



Article π -Hole Tetrel Bonds—Lewis Acid Properties of Metallylenes

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Abstract: The MP2/aug-cc-pVTZ calculations were performed on the dihalometallylenes to indicate their Lewis acid and Lewis base sites. The results of the Cambridge Structural Database search show corresponding and related crystal structures where the tetrel center often possesses the configuration of a trigonal bipyramid or octahedron. The calculations were also carried out on dimers of dichlorogermylene and dibromogermylene and on complexes of these germylenes with one and two 1,4-dioxide molecules. The Ge···Cl, Ge···Br, and Ge···O interactions are analyzed. The Ge···O interactions in the above mentioned germylene complexes may be classified as the π -hole tetrel bonds. The MP2 calculations are supported by the results of the Quantum Theory of Atoms in Molecules (QTAIM) and the Natural Bond Orbital (NBO) approaches.

Keywords: dihalogermylenes; coordination of Ge; π -hole tetrel bond; the Quantum Theory of Atoms in Molecules (QTAIM); the Natural Bond Orbital (NBO)

1. Introduction

Carbenes are often defined as neutral compounds containing a divalent carbon atom [1]. The latter center possesses only six electrons in the valence shell. Two non-bonding electrons of this carbon can be located in two different orbitals; their spins are parallel for the $\sigma^1 p_{\pi}^{-1}$ triplet state (³B₁ state). The singlet carbenes are characterized by the opposite spin nonbonding electrons. These electrons may occupy the same σ or p_{π} orbital for the σ^2 or p_{π}^2 configuration, respectively, this corresponds to two ¹A₁ states. In general, the σ^2 configuration is more stable than the p_{π}^2 configuration [2]. The $\sigma^1 p_{\pi}^{-1}$ configuration corresponding to the excited singlet ¹B₁ state may also occur.

The divalent character of the carbon atom is often contested because of substituents influencing electron charge transfer which in consequence may result in the double carbonheteroatom bond features in stable singlet carbenes [2]. The early study on dibromocarbene is an example [3–6]; it was stated that the ylide form of this compound is characterized by the overlap of the vacant p orbital of carbon and the filled p orbital of bromine. In the past, these features led to numerous discussions and controversies of the carbene character of various compounds. This is why other definitions were proposed. The definition of Bertrand and co-workers [2] may be mentioned, namely that carbenes are "compounds with a neutral dicoordinate carbon atom featuring either two singly occupied nonbonding orbitals (triplet state) or alternatively both a lone pair and an accessible vacant orbital (singlet state)."

Carbenes play a crucial role as transient intermediates; for example their important role in numerous chemical processes was analyzed [2]. In numerous studies much attention is also paid to the metallylenes that are heavier analogues of carbenes, such as silylenes (R_2Si), germylenes (R_2Ge), stannylenes (R_2Sn), and plumbylenes (R_2Pb) [7]; two R substituents attached to the tetrel center here need not be the same. It is often assumed that the valency of such heavier analogues is two. It was also pointed out that in contrast to the carbenes, their heavier analogues have a lower ability to form hybrid orbitals [7].



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Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Thus they are characterized by the $(ns)^2(np)^2$ valence bond configuration (or close to that one), for the singlet state two nonbonding electrons occupy the ns orbital or the orbital characterized by the low contribution of the p orbital character. Hence the lone pair electrons of such heavier analogues are expected to be inert due to the very high s-character of the corresponding orbital.

In summary, the former studies reveal that the heavier analogues of carbenes, metallylenes, possess the Lewis acid character due to the vacant p orbital but rather not the Lewis base properties in spite of the existence of lone electron pair. However carbon atoms of carbenes may act as the Lewis base centers since they donate electrons in various interactions and reactions, the hydrogen bonds were a subject of investigations, for example [8–12]. This is why the aim of this study is to analyze the Lewis acid and Lewis base properties of carbenes and their heavier analogues. In particular, the acidic properties of germylenes are discussed here since the experimental studies on these systems are well known; one can mention the X-ray crystal structures evidence of the Lewis acid properties of dihalogen germylenes.

Cambridge Structural Database [13,14] searches were performed in this study to describe interactions which reveal acidic properties of metallylenes. Next, for some of the systems, ab initio and DFT calculations were performed that were supported by the results of the Quantum Theory of Atoms in Molecules (QTAIM) approach [15,16] and the Natural Bond Orbital (NBO) method [17,18].

