

# Bonding Properties of Amidinate Complexes of the Group 14 Elements Silicon, Germanium, Tin, and Lead in Their Divalent and Tetravalent Oxidation States<sup>†</sup>

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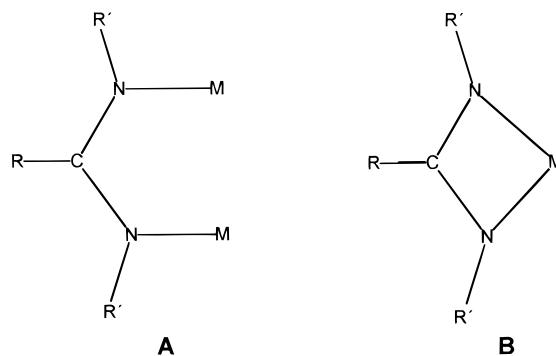
The mono- and bidentate formation of the amidinate ligands toward the main group elements silicon, germanium, tin, and lead is studied with quantum chemical methods. In accordance with the experimental investigations the bisamidinate complexes of the higher element homologues Pb and Sn in their divalent oxidation states adopt  $C_2$  symmetrical structures, with a distorted trigonal bipyramidal ( $\Psi$ -tpb) arrangement. The formation of a pseudo-trigonal bipyramid is less favorable with the lighter elements Si and Ge; the resulting structures easily undergo Jahn–Teller distortion to  $C_1$  symmetrical structures in which the axial bonds become unsymmetrical. A structural rearrangement from  $C_2$  to  $C_{2v}$  symmetry is even feasible and causes a facile degenerate rearrangement in which the nitrogens in the amidinate ligands become positionally equivalent. The effect of substituents on these different structures is discussed. An analysis of the electron distributions (natural bond orbital populations, Laplacian of the charge densities) establishes for these compounds a strongly positive charged central atom ( $M = \text{Si, Ge, Sn, Pb}$ ), weakly chelated by the surrounding amidinate ligands. The equilibrium between chelated and covalent bound structures is discussed on the basis of a bond stretch formalism. Structural predictions are also made for ligands isoelectronic to the amidinate anion  $[\text{HNCR}'\text{NR}]^-$ , (e.g.,  $[\text{HPCHPH}]^-$ ,  $[\text{HNSiHNNH}]^-$ , and  $[\text{OCHO}]^-$ ). Accordingly, bisamidinate-like structures are promoted with increasing difference in electronegativity between the central atom (Si, Ge, etc.) and the neighboring chelating atom ( $\text{P} < \text{N} < \text{O}$ ). The design of structures with a tetrahedral environment of the central atom in which the nonbonding s-orbital is stereochemically not active is discussed. Such conformations possess large open shell character as tested by the electron correlated methods and MCSCF calculations and are promoted by chelating ligands with an inherent weak  $\pi$ -allylic system. The matter is tested for silicon as central atom for the homologous bisamidinate complex.

## Introduction

The coordination chemistry of the amidinate ligand  $[\text{RNCR}'\text{NR}]^-$  ( $\text{R, R}' = \text{H, alkyl, aryl, SiMe}_3$ , etc.) is well established, especially for transition metal complexes.<sup>1,2</sup> For these the most common are the bridging (**A**) and chelating (**B**) forms (Scheme 1).

For the group 14 elements the amidinate chemistry has been hitherto reported in detail for tin and lead.<sup>3–8</sup> Silicon and germanium compounds are scarcely known, but recently their chemistry has begun to be explored in the prolific work of Karsch et al.<sup>9,10</sup> For silicon bidentate coordination has been deduced earlier on the basis of nuclear magnetic resonance investigations.<sup>11</sup> The importance of the amidinate chemistry of group 14 elements, in particular of silicon, lies in their use for CVD methods<sup>12</sup> and for the synthesis of catalysts.

## Scheme 1

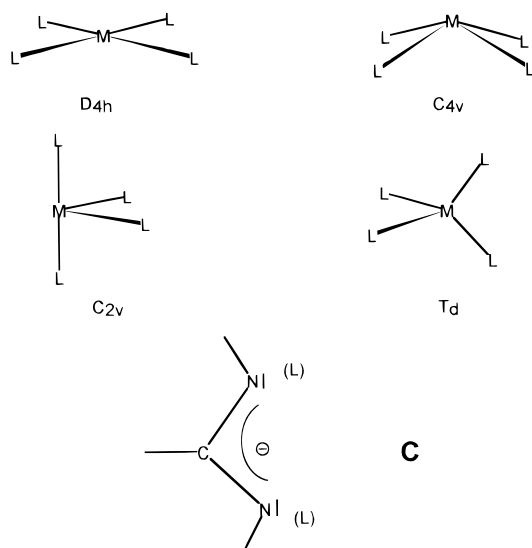


On the basis of these aspects we investigated in detail the class of main group amidinate complexes by quantum chemical methods. We will report here the results of ab initio calculations on amidinate complexes of silicon, germanium, tin, and lead in their (formal) divalent and tetravalent oxidation states, utilizing effective core potentials for the description of the higher main group elements. Our study focuses on the following aspects: (a) mono- versus bisamidinate complexation, (b) an analysis of the complexes with regard to various geometrical arrangements, tetrahedral ( $D_{2d}$ ), planar ( $D_{2h}$ ), or pyramidal ( $C_{2v}$ ,  $C_2$ ) at the

