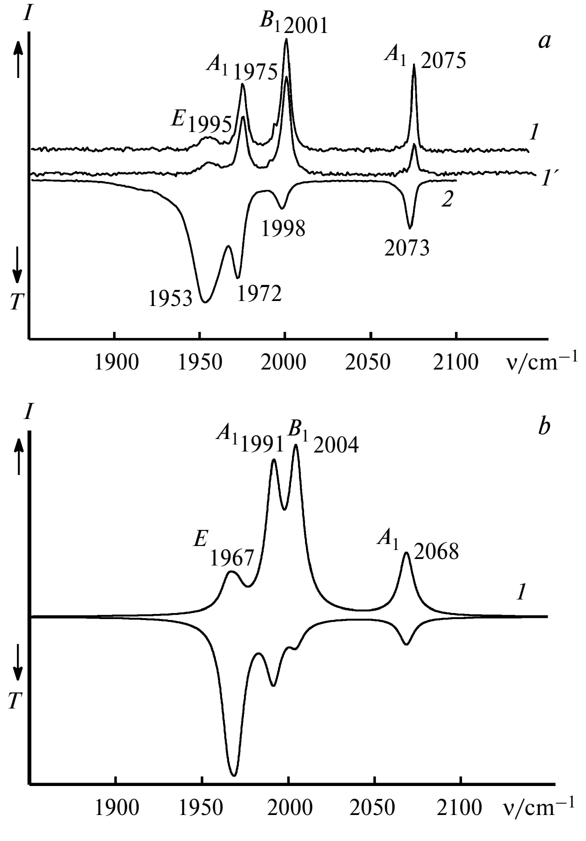


Fig. 1. The Raman (*1*, *1*′) and IR spectra (*2*) of complex **3**: experimental (*a*) (polarization measurements for a solution in hexane: parallel (*1*) and perpendicular (*1*′) polarization) and calculated by the DFT PBE/6-311G(d,p) method (*b*). *I* is the intensity and *T* is transmission.

The theoretical and experimental vibrational frequencies are in reasonable agreement despite the fact that no scaling factors were applied. Moreover, calculations reproduce the Raman and IR intensities quite correctly, as is illustrated in Fig. 1. Calculations of the potential energy distribution over normal coordinates were carried out with the NCA99 program.[28]

Results and Discussion

The Raman spectra of the complexes studied were obtained in the whole frequency range for solid samples and their solutions in hexane and THF. For the solutions, the depolarization ratios of the Raman lines were estimated qualitatively. The IR spectra of solutions of compounds **1**—**6** in hexane and THF were measured in the ν(CO) region. Complexes **3**, **5**, and **13** were characterized by X-ray analysis for the first time. The geometries of complexes **1**—**12** were optimized, normal coordinate analysis (NCA) was performed, and the energies of the M—E and E←O bonds were estimated using quantum chemical methods.

Type-B complexes. The IR spectra of solutions of compounds **1**—**4** measured in this work agree with those reported earlier; however, in some studies the assignment of bands was erroneous. For correct band assignment, we used the Raman data and the results of NCA.

The Raman spectra of all solid type-B complexes (**1**—**4**) exhibit five lines in the ν(CO) region (Table 3, Figs 2 and 3). Thus, it is evident that the local symmetry of the carbonyl fragment $(CO)_5M$ in the crystals is lower than C_{4v}. The IR and Raman spectra of solutions of complexes **1**—**4** in hexane exhibit four lines at about 2075, 2000, 1970, and 1950 cm^{-1} (see Fig. 1), which means that the E symmetry mode remains degenerate. Therefore, this splitting observed in the spectra of solid samples is due to the crystal field effect only. The solvent effect manifests itself in a regular broadening of all spectral lines and a slight shift toward high-frequency region.

Calculations of the ν(CO) stretching vibrations of the $L—M(CO)_5$ fragment assuming a C_{4v} local symmetry predict the following order of mode frequencies: $A_1{}^1 > B_1 > A_1{}^2 > E$. Indeed, the highest-frequency polarized Raman line observed in the experimental spectra at about 2070 cm^{-1} corresponds to the totally-symmetric mode ($A_1{}^1$) involving in-phase vibrations of all CO groups. This mode frequency in the spectra of all tungsten complexes is about 10 cm^{-1} higher compared to those of the corresponding Cr complexes (see Table 3). An intense Raman line at about 2000 cm^{-1} belongs to the B_1 symmetry type, as is confirmed by its high depolarization ratio. Theoretically, this mode is forbidden in the IR spectrum, and its appearance in the spectra of the compounds under study as a weak band (see Fig. 1) is probably due to a slight

Table 3. CO stretching frequencies (ν/cm^{-1}) in complexes $(CO)_5MECl_2 \cdot n$THF **1—6** and **11**

Complex	Spectrum					
	Raman			IR		
	I	II	III	II	III	IV
1	2071 m	2071 s	2067 s	2071 m	2063 m	—
	1995 s	1998 s	1988 s	2000 w	1980 m	—
	1963 w	1972 m	1950 sh	1972 m	1950 sh	—
	1953 m	1953 m	1940 m	1953 s	1940 s	—
	1923w	—	—	—	—	—
2	2080 m	2080 s	2077 s	2080 m	2073 m	—
	1993 s	1997 s	1987 s	2000 w	1977 m	—
	1962 w	1970 m	1953 sh	1968 sh	1944 s	—
	1949 m	1955 m	1935 m	1955 s	1930 sh	—
	1918 sл	—	—	—	—	—
3	2071 c	2075 s	2070 s	2073 m	2060 w	2070 m
	1986 m	2001 s	1990 s	1998 w	1980 w	1950 m
	1971 w	1975 m	1953 w	1972 s	1941 s	1930 s
	1945 m	1955 w	—	1953 s	—	—
	1935 w	—	—	—	—	—
4	2078 m	2084 s	2082 s	2081 m	2076 m	—
	1982 s	1999 s	1992 s	1997w	1986 w	—
	1969 w	1971s	1948 m	1968 m	1946 s	—
	1937 m	1953 m	—	1955 s	—	—
	1927 m	—	—	—	—	—
5	2061 m	2065 s	—	2065 m	—	—
	1980 s	1985 s	—	1987 w	—	—
	1955 w	1953 m	—	1950 s	—	—
	1942 w	—	—	—	—	—
	1927 w	—	—	—	—	—
6	2073 m	2075 s	—	2075 m	—	—
	1976 s	1984 s	—	1984 w	—	—
	1953 w	1947 m	—	1949 s	—	—
	1937 w	—	—	—	—	—
	1908 m	—	—	—	—	—
11	—	—	—	—	—	2075 s
	—	—	—	—	—	1985 m
	—	—	—	—	—	1960 s