2. Computational Details

The calculations were performed with the Gaussian16 set of codes [19]. The MP2 method [20] and the Dunning style aug-cc-pVTZ basis set [21,22] were applied to perform optimizations of complexes analyzed in this study. Frequency calculations have been carried out at the same MP2/aug-cc-pVTZ level to confirm that the structures optimized correspond to energetic minima. The calculations for species containing heavier atoms (Br, Ge, Sn or Pb) were done with quasi-relativistic small-core effective core potentials (ECPs) [23] and the corresponding Peterson AVTZ basis set [24] for these atoms. First of all the dihalometallylenes, ZX_2 (Z = C, Si, Ge, Sn and Pb; X = Cl and Br) monomers were optimized to further analyse their properties. Next, the larger systems were also optimized, GeCl₂ and GeBr₂ dimers as well as the complexes of GeCl₂ and GeBr₂ with one or two 1,4-dioxane molecules. It is worth mentioning that all monomers corresponding to the total energetic minima are the singlet ¹A₁ states, the same concerns the GeCl₂ and GeBr₂ species in dimers as well as in other complexes analysed in this study.

The interaction and binding energies, E_{int} and E_{bin} , were calculated for complexes analysed. The former one is the difference between the energy of complex and the energies of monomers with geometries taken from the complex. For the binding energy, the energies of monomers correspond to their optimized geometries [25]. Hence, the E_{bin} energy contains the deformation energy term, E_{def} , ($E_{bin} = E_{int} + E_{def}$) [26]. The basis set superposition error (BSSE) corrections [27] were also calculated and included in the E_{int} and E_{bin} energies.

The NBO method [17,18] was used to calculate the atomic charges as well as the energies of orbital-orbital interactions; the NBO 6.0 program [28] implemented in the ADF2019 set of codes [29] was applied to perform NBO calculations. Hence, for all systems optimized at the MP2/aug-cc-pVTZ level where the NBO characteristics are discussed, the BP86-D3/TZ2P calculations were performed with the ADF 2019.302 program codes. Ref. [29] It means that the BP86 functional [30,31] with the Grimme dispersion corrections [32] and the uncontracted Slater-type orbitals (STOs) as basis functions with triple- ζ quality [33] for all elements were applied. Relativistic scalar ZORA corrections [34] were applied for systems containing heavier atoms (Br, Ge, Sn and Pb).

The Quantum Theory of Atoms in Molecules', QTAIM [15,16] was applied to analyze characteristics of the bond critical points corresponding to intermolecular interactions. The QTAIM calculations were performed with the use of wfn-files obtained from the former MP2/aug-cc-pVTZ calculations. The AIMAll program [35] was used to perform

QTAIM calculations and to visualize molecular graphs and EP surfaces while the Jmol [36] program was applied to show the fragments of crystal structures.

3. Results and Discussion

3.1. Crystal Structures

The search through the Cambridge Structural Database, CSD [13,14] (September 2021 release) was performed here to find crystal structures containing species with the tetrel (14th group element) formally divalent center being in contact with the electron donor. The aim of this search was to check the Lewis acid properties of such tetrel sites in metallylenes. The main groups' elements of the second and third periods were taken into account as the Lewis base centers: N, O, F, P, S and Cl. The following criteria for this search were applied; 3D coordinates determined, no disordered structures, no errors, no polymeric structures, R-factor less or equal to 10% and only single crystal structures. The distance between the tetrel and Lewis base centers was assumed to be shorter than the sum of the corresponding van der Waals radii. The radii proposed by Bondi [37] that are inserted in the CSD set of codes were applied here. Thirty-one crystal structures were found that fulfil the above search criteria; 17 germylenes, 10 stannylenes, and 4 plumbylenes. There are no carbenes and silylenes crystal structures which fulfil the above mentioned criteria. This is partly caused by the energetic instability of the majority of carbenes [2].