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## Scheme 2

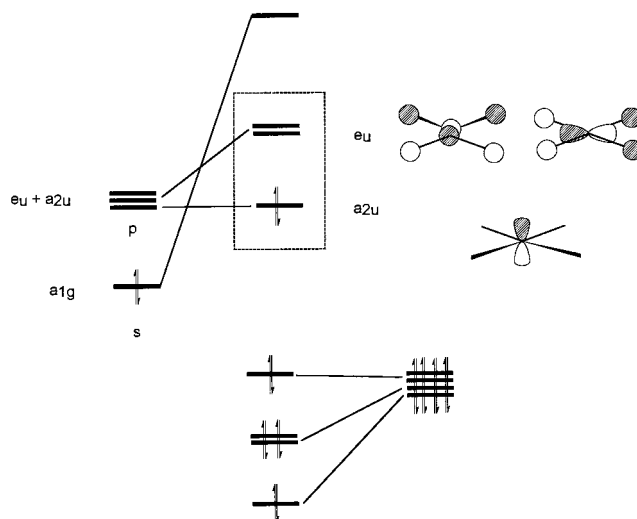


central atom, and (c) the degenerate, positional rearrangement of the bisamidinate complexes. In addition we will reveal (d) the particular role of the ligand on the preferred equilibrium geometry of the resulting complex. It will be shown that the actual geometries of the divalent bisamidinate complexes depend strongly on the choice of the ligands. It is possible to change the equilibrium structures from a pseudo-trigonal bipyramidal ( $\Psi$ -tbp) environment to corresponding tetrahedral structures. On this basis new bonding facets for the amidinate complexes emerge. Details of the quantum chemical methodology are given in the Theoretical Section of this article.

## Results and Discussion

**a. Ligand Field of p-Block Elements.** It is very instructive to begin the analysis with a consideration of the complexation of the central element M (Si, Ge, Sn, Pb) in a ligand field.<sup>13</sup> A priori in the discussion the following different structures have to be included (Scheme 2).

A central atom M constituted of a group 14 element (Si, Ge, Sn, Pb) can be surrounded by a planar ( $D_{4h}$ ), pyramidal ( $C_{4v}$ ), pseudo-trigonal bipyramidal ( $C_{2v}$ ), or tetrahedral ( $T_d$ ) environment by ligands L which at times refer to two-electron donors. In the experiment the ligands L are the amidinate ligands C. [As a consequence, which will be evaluated in detail in a later section of our article, the resulting amidinate geometries are confined to lower symmetry equivalents,  $D_{4h} \rightarrow D_{2h}$ ,  $C_{4v} \rightarrow C_{2v}$ ,  $C_{2v} \rightarrow C_2$ ,  $T_d \rightarrow D_{2d}$ .] To first order in this simplified view the two-electron donors are represented by the nonbonding lone pairs at the nitrogens of the amidinate ligands. In practice however, the molecular orbital system of the latter possesses  $\sigma$ - and  $\pi$ -type donor orbitals, composed of nonbonding orbitals at the nitrogens and  $\pi$ -orbitals at the heteroallyl system. In more detail these will be analyzed in the next section. Experimentally the trigonal bipyramidal structure ( $\Psi$ -tbp) of the bisamidinate compounds is shown to be the most stable species. It is a geometry with an active nonbonding lone pair orbital at the central atom M. However we will explore on the basis of the ab initio calculations other structural types with a tetrahedral geometry at M. These can be induced by a suitable choice of substituents which are isoelectronic to the amidinate ligand, but possess weaker allylic  $\pi$ -systems.



**Figure 1.** Interaction between  $M^{2+}$  and  $4H^-$ , resulting in  $MH_4^{2-}$  ( $D_{4h}$  symmetry).

We begin our considerations with an analysis of the molecular orbital system of the planar structure (with  $D_{4h}$  symmetry). If we consider for the sake of simplicity first the ligand L as a simple two-electron  $\sigma$ -donor ( $H^-$ ) (it refers at times to one nitrogen atom in the amidinate ligand) in the ligand field,<sup>14</sup> the s- and p-orbitals of the central atom are confined to  $a_{1g}$  (s),  $a_{2u}$  ( $p_z$ ), and  $e_u$  ( $p_x, p_y$ ) representations.<sup>15</sup> Overall the resulting  $ML_4$  refers formally to a  $MH_4^{2-}$  system of which the molecular orbitals are well described.<sup>16</sup> Interaction with the  $\sigma$ -type ligand orbitals causes a destabilization of the s- and  $p_x, p_y$ -orbitals at M, while its  $p_z$ -orbital is not effected, as shown in an interaction diagram in Figure 1. The considerations are extracted from EH calculations.