Note: I — solid, II — solution in hexane, III — solution in THF, IV — solution in CH_2Cl_2.[13b]

deviation of the equatorial carbonyl groups from planarity.[18] The band at nearly 1970 cm^{-1} has a medium intensity in the IR and Raman spectra and belongs to the $A_1{}^2$ symmetry type. An interestung feature of this Raman line in the solution spectra of all the complexes studied is its high depolarization ratio ($\rho \approx 0.8$), which is abnormal for totally-symmetric, pure stretching vibrations (typical ρ values lie in the range from 0 to 0.3). This can be due to the eigenvector of this mode in which equatorial CO groups are stretched (or shortened) out-of-phase with the axial CO group. Abnormal ρ values of the totally-symmetric ν(CO) vibrations of this symmetry type in the spectra of metal carbonyls were reported earlier[18] and explained by large contributions from those components of the CO bond polarizability tensor that are normal to this bond. Finally, a band of degenerate ν(CO) vibration, the most intense in the IR spectrum, is situated in the region ~1950 cm^{-1}.

In the lower-frequency spectral region, the stretching and deformational modes of the E—Cl bonds, the ν(M—C) stretching, and the M—C≡O deformational modes are present. Their assignment can be made based on the analysis of the published data for the related compounds $(CO)_6M$,[18] R_2ECl_2,[29,30] and ECl_2,[31—33] as well as on the results of our calculations. For instance, strong lines in the region 400—600 cm^{-1} correspond to the ν(M—C) stretches and M—C≡O deformations; according to calculations, these vibrations are heavily mixed. The stretching vibrations of the E—Cl bonds are situated in the region near 350 cm^{-1}. The vibrational frequencies of the metal—metal bond, ν(E—M), should be even lower; however, no reliable information on them is available at the moment. The authors of Ref. 34 have assigned the vibrations of M—E^{IV} ordinary bonds in the spectra of compounds $(CO)_nM—ER_3$ as the bands in the region 150—250 cm^{-1}. One could assume that, owing to high polarizability of heavy atoms, the ν(M—E^{II}) vibration should manifest itself as an intense Raman line. However, only a few lines of medium intensity were observed in this spectral region (Fig. 2). This can be explained by the results of NCA calculations according to which the vibration of the M—E bond is strongly coupled. In fact, this bond stretching coordinate participates in a number of normal modes, *e.g.*, in those with the frequencies 157, 195, and 253 cm^{-1} for complex **3** and with the frequencies 156 and 188 cm^{-1} for complex **2**.

The presence of a coordinated THF molecule in complexes **1—4** is evidenced by a very weak line in the region ~920 cm^{-1}, which corresponds to the "breathing" mode of THF, whose frequency in the Raman spectra of solid samples is somewhat shifted compared to that in the spectrum of "free" liquid THF (see inset in Fig. 2). Note that the intensity of the spectrum corresponding to the remaining part of the complex is much stronger than that of the THF ligand. The vibration of the E^{II}←O coordination bond cannot be identified because of its mixed origin. However, the nature of this bond can be assessed based on the X-ray data.

The structures of complexes **2** and **4** were reported earlier.[3,5b] Figure 3 shows the structure of compound **3**; we determined it by X-ray analysis. The Ge coordination polyhedron in complex **3** is a distorted tetrahedron, the Ge—O coordination bond length equal to 1.948(2) Å is close to that in the isostructural complex **4** with $W(CO)_5$ (1.947 Å) and nearly 0.05 Å longer than the bond in a similar complex of $(CO)_5CrGeCl_2$ with 3,4-dihydro-2,2-dimethyl-2*H*-pyrrolle *N*-oxide (1.890 Å).[4] A comparison of the geometric parameters of the last-mentioned complex and complex **3** suggests that the change in the