There are six crystal structures where dihalometallylenes form complexes with Lewis base units through the tetrel center. Figure 1a presents an example, this is the fragment of the crystal structure of the complex of dichlorogermylene with 1,4-dioxane. The germanium center is characterized here by the octahedron configuration since it has six closest contacts; two bonds with chlorine atoms, equal to 2.2813(5) Å, and four intermolecular contacts; two with oxygen centers of two 1,4-dioxane molecules, equal to 2.3989(12) Å, and two with chlorine centers of two neighboring GeCl₂ molecules, amounting to 3.463(1) A [38]. It seems that in these four intermolecular contacts, the germanium center acts as the Lewis acid. A similar situation occurs in the crystal structure of the dichlorogermylene complex with tetrahydrofuran. Figure 1b presents the fragment of this structure. Here, the germanium center possesses the trigonal bipyramid configuration. Two Ge-Cl bond lengths are equal to 2.442(2) and 2.438(2) A. Three intermolecular contacts are observed, one Ge \cdots Cl contact with the neighboring GeCl₂ molecule, equal to 3.846(2) Å, and two Ge \cdots O contacts with tetrahydrofuran molecules, amounting to 2.410(2) and 2.459(2) A [39]. One may also consider the octahedron configuration of the germanium center here, since it possesses a lone electron pair. However, this configuration is hardly accepted since the electron pair is characterized mainly by the s-character of the corresponding orbital (over 90%) that makes it rather non-directional and non-reactive.

There are other crystal structures of dihalometallylenes resulting from the CSD [13,14] search; another solution of the mentioned above crystal structure of 1,4-dioxane dichlorogermanium, the crystal structures of 1,4-dioxane dibromo-germanium, bis(μ -chloro)-ditin(ii) bis(tetrachloro-aluminum(iii)) 1,2,3,4-tetramethylbenzene solvate and bis(μ -chloro)di-tin(ii) bis(tetrachloro-gallium(iii)) 1,2,3,4-tetramethylbenzene solvate. It is interesting that for all these dihalometallylenes crystal structures, the octahedron or trigonal bipyramid configuration of the tetrel center may be assumed. An interesting situation is observed for the last mentioned above tin crystal structure where the benzene ring may be assumed as one of coordination centers [40].

There are other examples of crystal structures of metallylenes. Figure 2 presents the fragment of the structure of (N-(n-propyl)-2-(n-propylamino)troponiminato-N,N')-tin(ii) trifluoromethanesulfonate [41]. This is the stannylene structure where the divalent tin center forms two bonds with the nitrogen atoms. Additionally two Sn···O intermolecular contacts are formed with the trifluoromethanesulfonate molecules. Figure 3 presents the structure of N,N'-bis(3-(dimethylamino)propyl)benzimidazolin-2-stannylene [42]. The tin center forms two bonds with nitrogen atoms here. However, two Sn···N contacts are also observed, one intermolecular contact and an intramolecular one.



Figure 1. The fragments of the crystal structures; (**a**) 1,4-dioxane dichloro-germanium, (**b**) dichloro-germanium(ii) tetrahydrofuran solvate. The closest intermolecular contacts are indicated.



Figure 2. The fragment of the crystal structure of (N-(n-propyl)-2-(n-propylamino)troponiminato-N,N')-tin(ii) trifluoromethanesulfonate. The closest intermolecular contacts are indicated.

There are other interesting cases among 31 structures resulting from the above mentioned search. However few characteristics are common, the tetrel center may be assumed to be divalent since metallylenes are discussed here. And usually there are at least two additional contacts of the tetrel center with the Lewis base sites, in directions perpendicular,



or nearly so, to the plane of two covalent bonds to the tetrel atom. This is discussed later, that these contacts may be classified as the π -hole tetrel bonds.

Figure 3. The fragment of the crystal structure of N,N'-bis(3-(dimethylamino)propyl) benzimidazolin-2-stannylene. The closest contacts are indicated, an intermolecular contact and an intramolecular one.

3.2. Dihalometallylenes—Lewis Acid and Lewis Base Sites

It was discussed in the previous section that in structures of metallylenes, the tetrel center is in contact with the Lewis base centers by areas located at planes containing bonds to this center. The Lewis acid properties of metallylenes were also discussed in earlier studies. On the other hand, the Lewis base properties, are revealed in carbenes but rather not in their analogues containing heaver elements of the 14th group. It is worth mentioning, however, that the Lewis base properties of carbenes and silylenes were analyzed theoretically and the formation of hydrogen bonds with carbon and with silicon acting as the proton acceptor centers was discussed [11].

This is why the Lewis acid and Lewis base properties of tetrel centers in metallylenes are analyzed here in detail. The simple dihalometallylenes species were chosen for such analysis. This seems to be justified since the crystal structures of these compounds make up about 20% of the total number of crystal structures of metallylenes (see the former section). The preliminary analyses of properties of these systems are performed here; the interpretations of results seem to be clear due to the simple structure of these dihalogens.