In this simplified picture two electrons are arranged on each ligand, while two more electrons remain at the central atom, i.e., in the s-orbital. In other words the central atom adopts formally a divalent oxidation state. The ligands possess a block of molecular orbitals that are doubly occupied. Upon mutual interaction the orbitals are lowered while the orbitals at the central atom are raised in energy. For symmetry reasons only the  $a_{1g}$  (s) and the  $e_u$  set ( $p_x, p_y$ ) orbitals are destabilized. As a result, a closed shell system is obtained with the  $p_z$ -orbital as HOMO and the  $p_x, p_y$ -orbitals as LUMO (dashed lines in Figure 1). Overall these considerations refer to a  $M^{2+}$  central atom surrounded by four  $H^-$  atoms, resulting in a hypothetical  $MH_4^{2-}$  system.<sup>16</sup>

In the  $C_{4v}$  symmetrical arrangement of ligands the frontier orbitals can mingle with each other such that s-character is admixed to the HOMO, and it becomes a nonbonding lone pair. The bonding situation is depicted in Scheme 3.

The possible interaction between the HOMO and the LUMOs at the given  $C_{4v}$  symmetry causes an increase of the energy differences among these orbitals, thus an increase in the closed shell character of the  $C_{4v}$  symmetrical structure, as compared with the  $D_{4h}$  symmetrical congener.

In the pseudo-trigonal bipyramid ( $C_{2v}$  symmetry) the action of the ligand field with the s- and p-orbitals at M is sketched in Scheme 4.

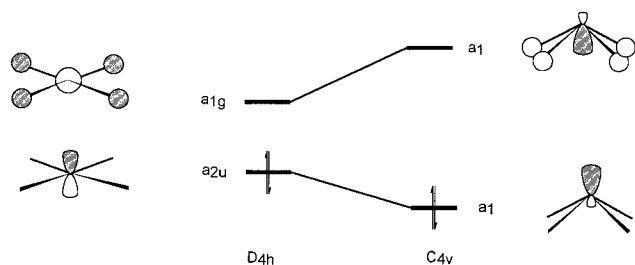
(14) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985.

(15) Engelke, F. *Aufbau der Moleküle*; Teubner: Stuttgart, 1985.

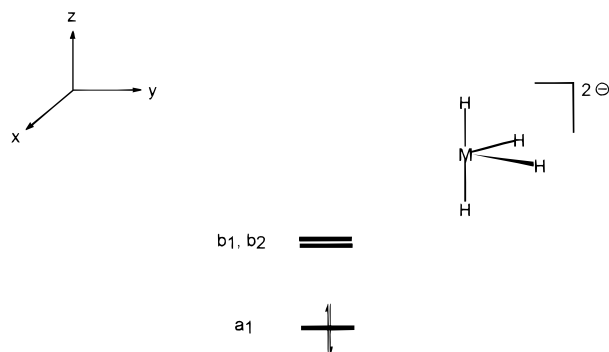
(16) The molecular orbital system of a  $MH_4$  unit is lucidly described in the textbook: Gimarc, B. M. *Molecular Structure and Bonding*; Academic Press: New York, 1979.

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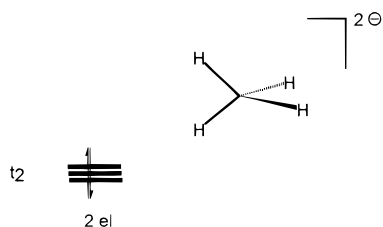
Scheme 3



Scheme 4



Scheme 5



According to the symmetry considerations<sup>15</sup> the p-orbitals at M split into  $a_1$ ,  $b_1$ , and  $b_2$ . In more detail the resulting molecular orbitals are part of the full set of molecular orbitals of the trigonal bipyramid.<sup>16,17</sup> The equatorially located ligands force M to form three  $sp^2$ -orbitals; two refer to two-electron bonds while the third one is the nonbonding lone pair  $sp^2$ -orbital at M. The  $p_z$ -orbital forms a bonding ( $a_1$ ) and antibonding ( $a_1$ ,  $b_2$ ) set of orbitals with s and  $p_z$  at M. We note that overall the resulting axial bonds refer to a three-center bond occupied by four electrons.<sup>17</sup>