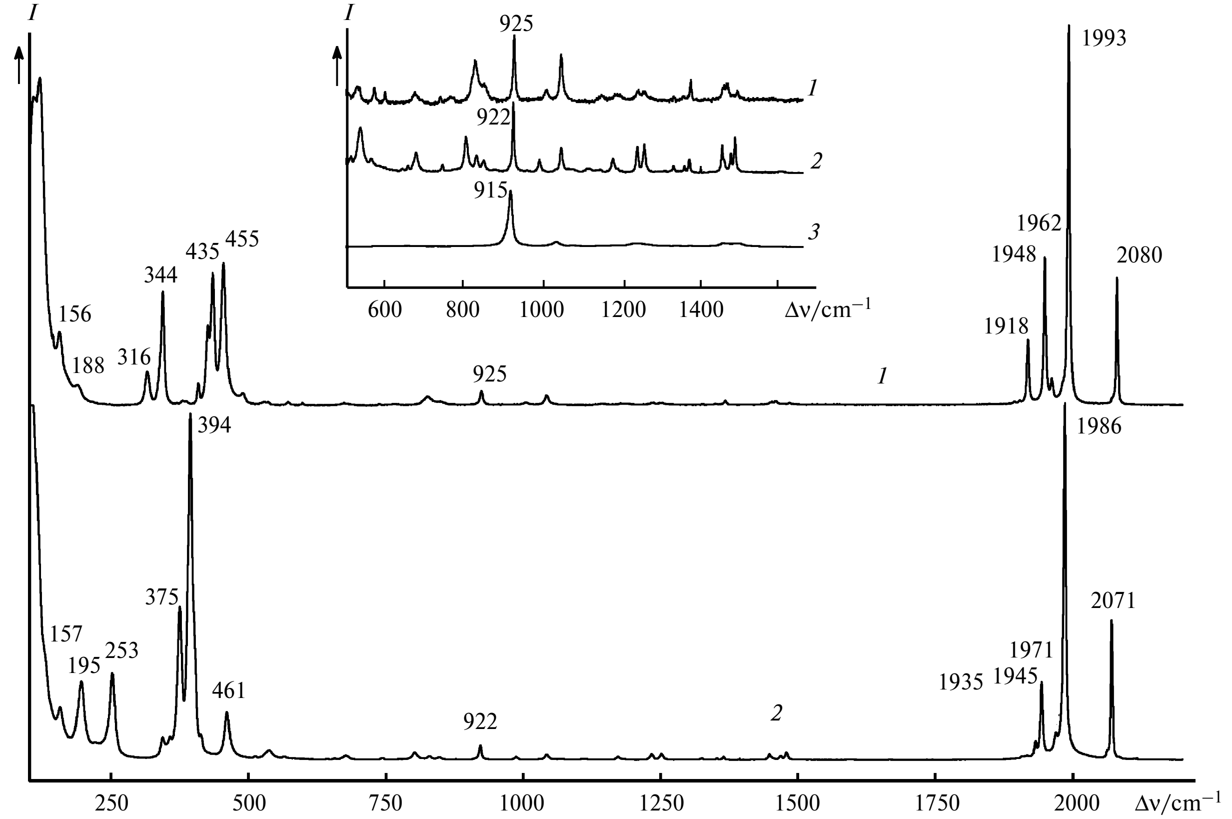


Fig. 2. The Raman spectra of solid samples of complexes **2** (*1*), **3** (*2*), and liquid THF (*3*) (intensities of spectral lines were approximately normalized to the intensity of the THF line near 920 cm^{-1}).

nature of the O-ligand at the Ge atom has no effect on the lengths of other bonds in the Ge coordination polyhedron. In particular, the Ge—Cl bond lengths in these compounds differ by at most 0.02 Å, while the Ge—Cr bond lengths are essentially the same (2.388 Å).

The E←O coordination bonds in these complexes are very short, *viz.*, 1.95 Å for Ge←O in complexes **3** and **4** and 2.22 Å for Sn←O in complex **2** (*cf.* 2.399 and 2.527 Å for the corresponding bonds in the complexes with 1,4-dioxane[33]). The average length of the E—O covalent bond in dioxygermylenes and dioxystannylenes is ~1.85 Å and ~2.05 Å, respectively.[35] The strength of the E←O coordination bond in the type-B complexes is also confirmed by the fact that compounds **1**—**4** are sublimed in high vacuum (10^{-5} Torr) without decomposition and that, according to vibrational spectroscopy data (see Table 3), no THF molecule is eliminated upon dissolution of type-B complexes in hexane. DFT quantum chemical calculations (Table 4) estimate the energy of the E←O bond in these complexes as rather high, *viz.*, at about 20 kcal mol^{-1}.

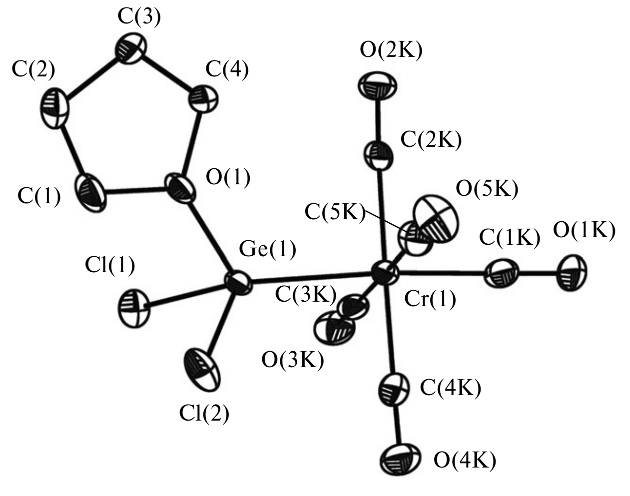


Fig. 3. Molecular structure of complex $(CO)_5CrGeCl_2 \cdot THF$ (**3**).

Type-C complexes. We succeeded in growing crystals of complexes with two THF molecules only for stannylenes. Compounds $(CO)_5MSnCl_2 \cdot 2THF$ (M = Cr (**5**), W (**6**)) were obtained from complexes **1** and **2** using a modified procedure.[3] To confirm that complex **6** is identical to the complex known earlier,[3] the unit cell parameters of the crystals of compound **6** were checked. The structure of a new compound **5** was proved by X-ray analysis (Fig. 4). Compounds **5** and **6** are unstable; when stored under argon at room temperature, one THF molecule is slowly eliminated to give the corresponding type-B complex.

By and large, complex **5** is structurally similar to complex **6**; the differences in the geometry of the Sn coordina-

Table 4. Thermodynamic parameters of THF addition reactions to complexes $(CO)_5CrECl_2 \cdot n$THF (n = 0, 1) calculated by the PBE0/cc-pVTZ-pp/6-311G(d,p) method

Compound	E_{tot}/au	ZPVE	ΔE_{tot}	ΔH_r	ΔG_r
			kcal mol^{-1}		
$(CO)_5CrSnCl_2$	−2745.0477072	29.14	—	—	—
$(CO)_5CrSnCl_2 \cdot$THF	−2977.32158751	104.13	−22.01	−21.74	−9.02
$(CO)_5CrSnCl_2 \cdot$2THF	−3209.57901353	178.88	−11.88	−9.85	−0.61
$(CO)_5CrGeCl_2$	−4607.41978059	29.56	—	—	—
$(CO)_5CrGeCl_2 \cdot$THF	−4839.69010933	104.79	−19.54	−19.47	−6.09
$(CO)_5CrGeCl_2 \cdot$2THF	−5079.93623482	179.52	−4.85	−3.06	+7.47

tion polyhedron are insignificant. In both complexes the Sn atom is at the center of a distorted trigonal bipyramid, the angle O(1)—Sn—O(2) in **5** and its analog **6** is 157.69(5) and 160.1, respectively.