The analysis of donor-acceptor properties may be performed on the basis of the σ -hole and π -hole concept [43–45]. The σ -hole is characterized by the depletion of the electron charge in the extension of the bond to the considered center; this may lead to the positive electrostatic potential (EP) at this area. This results in the Lewis acid properties of such a center. The σ -holes were detected at the 14, 15, 16, 17 and 18 groups elements, in the elongation of the bond to the corresponding center. Thus, these elements may act as Lewis acids, in spite of the majority of them being electronegative ones, they form tetrel, pnicogen, chalcogen, halogen and aerogen bonds, respectively, interacting with electron rich sites [43–50]. The π -holes are also areas of the electron charge depletion that may lead to the positive EP and Lewis acid properties of corresponding centers; such areas are located in surfaces related to planes of species or molecular fragments [44,45,51,52]. It was stated that "a positive π -hole is a region of positive electrostatic potential that is perpendicular to a portion of a molecular framework" [51]. The detailed analysis of natures and characteristics of π -holes was performed; the categorization of these sites was also provided [51,52]. One can also mention studies where the σ - and π -holes are characterized in terms of molecular orbitals [53,54].

Scheme 1 presents the GeBr₂ molecule, representing dihalometallylene species, the possible Lewis acid and Lewis base sites that may occur here are presented. The σ -holes and π -holes may occur and they may be connected with the Lewis acid properties. The σ -holes may occur at the bromine centers in the extensions of the Ge-Br bonds that may further

form halogen bonds [55,56]. However the σ -holes may also be observed at Ge center in the elongations of the Br-Ge bonds. The π -holes occur at the Ge center in the surface related to the plane of the GeBr₂ molecule. Additionally, the existence of the Ge lone electron pair may result in its Lewis base properties.



Scheme 1. The Lewis acid-base sites for the dihalometallylene (example of dibromogermylene is presented). The designations of this scheme are the same as those in Table 1.

Table 1. The values of electrostatic potential, EP (in au), for dihalometallylenes; the results of MP2/aug-cc-pVTZ calculations, Z = C, Si, Ge, Sn, Pb; X = Cl, Br. L. pair designates the site corresponding to the location of the lone electron pair, the EP values at the σ -hole and π -hole sites of the tetrel (Z) and halogen (X) centers are given (see Scheme 1).

Compound	π -Hole (Z)	σ-Hole (Z)	L. Pair	σ-Hole (X)
CCl ₂	0.024	-0.015	-0.040	0.028
SiCl ₂	0.055	0.031	0.005	0.005
GeCl ₂	0.065	0.035	0.015	-0.008
SnCl ₂	0.079	0.048	0.025	-0.005
PbCl ₂	0.092	0.060	0.058	-0.035
CBr ₂	0.017	-0.020	-0.035	0.032
SiBr ₂	0.050	0.029	0.003	0.019
GeBr ₂	0.060	0.033	0.021	0.001
SnBr ₂	0.074	0.043	0.024	0.000
PbBr ₂	0.088	0.055	0.058	0.000

The above sites presented for the GeBr₂ molecule may also occur for other dihalometallylenes discussed in this study. Table 1 presents the electrostatic potential values at sites shown in Scheme 1 for the molecular surfaces characterized by the 0.001 au electron density. Figure 4 presents two examples of molecular surfaces of CCl₂ and SiBr₂ with the EP mapped. Table 1 shows that the greatest positive EP values are observed for the sites related to π -holes. For both series, dichlorometallylenes and dibromometallylenes, the EP value at the π -hole site increases with the increase of the atomic number of the tetrel element. The greatest positive EP value is observed for the PbCl₂ species. This is in line with previous studies, for example, it was stated that "both σ -holes and π -holes become more positive in going from the lighter to the heavier atoms in a given Group of the periodic table ... " [51].



Figure 4. The molecular graphs of (**a**) CCl_2 and (**b**) $SiBr_2$. The surfaces of the electron density of 0.001 au are presented with the maps of the electrostatic potential (EP), the blue color corresponds to the positive EP value while the red color corresponds to the negative EP value.

Let us consider the possible σ -hole located at the halogen center. It is observed for the carbon and silicon dihalogens (accompanied by the positive EP values). For other heavier tetrel species, the close to zero EP-values or even negative EP values are observed in elongations of Z-X bonds (Z—tetrel center, X—halogen center). This is because chlorine and bromine elements are characterized by much greater electronegativity than heavier tetrel elements, in these cases, the greater shifts of the electron charge to halogen centers are observed. The Cl-center is more electronegative than the bromine one and hence, for the heavier tetrel atoms, the negative EP values at chlorine centers at sites corresponding to the σ -holes are observed while the corresponding EP values for bromine sites are positive and close to zero.