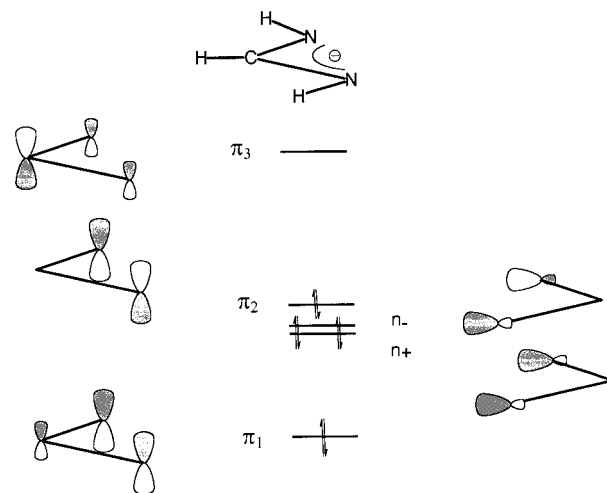
Of further interest is the tetrahedral geometry ( $T_d$ ), as shown in Scheme 5.

The p-orbitals form the  $t_2$ -set which is occupied by two electrons. Consequently for this geometry an open shell configuration should result. How to cope with such an arrangement in order to bring it to a stable geometry will be evaluated in section c in more detail.

**b. Monoamidinate Formation.** Hitherto the considerations are restricted to  $\sigma$ -effects, i.e.,  $\sigma$ -donation of the lone pair orbitals toward the empty p-orbitals at the central atom. We will now study the amidinate complexation. It is informative to begin with a first analysis of monoamidinate formation. Experimentally, these compounds are known in a high oxidation state as trichloro compounds.<sup>5</sup> The relevant frontier orbitals of an amidinate fragment are as follows (Scheme 6).

The amidinate ligand  $[\text{HNCHNH}]^-$  possesses an allylic system, formed by the orbitals  $\pi_1$  to  $\pi_3$ . In addition two lone

Scheme 6



pair orbitals,  $n_+$  and  $n_-$ , are present. These refer to approximate  $sp^2$  hybrid orbitals. Consequently they are slightly below the energy of the nonbonding  $\pi_2$  molecular orbital.

The formation of a monoamidinate complex with the element M was studied first with EH calculations. The interaction of the  $\sigma$ -type orbitals ( $n_+$ ,  $n_-$ ) with the orbitals at M is essentially larger than the  $\pi$ -type ( $\pi_1$  to  $\pi_3$ ) interactions. Thus it gives support for the simplified considerations emerging from the ligand field model. Further details will not be given here.

A modeling of the monoadduct formation using effective core potentials (MP2/ECP-31G\* level of optimization, see Theoretical Section) gives the following equilibrium bonding parameters (Figure 2).

With respect to the parent anion (all bond lengths are in angstroms, bond angles in degrees) the coordination causes a considerable shrinking of the angle  $\angle\text{NCN}$  and the corresponding CN bonds of the ligand are elongated (ca. 0.1 Å) upon coordination. The compression in the angle  $\angle\text{NCN}$  increases in the order of the decreasing atomic size of the element M ( $\text{Pb} < \text{Sn} < \text{Ge} < \text{Si}$ ). A vibrational analysis supports M = Sn and Pb structures (with  $C_{2v}$  symmetry) as true energy minima on the corresponding electronic hypersurfaces. For M = Si and Ge at times one weak imaginary vibration is observed, which refers to the induction of  $C_2$  symmetrical distortion of the  $C_{2v}$  symmetrical geometries. The tendency for symmetry reduction  $C_{2v} \rightarrow C_2$  is rather weak (Si  $\Delta E = -0.2$ , Ge  $\Delta E = -0.3$  kcal/mol, at the MP2 level with zero-point vibrational energy corrections). We should note here that a similar  $C_2$  symmetrical distortion (from  $C_{2v}$  to  $C_2$  symmetry) has recently been discussed for (isoelectronic) lithium coordinated allyl anions.<sup>18</sup>

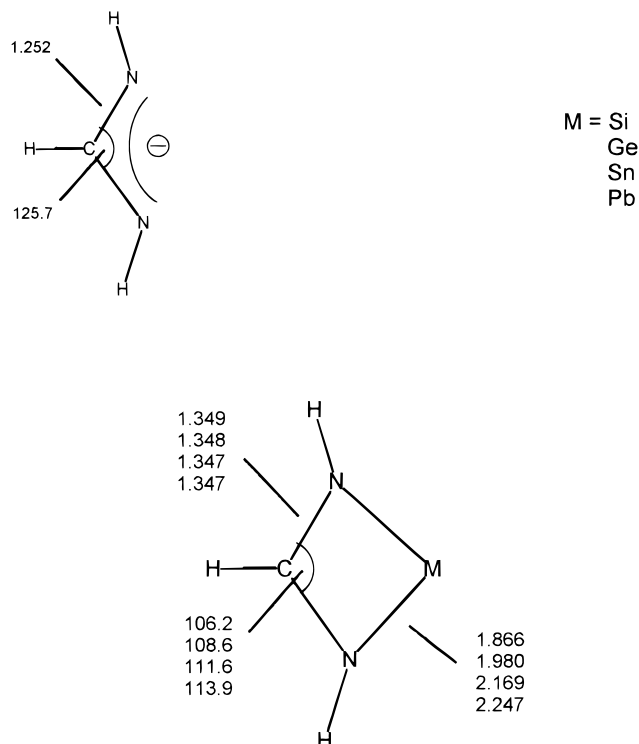
It is of interest to inspect also the results of the population analysis of the monodentate complexes (Figure 3).