In structure **6**, the lengths of the Sn—O(1) and Sn—O(2) coordination bonds differ by 0.05 Å (2.355 and 2.305 Å). In structure **5**, they differ somewhat more, *viz.*, by 0.09 Å (2.337(1) and 2.425(1) Å) (Table 5), although the DFT optimized structures of compounds **5** and **6** have almost equal Sn←O bonds 2.401 Å long. The distinctions between **5** and **6** can be explained by the effect of the system of weak intermolecular contacts formed by both coordinated THF molecules. No strong intermolecular interactions in the crystal of **5** were revealed; the H···Cl and H···O distances are close to the sum of the corresponding van der Waals radii.

Compounds **5** and **6** were characterized by IR and Raman spectroscopy. Based on positions of the ν(CO) lines, they are significantly different from complexes **1** and **2** (Fig. 5). Namely, the ν(CO) bands of the $A_1{}^1$, $A_1{}^2$ and B_1 symmetry types in the spectra of **5** and **6** are shifted toward the low-frequency region by 8 and 15 cm^{-1}, respectively. According to X-ray data,[3] the addition of the second THF molecule affects the Sn—Cl bond lengths and thus the corresponding stretching vibration frequencies in **5** and **6**, namely, the ν^s(Sn—Cl) band is shifted by ~10 cm^{-1} toward the low-frequency region, while the ν^{as} is shifted by about 5 cm^{-1} toward the high-frequency region compared to the spectra of **1** and **2**, respectively. At the same time, the frequencies of the M—C stretching vibrations and M—C—O deformation vibrations remain almost unchanged.

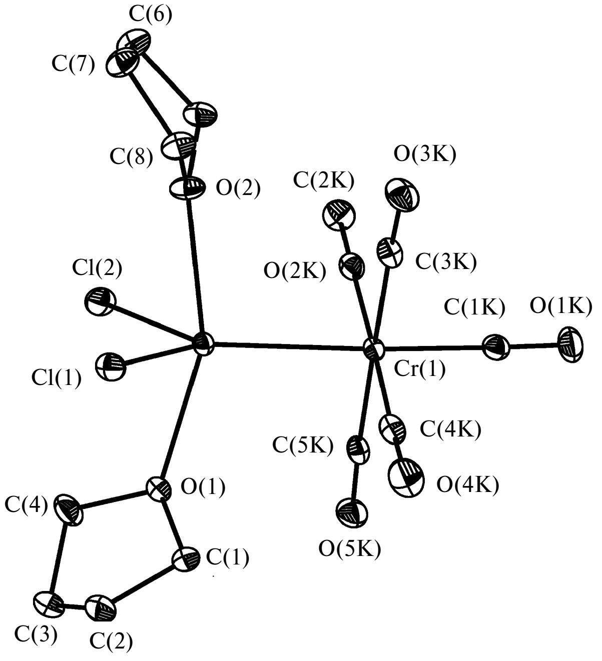


Fig. 4. Molecular structure of complex $(CO)_5CrSnCl_2 \cdot$ 2THF (**5**).

We failed to obtain type-C solid complexes of dichlorogermylene with two THF molecules (**7** and **8**) using the procedure described above; as a result, only the starting compounds **3** and **4** were isolated. This is in agreement with the results of DFT calculations (Table 4) of the enthalpies ΔH_r and the Gibbs free energy ΔG_r for the THF addition reactions:

$$(CO)_5MECl_2 + THF \rightarrow (CO)_5MECl_2 \cdot THF, \quad (1)$$

$$(CO)_5MECl_2 \cdot THF + THF \rightarrow (CO)_5MECl_2 \cdot 2THF. \quad (2)$$

For the germylene complex **7**, the enthalpy of reaction (2) is −3.06 kcal mol^{-1}, which is much smaller than the corresponding value for the stannylene complex **5** (−9.85 kcal mol^{-1}). As to the free energy, calculations

Table 5. Bond lengths (d) in complexes **5** and **6** according to X-ray data

Bond	d/Å	
	5	**6**[3]
Sn—O(1)	2.3374(14)	2.356(8)
Sn—O(2)	2.4247(14)	2.350(8)
Sn—Cl(1)	2.3721(5)	2.371(2)
Sn—Cl(2)	2.3714(5)	2.36(2)
Sn—M	2.5733(3)	2.737(1)

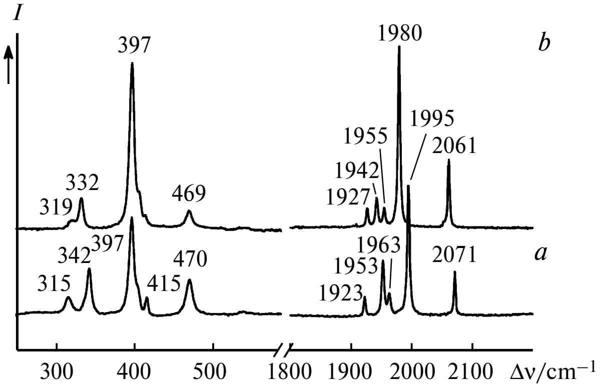


Fig. 5. A comparison of the Raman spectra of crystalline complexes $(CO)_5CrSnCl_2 \cdot THF$ (**1**) (*a*) and $(CO)_5CrSnCl_2 \cdot 2THF$ (**5**) (*b*).

predict a positive ΔG_r value (+7.47 kcal mol^{-1}) for **7** in the gas phase and a negative ΔG_r value (–0.61 kcal mol^{-1}) for **5**. It should also be noted that the only THF molecule in the type-B complexes is coordinated much stronger than each of the two THF molecules in the type-C complexes.

However, since calculations predict the possibility for the type-C complexes of germylenes to exist (a corresponding minimum on the potential curve was located), one could assume that complexes **3** and **4** can add the second THF molecule in the solutions in THF at room temperature, *i.e.*, the following equilibrium can exist

$$(CO)_2MGeCl_2 \cdot THF + THF \rightleftharpoons (CO)_5MGeCl_2 \cdot 2THF$$

with participation of molecules **7** and **8**, respectively. To check this assumption, we prepared solutions of complexes **3** and **4** in THF and measured their IR and Raman spectra (Fig. 6). In the ν(CO) region, the spectra of these solutions exhibit a common decrease in frequencies compared to the spectra of solutions in hexane. Some bands are split into doublets; the frequency of one component of the doublet is close to that of the type-B complexes, while the second component has a lower frequency (as in the spectra of the solutions of the C-type complexes of stannylenes, see Table 3). This suggests that the solutions in THF do contain the desired complexes **7** and **8**.