In the case of tetrel centers and the sites corresponding to locations of electron pairs, the negative EP values are only observed in carbon dihalogens, while for heaver tetrel centers they are not; this may be connected with the greater s-character contribution in the lone electron pair orbital in heaver tetrels; this is discussed later in this article. It seems also that there are not special areas corresponding to the σ -holes at the tetrel centers in extensions of the X-Z bonds. At the latter sites, the negative values are observed for carbon species while for the remaining dihalogens, the positive EP values are observed at these sites but it is probably connected with the large areas of π -holes.

Table 2 presents few other selected characteristics of the above discussed dihalometallylenes. The negative atomic charge of the tetrel center is observed only for carbenes, while for other tetrel elements this charge is positive, it increases with the increase of the atomic number of this element. This is in line with the results presented in Table 1. The sites of the clear negative EP corresponding to lone electron charges are observed only for carbenes. The Lewis base properties of carbenes were described in former studies [8–12]. In general, in the case of the metallylenes analyzed here (Tables 1 and 2), the positive EP corresponding to the π -hole increases with the increase of the tetrel atomic charge. It was stated above, that the lone electron pair site connected with the negative EP occurs only for carbon, this corresponds to the lowest s-character of the lone pair orbital (and the greatest contribution of the p-character), and with the highest value of polarization (Table 2). The latter term is understood here as the percentage contribution of the bond orbital charge at the tetrel center. The electron charge shifts from the tetrel center to the halogen increase with the increase of the atomic number of the tetrel element. The latter leads to the above mentioned increase of the atomic charge of the tetrel center and the increase of its EP value at the π -hole.

Table 2. The NBO characteristics of the dihalometallylenes; charge of the tetrel center is given (au), Lp-s is the percentage of the s-character of the lone electron pair orbital, Pol is the polarization of the tetrel-halogen (Z-X) bond defined as the percentage of the electron density of the bond orbital at the tetrel center. These are the BP86-D3/TZ2P results of calculations for systems optimized at the MP2/aug-cc-pVTZ level. T-S designates the difference in energy between the triplet and singlet states (in kcal/mol, MP2/aug-cc-pVTZ level).

Compound	Charge	Lp-s	Pol	T-S
CCl ₂	-0.098	74.3	38.0	19.3
SiCl ₂	0.784	86.4	21.1	51.4
GeCl ₂	0.826	90.8	20.7	62.9
SnCl ₂	1.029	92.2	17.3	62.9
PbCl ₂	1.081	95.2	16.5	79.6
CBr ₂	-0.215	79.4	39.7	15.9
SiBr ₂	0.634	88.0	23.9	46.9
GeBr ₂	0.670	91.7	23.5	56.9
SnBr ₂	0.880	92.7	20.0	57.6
PbBr ₂	0.938	95.4	19.1	71.4

The difference between the energy of the triplet state of the tetrel dihalogen and the corresponding singlet state is also presented in Table 2, indicating that the singlet is more stable. The latter difference increases with the increase of the atomic number of the tetrel element; this is in line with other studies [1,2,7].

3.3. Complexes of Dihalometallylenes

In this study, emphasis is put on interactions of dihalometallylenes. Here, it was pointed out before, that an important part of crystal structures of metallylenes concerns these dihalogens. For these structures, the octahedron configuration of the tetrel center is often observed. The crystal structure of the complex of dichlorogermylene with 1,4-dioxane is an example [38]. The germanium center forms two Ge-Cl formally covalent bonds and two Ge···Cl interactions (Figure 1a). Figure 1a shows that in this structure, the layer of $GeCl_2$ molecules is inserted between the layers of 1,4-dioxane molecules. Two GeCl₂ molecules neighboring to each other are linked by two Ge····Cl interactions. It is interesting that the layer of dichlorogermylene molecules is approximately flat. Referring to the possible Lewis acid and Lewis base sites in the dihalometallylenes (see Scheme 1), one can expect that two Ge \cdots Cl interactions in the neighboring molecules are governed by the negative EP at chlorine and the positive EP corresponding to the site related to the possible germanium σ -hole. Additionally, the Ge-center of each GeCl₂ molecule in the crystal structure is stabilized by two Ge...O interactions with two 1,4-dioxane molecules. The interactions similar to those observed in the crystal structure of the dichlorogermylene complex with 1,4-dioxide are observed in the crystal structure of the bromine analogue—the complex of dibromogermylene with 1,4-dioxide [57]. The Ge-center in the latter structure possesses the $Ge \cdots Br$ and $Ge \cdots O$ contacts. The space groups, packing and, in general, arrangements of molecules are the same in both the above mentioned structures, chlorine and bromine; even similar cell dimensions are observed; one may classify them as the isotypic structures. It is worth mentioning that an experimental (vibrational Raman and IR spectra have been reported) and theoretical study on dihalogermylene and dihalostannylene complexes with 1,4-dioxide and triphenylphosphine was performed [58]; in the case of the complexes of 1,4-dioxide, similar octahedron configurations of the germanium center were observed. Examples of such configurations were described above (see Figure 1a).