The metals bear charges that are larger than +1. In other words electron density is withdrawn from M to the neighboring nitrogen atoms. The bond orders of the MN bonds (Wiberg bond indices) are approximately 0.5. In the ligand the double-bond character of the allyl system is preserved. Overall the population analysis supports the formulation of these complexes within a donor-acceptor description as presented in Scheme 7.

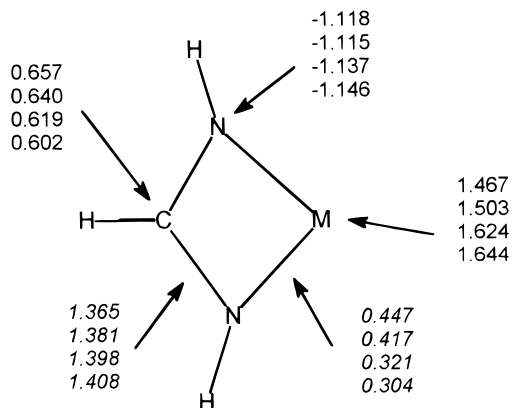
A similar view on bonding has been invoked in an analysis of the anionic Arduengo-type carbenes with the group IIIA

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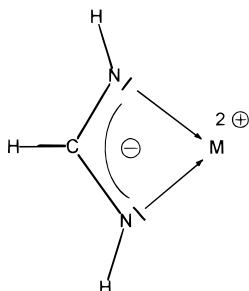


**Figure 2.** Equilibrium parameters (bond lengths in angstroms, bond angles in degrees) of monoamidinate adducts.

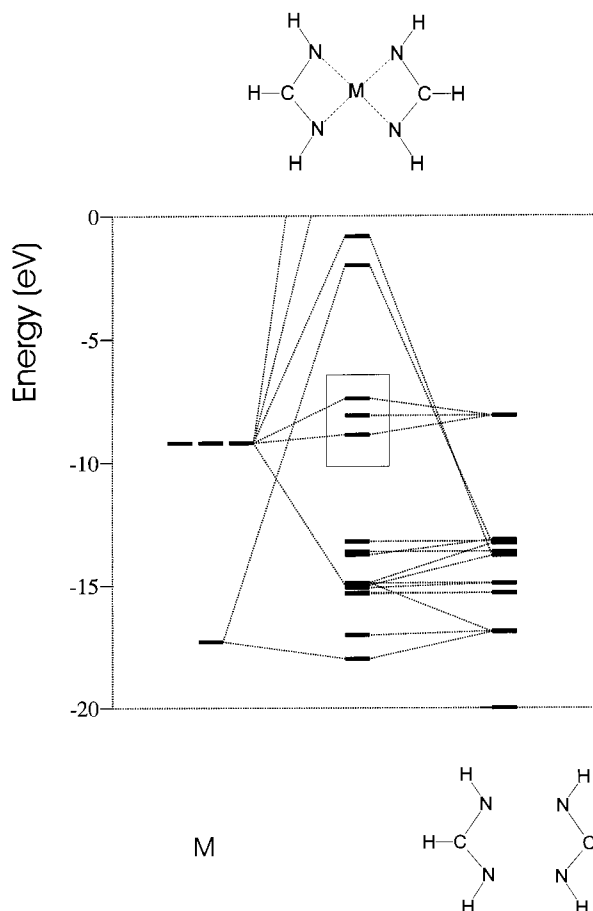


**Figure 3.** Population analysis of monoadducts; NBO charges and Wiberg bond indices (in *italics*).

#### Scheme 7



elements boron to indium.<sup>19</sup> The donor–acceptor formulation is in accord with further analysis of the Laplacian of the electron density distribution,<sup>20</sup> as well as a supplementary analysis of



**Figure 4.** Planar bisamidinate formation ( $D_{2h}$  symmetry) of  $M = \text{Si}$ , from EH calculations.

the electron localization function (ELF).<sup>21</sup> Details will not be given here.

While the amidinate ligand is now a well-established reagent,<sup>2</sup> in particular in the form of the N-silylated benzamidine derivative,<sup>22</sup> we will reveal that other valence isoelectronic chelating ligands exist, which promise hitherto unknown bonding facets on the structures of the resulting complexes.