The existence of a similar-type equilibrium for complexes of dihalogermylenes (stannylenes) in solutions in acetonitrile was proved by two of us (M.P.E., O.M.N.) earlier[36] by electrochemistry methods.

Instability of solid complexes **7** and **8** (unlike complexes **5** and **6**) can be explained by the smaller size of the coordination sphere and by lower Lewis acidity of the Ge atom compared to the Sn atom.

Comparison of donor-acceptor properties of ligands in the series A, B, and C. There is an approach[2,15,17,18] for assessment of the overall donor ability of ligands based on the position of the ν(CO) line belonging to the $A_1{}^1$ symmetry type. According to this criterion, all $Cl_2E \cdot n$THF (E = Ge, Sn; n = 0, 1, 2) ligands are strong donors toward the metal carbonyl fragment and their donor ability is comparable with that of phosphines and arsines.[18,19] A decrease in the ν(CO) frequencies on going from the A-type complexes to B-type ones owing to enhancement of the donor ability of the ligand was reported[13b] in a comparative study of the IR spectra of complexes **11** and **3**. Coordination of the oxygen atom of the second THF molecule to the p_z-orbital of the carbenoid atom should be accompanied by further decrease in the π-acceptor ability of the ligand, which manifests itself as changes in the molecular geometry and ν(CO) frequencies. Indeed, a comparison of experimental results obtained for complexes **1** and **2** with those obtained for **5** and **6** clearly demonstrates a regular elongation of Sn←O bonds from 2.22 Å in **2** to ~2.35 Å in **5** and **6** and some elongation of the W—Sn bond by 0.026 Å on going from the type-B compounds to type-C complexes (see Ref. 3). This is accompanied by a decrease in the ν(CO) frequencies (see Table 3, Fig. 5).

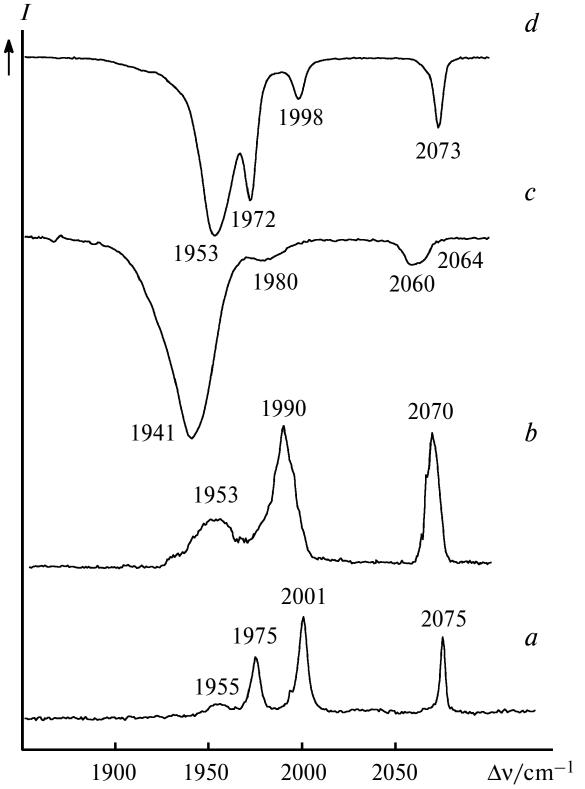


Fig. 6. The Raman spectra of solutions of complex **3** in hexane (*a*) and THF (*b*) and the IR spectra of solutions of complex **3** in THF (*c*) and hexane (*d*).

There is a method[15] of qualitative assessment of the π-acceptor ability using the mutual position of the ν(CO) bands of the E and $A_1{}^2$ symmetry types. This approach is based on the assumption that the E modes are generated by only the equatorial CO groups while the $A_1{}^2$ mode is due to the axial CO group only; the latter mode experiences the *trans*-effect of the ligand to the greatest extent. However, it is well known that the totally-symmetric ν(CO) vibrations of the A_1^1 and A_1^2 symmetry types are coupled.[17] Indeed, according to our calculations, the A_1^1 mode of complex **3** involves the stretching coordinates of not only the equatorial C—O bonds (contribution to the potential energy distribution is 76%), but also of the axial bond (17%); for the A_1^2 mode, these contributions are 20 and 71%, respectively. Nevertheless, this approach to assessment of the π-acceptor ability of the ligand "works" quite correctly. Transition from type-A complexes to type-B ones can be followed by comparing the IR spectra of complexes **11** and **3** using the published data.[13] On going from the spectra of solutions of type-B complexes (**1**—**4**) to those of the type-C complexes (**5**—**6**) the lines of the *E* and A_1^2 modes become even closer (Table 6, Fig. 7), which additionally confirms a decrease in the π-acceptor ability of the ligand.

Thus, the data from Tables 3 and 6 suggest that the addition of one and then two molecules of a Lewis base (THF) to the E^{II} atom of the complex (CO)$_5$MECl$_2$ is accompanied by a gradual decrease in the contribution of the π-component to the formation of the $\text{M}\overset{\cdots}{-}\text{E}^{\text{II}}$ bond leading to a slight elongation of this bond and, according to calculations, to a decrease in its energy.

It is important that the spectra of all complexes **1**—**6** exhibit inversion of the E—Cl stretching frequencies ($\nu^s > \nu^{as}$),[33b] which appear in the region near 350 cm^{-1} (Table 7). This indicates that the E^{II} atom in these complexes preserves its carbenoid nature despite the tetra- and penta-coordination environment.

Complex [(CO)$_5$WSn(Cl)(μ-OH)$_2$SnCl$_2$(μ-OH)]$_2$ · · 6THF (13). Our first attempts to grow crystals of compound (CO)$_5$WSnCl$_2$ · 2THF (**6**) by slow evaporation of the solvent (hexane/THF mixture) in air over a period of 3—4 days unexpectedly resulted in complex **13** whose Raman spectrum was significantly different from that of complex **6** (Fig. 8). The salient features of the spectrum of complex **13** are four very strong lines in the ν(CO) region, three ν(Sn—Cl) lines, and more intense lines of the THF internal vibrations. The structure of complex **13** was established by X-ray analysis (Fig. 9).