The dimers of dichlorogermylene and dibromogermylene are analyzed in detail here; the complexes of dichlorogermylene and dibromogermylene with one and with two molecules of 1,4-dioxide are also taken into account. Table 3 presents the energetic parameters of these complexes, the deformation, binding and interaction energies are given; two latter ones corrected for BSSE. The BSSE correction is large in spite of the saturated triple- ξ (triple-zeta—TZ) aug-cc-pVTZ basis set applied; the values from 4.9 kcal/mol to 10.0 kcal/mol are observed.

Table 3. MP2/aug-cc-pVTZ results of calculations (in kcal/mol); E_{int}BSSE—interaction energy corrected for BSSE, E_{bin}BSSE—binding energy corrected for BSSE, E_{def}—deformation energy, BSSE—basis set superposition error correction.

E _{int} BSSE	E _{bin} BSSE	E _{def}	BSSE
-32.5	-15.8	16.7	6.7
-32.0	-18.2	13.8	10.0
-19.5	-17.4	2.0	6.8
-19.3	-17.2	2.1	9.4
-11.9	-9.2	2.7	4.9
-11.9	-9.1	2.8	7.1
	E _{int} BSSE -32.5 -32.0 -19.5 -19.3 -11.9 -11.9	$\begin{array}{ c c c c c c c } \hline E_{int}BSSE & E_{bin}BSSE \\ \hline & -32.5 & -15.8 \\ & -32.0 & -18.2 \\ & -19.5 & -17.4 \\ & -19.3 & -17.2 \\ & -11.9 & -9.2 \\ & -11.9 & -9.1 \\ \hline \end{array}$	$\begin{array}{ c c c c c c c } \hline E_{int}BSSE & E_{bin}BSSE & E_{def} \\ \hline & -32.5 & -15.8 & 16.7 \\ & -32.0 & -18.2 & 13.8 \\ & -19.5 & -17.4 & 2.0 \\ & -19.3 & -17.2 & 2.1 \\ & -11.9 & -9.2 & 2.7 \\ & -11.9 & -9.1 & 2.8 \\ \hline \end{array}$

The corrected interaction energies for dimers of dihalogens, $(GeCl_2)_2$ and $(GeBr_2)_2$ are large since their absolute values exceed 30 kcal/mol. However, the absolute values of binding energies for these dimers are about two times smaller due to large deformation energies. Figure 5 presents the molecular graph of the dimer of dibromogermylene which is not a planar system like it is observed in the corresponding crystal structure of the dibromogermylene complex with 1,4-dioxide; similarly the planar (GeCl₂)₂ dimers are observed in the isotypic chlorine analogue. The large deformations of dibromogermylene molecules occur when the dimer is formed. A similar situation is observed for the theoretically analyzed dimer of dichlorogermylene, the structure is not planar and it is similar to the one presented in Figure 5. In both dimeric structures theoretically analyzed, $(GeCl_2)_2$ and $(GeBr_2)_2$, the germanium centers are coordinated by three halogen centers. This seems to be close to the tetrahedral structures if one also takes into account the lone electron pair of the germanium center. Figure 5 presents the bond paths (BPs) and corresponding bond critical points, each of two Ge-centers is connected by BPs with three bromide attractors. The same arrangement of attractors and bond paths with corresponding BCPs is observed for the $(GeCl_2)_2$ structure.



Figure 5. The molecular graph of (GeBr₂)₂; big circles correspond to the attractors (grey—germanium, brown—bromine), small green circles to the bond critical points and red circles to the ring critical points; solid and broken lines indicate bond paths.