**c. Bisamidinate Formation.** The monoadduct formation of an amidinate ligand (or a valence isoelectronic congener) with a main group element M leads to coordinatively unsaturated complexes. In the experimental situation the coordination sphere is further saturated with chlorines<sup>4–6</sup> and/or further addition of a second amidinate ligand. In the present section we will analyze bonding in the bisamidinate complexes,<sup>8</sup> resulting in a formal divalent oxidation state of the central atom M.

It is again informative to start the analysis with an analysis of bonding in the planar bis-coordinated structure. The relevant frontier orbitals of the ligands are constituted by positive and negative combinations of the molecular orbitals of the individual ligands (see Scheme 2). A corresponding interaction diagram, extracted from EH calculations, of the ligand orbitals (fragment A) with those of the central atom (M) is given in Figure 4. The three frontier orbitals HOMO, LUMO, and LUMO+1 are indicated by solid lines.

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**Table 1.** Relative Energies (in kcal/mol) for Bisamidinate Complexes at Various Symmetry Restrictions

symmetry	Si	Ge	Sn	Pb
$C_2$	0.0	0.0	0.0	0.0
$C_1$	-0.9	-0.1		
$C_{2v}$	6.7	6.1	2.4	1.6
$D_{2h}$	39.2	75.0	81.2	140.6

The highest occupied molecular orbital (HOMO) is now constituted by the  $p_z$ -orbital at the central atom M destabilized by weak antibonding interaction with the  $\pi$ -type orbitals of the two ligands. On the other hand the lowest unoccupied molecular orbital (LUMO) refers to an antisymmetric combination of the  $\pi_2$  molecular orbitals of the ligands. Of interest is the energetically next higher molecular orbital (LUMO+1). It refers to the  $s$ -orbital at the central atom M which is mingling in an antibonding manner with the positive combination of  $\sigma$ -type orbitals at the ligands.

The planar,  $D_{2h}$  symmetrical structures are in fact not energy minima on the electronic hypersurfaces. Energy-optimized ab initio calculations of the various bisamidinate complexes were performed within the constraints of  $D_{2h}$ ,  $C_{2v}$ , and  $C_2$  symmetry. The resulting relative energies (MP2(fc)/ECP-31G(d), with zero-point energy vibrational corrections) are collected in Table 1. The lowest energy conformation is the  $C_2$  symmetrical  $\Psi$ -tpb geometry; its equilibrium bonding parameters (bond lengths in angstroms, bond angles in degrees) are recorded in Table 2.

In all cases of M the  $D_{2h}$  symmetrical structures are highest in energy. The tendency toward pyramidalization increases with increasing atomic weight of the central atom (Si < Ge < Sn < Pb). Interestingly the  $C_2$  and  $C_{2v}$  symmetrical structures are similar in energy. They become energetically more equivalent in the opposite order of M. The  $C_{2v}$  symmetrical structures are first-order saddle points, thus transition-state geometries for the rearrangement  $C_2 \rightarrow C_{2v} \rightarrow C_2$ , etc. One must note that in the  $C_{2v}$  geometries the amidinate ligands are equivalent. Our findings are in conformity with the results of the experimental investigations<sup>8</sup> which in solution evidence facile rearrangements of the ground-state structures. The  $C_2$  symmetrical geometries adopt in their lowest energy conformations distorted pseudo-trigonal bipyramids ( $\Psi$ -tpb), as has been established by X-ray investigations. The angle of the two axial bonds  $\angle\text{NMN}$  decreases with increasing atomic weight of M (Si < Ge < Sn < Pb). This reflects the tendency to approach the  $C_{2v}$  symmetrical geometries. For all cases the axial bonds are longer than the equatorial ones. Our investigations predict for M = Si and Ge with the parent amidinate ligands (i.e., all substituents at the nitrogen and carbon atoms are hydrogens) an easy distortion from  $C_2$  to  $C_1$  symmetry; thus the two axial MN bonds become unsymmetrical (Si 1.944, 3.102 Å; Ge 2.217, 2.685 Å), although the energy differences between  $C_2$  and  $C_1$  symmetrical structures are negligible (see Table 1). The CN bonds in the complexes (1.33–1.35 Å) are almost the same as those in the free anion (1.352 Å,  $\angle\text{NCN} = 125.7^\circ$ ,  $C_{2v}$  symmetry). As will be shown in a later section of this work, substituents exert considerable effects on the various possible geometries of these species.

Hitherto, experimental investigations have only been reported for M = Ge.<sup>9</sup> These favor a  $C_2$  symmetrical geometry in the bisamidinate complex. The calculated equilibrium geometries, i.e., the MN bonds of the higher element homologues M = Sn and Pb, are slightly different from the results of the X-ray investigations. In practice the structures are protected by bulky substituents, to stabilize these compounds kinetically. On this basis the actual geometries may be superimposed by substituent

effects. Since we are interested in an analysis of principal bonding effects, our investigations will not be affected by this.