Table 6. ν(CO) frequency differences (cm^{-1}) between the modes of A_1^2 and *E* symmetry types in the spectra of solutions of complexes **1**—**6** (Raman spectra) and **11** (IR spectrum)

M	Complex	Solvent	Type	$\nu(A_1^2)$-$\nu(E)^1$
Ge	**11**	CH$_2$Cl$_2$	A[13b]	25
	3	CH$_2$Cl$_2$	B[13b]	20
	3	Hexane	B	19
	4	Hexane	B	18
Sn	**1**	Hexane	B	19
	2	Hexane	B	15
	5	Hexane	C	5
	6	Hexane	C	<10*

* Notation "$\nu(A_1^2)$-$\nu(E)$ <10 cm^{-1}" means that these spectral lines are unresolved because of close frequency values.

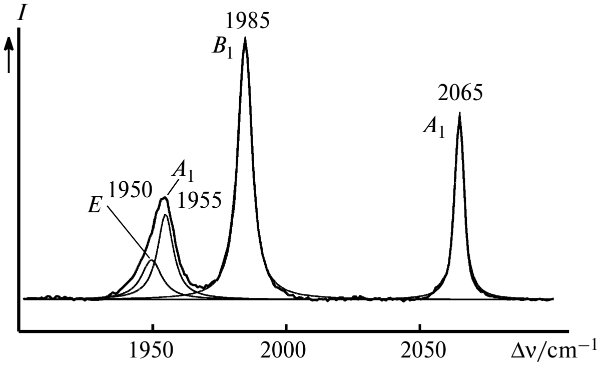


Fig. 7. The Raman spectrum of a solution of (CO)$_5$CrSnCl$_2$ · 2THF (**5**) in hexane (shown are the results of curve fitting analysis of a complex bandshape in the region near 1950 cm^{-1}).

The backbone of complex **13** is a cage built of four tin atoms and six oxygen atoms. This unusual structure provides an example of a compound containing Sn atoms with different coordination numbers. For four-coordinate atoms Sn(1) and Sn(1A), the Sn—O bond lengths fall in the range of values typical of divalent tin compounds. The Sn(1)—W(1) and Sn(1)—Cl(1) bonds are 0.08 and 0.04 Å shorter than the corresponding bonds in **6**. The coordination polyhedra of the Sn(2) and Sn(2A) atoms are distorted tetragonal bipyramids with the Sn(2)—O(1A) and Sn(2)—O(2) bonds (2.060(5) Å) that are somewhat shorter than the Sn(2)—O(3) bond (2.085(5) Å). A comparison of the Sn—O and Sn—Cl bond lengths for the octahedral Sn(2) atoms with those of the four-coordinate Sn(1) atoms shows that in the latter case they are much smaller. This suggests that complex **13** simultaneously contains both divalent (Sn(1) and Sn(1A)) and tetravalent (Sn(2) and Sn(2A)) tin atoms. To the best of our knowledge,

Table 7. Stretching frequencies of E^{II}—Cl bonds in the Raman spectra of solid samples of complexes **1**—**6**

Compound	$\nu^s_{\text{E—Cl}}$	$\nu^{as}_{\text{E—Cl}}$
	cm^{-1}	
GeCl$_2$ (Ar matrix)[31]	399	373
(CO)$_5$CrGeCl$_2$ · THF (**3**)	375	357
(CO)$_5$WGeCl$_2$ · THF (**4**)	376	357
SnCl$_2$ (Ar matrix)[31]	353	332
(CO)$_5$CrSnCl$_2$ · THF (**1**)	341	315
(CO)$_5$CrSnCl$_2$ · 2THF (**5**)	333	320
(CO)$_5$WSnCl$_2$ · THF (**2**)	343	315
(CO)$_5$WSnCl$_2$ · 2THF (**6**)	332	319

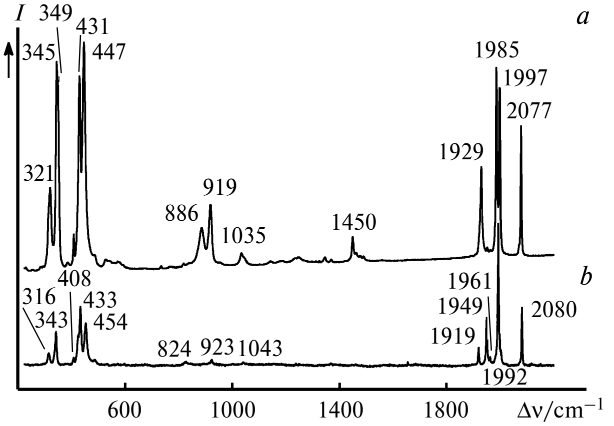


Fig. 8. A comparison of the Raman spectra of solid complexes **13** (*a*) and **6** (*b*).

there is only one example[37] of such a compound, *viz.*, bis(μ^3-oxo)-octakis(μ^2-trifluoroacetato-*O*,*O*′)-tetratin(II)-tin(IV). The hydroxyl groups in complex **13** form strong hydrogen bonds with the solvate THF molecules, the H···O and O···O distances being in the regions 1.72—1.79 and 2.552—2.640 Å, respectively.

Electronic structures of the complexes. To study the regularities of the geometry of the $SnCl_2$ and $GeCl_2$ complexes with tungsten and chromium carbonyls, we carried out quantum chemical calculations of isolated molecules **1**—**12**. A comparison of the optimized geometric parameters with the experimental data for complexes **2**—**6** showed that the E—O and E—M bonds in the isolated molecules are systematically longer than in the molecules in the corresponding crystals (Table 8).