The BSSE corrections and the deformation energies are smaller for the complexes of dichlorogermylene and dibromogermylene with 1,4-dioxide than for the above discussed dimers. This is why the absolute values of interaction energies for these complexes with 1,4-dioxide are much smaller than for corresponding dimers, while the absolute binding energies are comparable between themselves (see Table 3). The complexes of dichlorogermylene and dibromogermylene with two molecules of 1,4-dioxide are also considered here. The interaction and binding energies are defined here as the interaction of one 1,4-dioxide molecule with the system of dihalogermylene and another 1,4-dioxide molecule. This interaction with the subsequent 1,4-dioxide is much weaker than the one with the first 1,4-dioxide molecule (Table 3).

Table 4 presents selected QTAIM parameters corresponding to the coordination contacts discussed above. The characteristics of the bond critical points (BCPs) corresponding to the Ge···Cl/Br and Ge···O contacts are given. It was pointed out in numerous studies that the electron density at the BCP, $]\rho_{BCP}$, expresses the strength of interaction and that it is in agreement with the value of binding or interaction energy [59–62]. The greatest ρ_{BCP} values are observed here for the complexes of dihalogermylenes with the 1,4-dioxide, next for the dihalogermylene dimers and finally for the Ge···O interaction with the subsequent 1,4-dioxide molecule. The Laplacian of the electron density, $\nabla^2 \rho_{BCP}$, for all these contacts is positive, but the corresponding total electron energy density at BCP, H_{BCP}, is negative. It means that all intermolecular contacts are at least partly covalent in nature. Table 4 also presents delocalization indices, $\delta(A,B)$ [63,64], for the contacts described above. This parameter corresponds to the covalent character of interaction (see Equation (1)).

$$\delta(A,B) = -2 \int_{A,B} (2\Gamma(r_1,r_2) - \rho(r_1)\rho(r_2)) dr_1 dr_2$$
(1)

Table 4. The QTAIM characteristics (in au) of bond critical points—BCPs (corresponding bond paths are indicated); ρ_{BCP} —electron density at BCP, H_{BCP} —the total electron energy density at BCP, $\delta(A,B)$ —delocalization index corresponding to $A \cdots B$ bond path.

Species	$\mathbf{A}{\cdots}\mathbf{B}$	ρ _{BCP}	H _{BCP}	δ(A,B)
(GeCl ₂) ₂	Ge···Cl	0.060 - 0.064	-0.020 - 0.023	0.573-0.622
$(GeBr_2)_2$	$Ge \cdots Br$	0.055 - 0.059	-0.019 - 0.021	0.625 - 0.670
GeCl ₂ -C ₄ H ₈ O ₂	Ge···O	0.070	-0.020	0.415
GeBr ₂ -C ₄ H ₈ O ₂	Ge···O	0.071	-0.020	0.428
$GeCl_2 - (C_4H_8O_2)_2$	Ge···O	0.050	-0.010	0.306
$GeBr_2 - (C_4H_8O_2)_2$	$Ge \cdots O$	0.051	-0.010	0.317

 $\rho(\mathbf{r})$ and $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ are one- and two-electron densities, respectively, the integrations are carried out here through two atomic basins. In other words, the delocalization index $\delta(A,B)$ shows the number of electrons delocalized between two atoms (A and B). Thus, it may be treated as the degree of covalency and as the number of shared electrons. The greatest $\delta(A,B)$ values are observed for the Ge···Cl/Br contacts, next for the Ge···O ones, which are greater in a case of one 1,4-dioxide molecule in the complex, and smaller for complexes containing two 1,4-dioxide molecules.

Figure 6 shows molecular graphs of the complexes of dibromogermylene with one and with two 1,4-dioxane molecules. For the former complex, the Ge-attractor is connected by bond paths with bromide attractors. This corresponds to the Ge-Br covalent bonds. Additionally, this Ge-attractor is linked by the bond path with the oxygen attractor, this is an interaction possessing the characteristics of the covalent bond, here, it was pointed out before that it is partly covalent in nature. The latter complex with two molecules of 1,4-dioxane possesses the same characteristics as the complex with one such molecule; however, here, two Ge \cdots O bond paths are observed that correspond to partly covalent interactions.

To take into account the greater part of the crystal structure, the system containing three GeCl₂ molecules and two 1,4-dioxane molecules was optimized (because it is a larger system than previous complexes, the ω B97XD/6-311++G(d,p) level was applied here). Figure 7 presents the corresponding molecular graph. One can see that three germanium dichloride molecules are not located in the plane as it is observed for the corresponding crystal structure [38]. This shows that the π -hole Ge···O tetrel bonds are very important in crystals of dichlorogermylene and dibromogermylene complexes with 1,4-dioxide to stabilize the planar layer of the dihalogen molecules [37,57,58].