Finally we will record the population analysis for the  $C_2$  symmetrical geometries. They are given in Table 2 in parentheses. The trend for polar bond formation between the central atom M and the neighboring nitrogen atoms is even attenuated in the bisamidinate complexes as compared with monochelation. The central atom bears a positive charge, larger in magnitude than 1; all neighboring nitrogen atoms are bound to the central atom by fractional single bonds. They are even very weak for the axial bonds; for example, for M = Pb the axial bonds are 0.181, weaker than a half bond.

**d. Tetrahedral geometry.** All of the computed chelate structures adopt a  $\Psi$ -tpb geometry, **a**, in accord with the experimental investigations.<sup>8</sup> A  $C_{2v}$  symmetrical structure, **b**, is always close in energy. In both structural types the lone pair at the central atom M is stereochemically active. The experimental as well as the theoretical investigations did not give any hint to a tetrahedrally coordinated species, as drawn in **c** (Schemes 8, 9).

What is the reason for this? A first answer to this question has been already given by the ligand field considerations (see section a). For the tetrahedral environment an open shell configuration is expected. This view is also more substantiated by a Walsh diagram for rotation of the trigonal bipyramidal geometry to the tetrahedral geometry and is recorded in Figure 5.

Upon rotation from the  $\Psi$ -tpb geometry (Figure 5, left) toward the  $D_{2d}$ -shaped structure (right), the two molecular orbitals HOMO and LUMO become degenerate. They stem from the  $\pi_3$  molecular orbitals of the amidinate allylic system and refer to a degenerate set of nonbonding orbitals located at the amidinate ligands (see Scheme 9), **e**. At first glance such a geometry seems to be out of range for a stabilization with a suitable choice of the substituents. Nevertheless the canonical structure **e** differs from **d** in an essentially stronger MN bond; for example, the matter is substantiated in the enormous bond energy of a SiN bond,<sup>23</sup> which is known to increase with increasing number of electronegative atoms (substituents) attached to the same central atom.<sup>24</sup> Thus there is a strong driving force for induction of a tetrahedral geometry, as sketched in the canonical structure **e**. The MN bonds in the tetrahedral structures possess more  $s$ -character than in the trigonal bipyramidal geometries. A further factor that may promote **e** over **d** is given in ligands with a weaker  $\pi$ -system. The two canonical structures **e** and **d** differ in the released  $\pi$ -system of the latter.

In more detail for the latter case a covalent structure can be viewed as bond stretching<sup>25</sup> from a donor–acceptor complex to a covalently bound limiting structure, as drawn in **d** versus **e** for the bisamidinate complex. The canonical structure **d** is closed shell and can adequately be described by the given MP2 level. On the other hand the canonical structure **e** refers to a biradical structure. If structure **e** adopts  $D_{2d}$  symmetry, it would possess biradical character; that is, a triplet would be the energy lowest state. However if structure **e** further reduces to  $C_2$  symmetry, which can be induced by pyramidalization at the carbon atoms where the single electrons reside, a quasi closed shell system is promoted. The modeling of these structures by the quantum chemical calculations (see below) indicates that this is the case.

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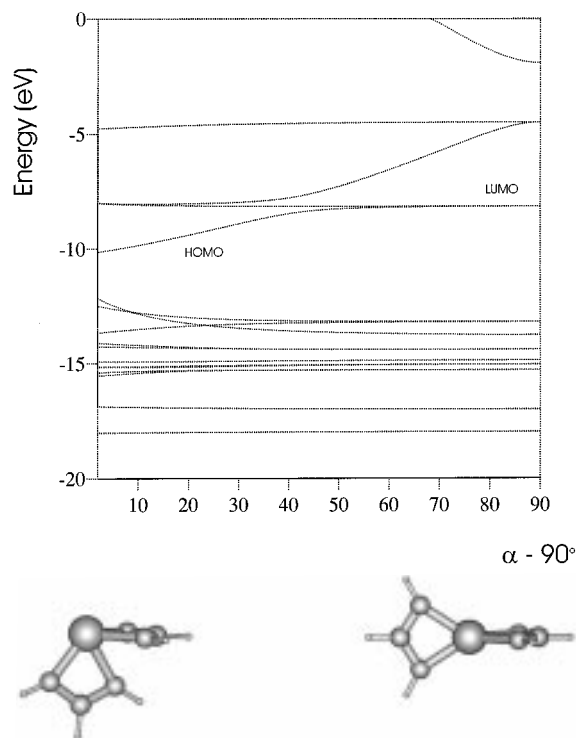
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**Table 2.** Equilibrium Geometries ( $C_2$  Symmetry) of Bisamidinato Complexes (Bond Lengths in Å, Bond Angles in deg), Wiberg Bond Indices between Bonds (in *Italics*), and Charges in Central Atom (in *Italics*, at Bottom)