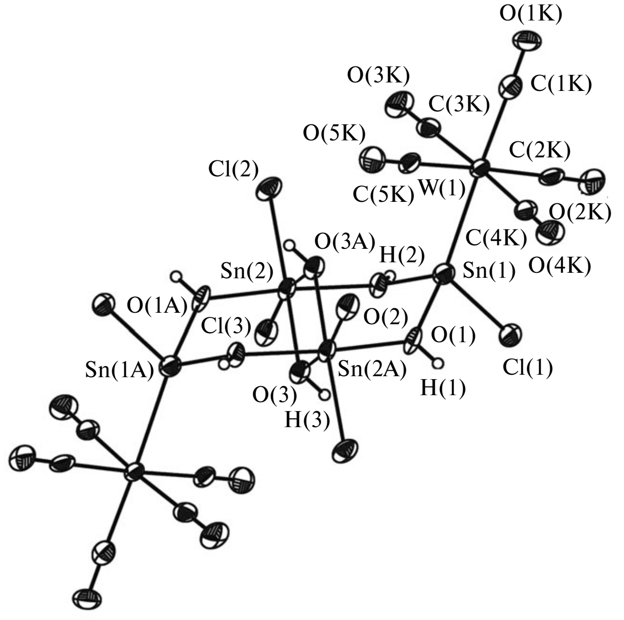


Fig. 9. Molecular structure of complex **13** (THF molecules are omitted).

The calculated Sn—O bond lengths vary in a rather narrow interval (2.251—2.401 Å) depending on the type of the complex and on the nature of the metal carbonyl fragment. For instance, the Sn—O bond lengths in $(CO)_5CrSnCl_2 \cdot 2THF$ (**5**) and $(CO)_5WSnCl_2 \cdot 2THF$ (**6**) are almost equal. This also holds for related complexes with one coordinated THF molecule. The limits for the Ge—O bond lengths are much wider (1.936—2.373 Å).

Table 8. Calculated and experimental bond lengths in complexes **1**—**12***

Compound	*r*(E←O)/Å		*r*(E—M)/Å		*r*(E—Cl)/Å	
	Calculations	Experiment	Calculations	Experiment	Calculations	Experiment
$(CO)_5CrGeCl_2$ (**11**)	—	—	2.320	—	2.159	—
$(CO)_5CrGeCl_2 \cdot THF$ (**3**)	2.081	1.948(2)	2.380	2.3880(6)	2.194	2.1906(10) 2.1994(10)
$(CO)_5CrGeCl_2 \cdot 2THF$ (**7**)	2.373	—	2.424	—	2.216	—
$(CO)_5WGeCl_2$ (**12**)	—	—	2.516	—	2.163	—
$(CO)_5WGeCl_2 \cdot THF$ (**4**)	2.086	1.948(8)	2.583	2.5335(13)	2.213 2.192(4)	2.192(3)
$(CO)_5WGeCl_2 \cdot 2THF$ (**8**)	2.361	—	2.644	—	2.221	—
$(CO)_5CrSnCl_2$ (**9**)		—	2.520	—	2.353	—
$(CO)_5CrSnCl_2 \cdot THF$ (**1**)	2.251	—	2.555	—	2.389	—
$(CO)_5CrSnCl_2 \cdot 2THF$ (**5**)	2.401	2.3374(14) 2.4247(14)	2.597	2.5733(3)	2.404	2.3721(5) 2.3714(5)
$(CO)_5WSnCl_2$ (**10**)	—	—	2.714	—	—	2.356
$(CO)_5WSnCl_2 \cdot THF$ (**2**)	2.257	2.223(6)	2.758	2.711(1)	2.388	2.352(3) 2.375(2)
$(CO)_5WSnCl_2 \cdot 2THF$ (**6**)	2.401	2.356(8) 2.350(8)	2.804	2.737(1)	2.415	2.364(2) 2.371(2)

* Experimental data were taken from Ref. 3 (**2**, **6**) and Ref. 5b (**4**).

For instance, replacement of the Cr atom by W in the complexes $(CO)_5MGeCl_2 \cdot THF$ causes the Ge—O coordination bond to shorten by about 0.1 Å. An increase in the coordination number of the E^{II} atom in the series A→B→C leads to elongation of the E—M bonds by 0.04—0.07 Å (see Table 8). The E—O bonds are also lengthened by 0.15—0.29 Å on going from the type-B to type-C complexes. Thus, in spite of a regular elongation of the calculated bond lengths compared to the experimental data,[3,4,5b] quantum chemical calculations of the molecular geometry reproduce the main trends in the structure of the complexes under study quite correctly.

A more detailed inspection of mutual influence of fragments in the complexes studied was performed using topological analysis of the calculated electron density distribution function in the framework of Bader´s theory "Atoms in molecules" (AIM). This approach has been used earlier[38] in studies of Arduengo´s heterocyclic carbene and silylene. According to the AIM theory, a saddle critical point of the (3, −1) type is a criterion for a chemical bond formation. The values of the electron density $\rho(\mathbf{r})$, its Laplacian $\nabla^2\rho(\mathbf{r})$, and the local energy density $E^e(\mathbf{r})$ at the (3, −1) critical point (topological parameters of a chemical bond) are the necessary criteria for the determination of the type of chemical bonding.

Topological analysis of the $\rho(\mathbf{r})$ function for the molecules under study allowed the (3, −1) critical points to be located in the regions of all expected chemical bonds. The topological parameters of the bonds formed by the E^{II} atom are listed in Table 9. The bonds formed by the E^{II} and M atoms are characterized by positive $\nabla^2\rho(\mathbf{r})$ values and negative $E^e(\mathbf{r})$ values, which corresponds, in the framework of the AIM theory, to the intermediate type of interatomic interactions. This theory makes it possible not only to study the nature of the bonds in the coordination site, but also to estimate their strength. The latter can be accomplished using a phenomenological correlation between the energy of the coordination bond and the potential energy density $V^e(\mathbf{r})$ at the (3, −1) critical point proposed by Espinosa, Molins, and Lecomte (EML)[27]:

$$E_{\text{bond}} = -1/2V^e(\mathbf{r}). \tag{3}$$

Correlation (3) was established using the data for hydrogen bonds with energies of at most 20 kcal mol^{-1}; however, as was shown recently,[39] it is also valid for stronger coordination interactions (up to 55 kcal mol^{-1}). Therefore, we used this correlation to estimate the strength of the E—O and E—M bonds.