Table 5 shows the natural bond orbital (NBO) approach [17,18] characteristics. One can see that the NBO charges of the germanium center in complexes with one or two 1,4-dioxane molecules only slightly differ from those of monomeric dihalogens. However, the charges of Ge-centers in dimers of dichlorogermylene and dibromogermylene are lower. It means

that the meaningful electron charge transfer from the neighboring halogens occurs here. In the case of the (GeCl₂)₂ and (GeBr₂)₂ dimers, the additional σ_{GeCl} or σ_{GeBr} bond orbital occurs, respectively. In the case of complexes with one 1,4-dioxide molecule, the additional σ_{GeO} bond orbital is observed. In other words, one can consider the germanium centers as trivalent ones. In the case of complexes with two 1,4-dioxide molecules, only two bond orbitals occur for each of the Ge-centers. The Ge···O interactions are too weak here to form bonds; instead the orbital-orbital n(O) $\rightarrow \pi_{Ge}^*$ interactions occur, thus the germanium centers are divalent. The huge energies of these interactions are observed, they exceed 80 kcal/mol (Table 5).



Figure 6. The molecular graphs of (**a**) GeBr₂-C₄H₈O₂ and (**b**) GeBr₂-(C₄H₈O₂)₂; big circles correspond to the attractors (red—oxygen, brown—bromine, grey—germanium, white—hydrogen), small green circles to the bond critical points and red circles to the ring critical points; solid and broken lines indicate bond paths.



Figure 7. The molecular graph of $(GeBr_2)_3$ - $(C_4H_8O_2)_2$; big circles correspond to the attractors (red—oxygen, green—chlorine, grey—germanium, white—hydrogen), small green circles to the bond critical points and red circles to the ring critical points; solid and broken lines indicate bond paths.

Table 5. The NBO BP86-D3/TZ2P results of calculations. The charge of Ge center is given and the extra bond orbital of the divalent Ge center changes into a trivalent one. In the latter case, the polarization (Pol) of the extra bond orbital is presented (percentage of the electron density at the Ge center). In complexes with two 1,4-dioxane molecules, the orbital-orbital overlap is given with the corresponding interaction of energy.

Species	Charge (Ge)	Extra Orbital	Pol
$(GeCl_2)_2 (GeBr_2)_2 GeCl_2-C_4H_8O_2 GeBr_2-C_4H_8O_2$	0.751–0.773	σ _{GeCl}	15.0–16.1
	0.574–0.593	σ _{GeBr}	17.5–18.8
	0.819	σ _{GeO}	7.8
	0.695	σ _{GeO}	8.1
Species	Charge (Ge)	Interaction	Energy
GeCl ₂ -(C ₄ H ₈ O ₂) ₂	0.818	$\begin{array}{c} n(O) \rightarrow {\pi_{Ge}}^{*} \\ n(O) \rightarrow {\pi_{Ge}}^{*} \end{array}$	84.2
GeBr ₂ -(C ₄ H ₈ O ₂) ₂	0.702		89.6

It is worth mentioning that the additional bond orbitals for complexes with one 1,4dioxide molecule and for the (GeCl₂)₂ and (GeBr₂)₂ dimers are strongly polarized. Table 5 shows the percentage of the charge of these orbitals (related to the germanium center). These results show that the electron charge is accumulated here at the halogen centers.

4. Summary and Conclusions

It seems that in the case of metallylenes, the electron donor properties are revealed for carbenes and hardly for silylenes. This is probably connected with the greater contribution of the p-character of the lone electron pair orbital of the tetrel center. For metallylenes that contain the heavier tetrel element, this lone pair possesses mostly the s-character that results in the lack of Lewis base properties of the tetrel center. This is nicely visible for the dihalometallylenes where the electrostatic potential maps show the Lewis base properties for carbenes and the strongest Lewis acid properties of the tetrel centers related to the areas of π -holes.

The Cambridge Structural Database search shows that for structures of metallylenes where the tetrel center acts as the Lewis acid, about 20% of structures are dihalometallylenes. The divalent tetrel center in the latter structures participates additionally in three or four interactions that possess the partly covalent in nature character. This corresponds to the trigonal bipyramid or octahedron tetrel configuration, respectively. In general, the additional σ -hole or π -hole interactions for the tetrel center often lead, if they are strong enough, to the change of one configuration into another one [65]. Here, the trigonal structures (two covalent bonds and one lone electron pair) of dihalometallylenes change into other configurations.

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