Application of the EML scheme to the E—O bonds in the compounds in question leads to a large spread in energy values (from 10 to 25 kcal mol^{-1}), which vary in the same order as the calculated bond lengths. Type-C complexes are characterized by lower energies of the E—O bonds compared to the type-B complexes, the difference being more pronounced for E^{II} = Ge; this agrees with the results of calculations of thermodynamic parameters (see Table 4).

The strongest E^{II}—M bond is found in the type-A complex with M = W and E^{II} = Ge (see Table 9). Successive coordination of THF molecules to the vacant p_z-orbital of

Table 9. Calculated topological parameters (listed are the average values) and energies of coordination bonds E—O and M—E in isolated complexes of the types A, B, C (**1—12**)

Bond	Type A (THF)				Type B (1 THF)				Type C (2 THF)			
	Cr—Ge	W—Ge	Cr—Sn	W—Sn	Cr—Ge	W—Ge	Cr—Sn	W—Sn	Cr—Ge	W—Ge	Cr—Sn	W—Sn
$\rho(\mathbf{r})$												
E—O	—	—	—	—	0.085	0.074	0.057	0.058	0.041	0.052	0.041	0.043
M—E	0.037	0.064	0.035	0.033	0.041	0.042	0.031	0.023	0.031	0.039	0.029	0.047
E—Cl	0.094	0.064	0.061	0.062	0.066	0.078	0.075	0.078	0.094	0.066	0.058	0.070
$\nabla^2\rho(\mathbf{r})$												
E—O	—	—	—	—	0.155	0.017	0.197	0.195	0.095	0.098	0.127	0.149
M—E	0.119	0.136	0.116	0.103	0.083	0.070	0.087	0.085	0.089	0.012	0.093	0.067
$E^e(\mathbf{r})$												
E—O	—	—	—	—	−0.023	−0.016	−0.004	−0.004	−0.004	−0.004	−0.003	−0.002
M—E	−0.009	−0.017	−0.007	−0.005	−0.010	−0.009	−0.006	−0.003	−0.007	−0.017	−0.004	−0.011
$V(\mathbf{r})$												
E—O	—	—	—	—	−0.085	−0.075	−0.057	−0.058	−0.032	−0.033	−0.032	−0.042
M—E	−0.048	−0.069	−0.042	−0.035	−0.041	−0.036	−0.035	−0.027	−0.037	−0.052	−0.032	−0.039
E_{bond}/kcal mol^{-1}												
E—O	0.0	0.0	0.0	0.0	26.6	23.4	17.9	18.1	9.9	14.4	10.0	13.1
M—E	14.9	21.6	13.2	11.1	12.8	11.2	10.9	8.4	11.6	16.2	10.0	12.4

the $\mathrm{E^{II}}$ atom, which formally manifests itself in an increase in the coordination number of this atom, leads by and large to weakening of the $\mathrm{E^{II}—M}$ bond, the effect also being more pronounced for $\mathrm{E^{II} = Ge}$. Generally, the energies of coordination bonds calculated using the empirical relationship (3) seem to be reasonable because they agree with the commonly accepted concepts.

In conclusion, we obtained the Raman and IR spectra of the following dichlorogermylene and dichlorostannylene complexes with chromium and tungsten carbonyls containing one molecule of a neutral base, THF (B type): $\mathrm{(CO)_5CrSnCl_2 \cdot THF}$ (**1**), $\mathrm{(CO)_5WSnCl_2 \cdot THF}$ (**2**), $\mathrm{(CO)_5CrGeCl_2 \cdot THF}$ (**3**), $\mathrm{(CO)_5WGeCl_2 \cdot THF}$ (**4**), and two THF molecules (C type): $\mathrm{(CO)_5CrSnCl_2 \cdot 2THF}$ (**5**) and $\mathrm{(CO)_5WSnCl_2 \cdot 2THF}$ (**6**), and complex $\mathrm{[(CO)_5WSn(Cl)(\mu\text{-}OH)_2SnCl_2(\mu\text{-}OH)]_2}$ (**13**) and interpreted them using quantum chemical calculations. Complexes **3**, **5**, and **13** were characterized by X-ray analysis. It was shown that the stretching vibrations of CO groups in the spectra of solutions of complexes **1**—**6** obey the selection rules for the C_{4v} local symmetry. The spectra of solid compounds point to the symmetry lowering of the $\mathrm{E—M(CO)_5}$ fragment due to the crystal field effects. For the type-A, type-B, and type-C complexes, the calculated and experimental bond lengths, the energies of the $\mathrm{M\overset{\cdots}{-}E^{II}}$ bonds, and the ν(CO) vibrational frequencies were compared. It was shown that successive addition of the first and then second THF molecule to the $\mathrm{(CO)_5M\overset{\cdots}{-}ECl_2}$ complexes is accompanied by filling of the $\mathrm{p_z}$-orbital of the carbenoid atom and, therefore, by a decrease in the contribution of the π-component to the $\mathrm{M\overset{\cdots}{-}E^{II}}$ bond, which causes an increase in the donor ability of the carbene-like ligand and a slight elongation and weakening of this bond. However, this bond still remains shorter than the $\mathrm{M—E^{IV}}$ ordinary bond. The ligand executes free rotation about the $\mathrm{M\overset{\cdots}{-}E^{II}}$ bond.

The energies of addition of the first and second THF molecules to the $\mathrm{(CO)_5M\overset{\cdots}{-}ECl_2}$ complexes were calculated. By and large, the energy of addition of the second molecule is much lower than that of the first molecule, which is consistent with elongation of the $\mathrm{E \leftarrow O}$ coordination bond in the C-type complexes compared to the B-type complexes. These energies are higher for the stannylene rather than germylene complexes; therefore, the dichlorostannylene complexes with two THF molecules can be isolated as crystals, whereas analogous dichlorogermylene complexes are assumed to exist only in THF solution.

Attempts to grow crystals of complex **6** in air unexpectedly led to complex **13**, which was characterized by X-ray analysis and Raman spectroscopy. It simultaneously contains two types of tin atoms, $\mathrm{Sn^{II}}$ and $\mathrm{Sn^{IV}}$.

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