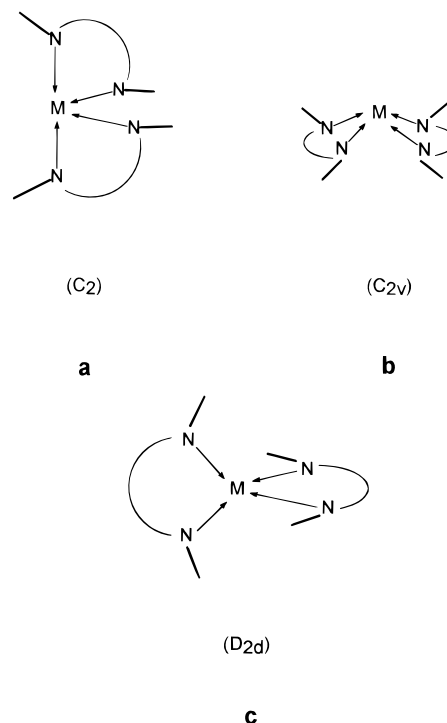
bonding parameter <sup>a</sup>	Si	Ge	Sn	Pb
M–N (ax)	2.175 ( <i>0.250</i> )	2.310 ( <i>0.204</i> )	2.422 ( <i>0.192</i> )	2.448 ( <i>0.181</i> )
M–N (eq)	1.874 ( <i>0.448</i> )	1.986 ( <i>0.422</i> )	2.184 ( <i>0.333</i> )	2.270 ( <i>0.309</i> )
$\angle$ N(ax)MN(ax)	139.2	134.6	127.8	126.2
$\angle$ N(eq)MN(eq)	101.1	97.2	95.2	94.4
NC <sup>b</sup>	1.334 ( <i>1.383</i> )	1.332 ( <i>1.537</i> )	1.334 ( <i>1.516</i> )	1.335 ( <i>1.507</i> )
NC <sup>c</sup>	1.351 ( <i>1.333</i> )	1.350 ( <i>1.333</i> )	1.349 ( <i>1.364</i> )	1.348 ( <i>1.383</i> )
charge at M	( <i>1.210</i> )	( <i>1.273</i> )	( <i>1.394</i> )	( <i>1.436</i> )

<sup>a</sup> ax = axial, eq = equatorial. <sup>b</sup> Adjacent to axial MN bonds. <sup>c</sup> Adjacent to equatorial MN bonds.

**Figure 5.** Walsh diagram for formation of a tetrahedral ( $D_{2d}$ ) geometry from the  $\Psi$ -tpb structure ( $C_2$ );  $\alpha$  is the angle between the bisectors of the  $\angle$ NMN angles of the two four-membered rings.

Experimentally, a variety of possible anionic ligands which are valence isoelectronic with the amidinate system have been reported during the last years (e.g., see the recent discussion in ref 18). We have probed the possible tetrahedral structure formation for the ligands  $[\text{HNSiHNNH}]^-$  (**D**) and  $[\text{HNP}_2\text{NH}]^-$  (**E**) with  $M = \text{Si}$ . The ligand **D** possesses a weaker  $\pi$ -system than the amidinate ligand, and **E** is even lacking a  $\pi$ -system. The results of the ab initio calculations are collected in Table 3.

The ab initio calculations (MP2/ECP-31G\*) were performed without any symmetry constraints. First of all they reveal that substituents at the amidinate ligand **C** either at the nitrogen or at the carbon atoms exert a strong effect on the resulting equilibrium geometry. A strong asymmetrical (**C** =  $[\text{HNCHNH}]^-$ ,  $R(\text{N}) = \text{H}$ ;  $R(\text{C}) = \text{H}$ ) or a more symmetrical (**C**,  $R(\text{N}) = \text{F}$ ,  $\text{CH}_3$ ,  $\text{SiH}_3$ ;  $R(\text{C}) = \text{H}$ ) structure for the two axial bonds is obtained. However, for the case of the amidinate ligand (**C**)  $\angle$ N<sub>ax</sub>MN<sub>ax</sub> is always larger than  $\angle$ N<sub>eq</sub>MN<sub>eq</sub>, indicating the formation of a  $\Psi$ -tpb structure. In contrast to this, the angle between axial and equatorial bonds for the ligands **D**,  $[\text{HNSiHNNH}]^-$ , and **E**,  $[\text{HNP}_2\text{NH}]^-$ , becomes equal. This evidences a considerable structural change from the  $\Psi$ -tpb to the tetrahedral structures. This is also substantiated by structural

**Scheme 8**

plots of the computed geometries, as shown in drawings generated with the Molden program<sup>26</sup> for two relevant geometries (Figure 6), the bisamidinate (top) and the bisilyamidinate (bottom) complexes.

The latter structure possesses strongly pyramidalized silicon atoms, a well-known facet of silyl radicals.<sup>27</sup>

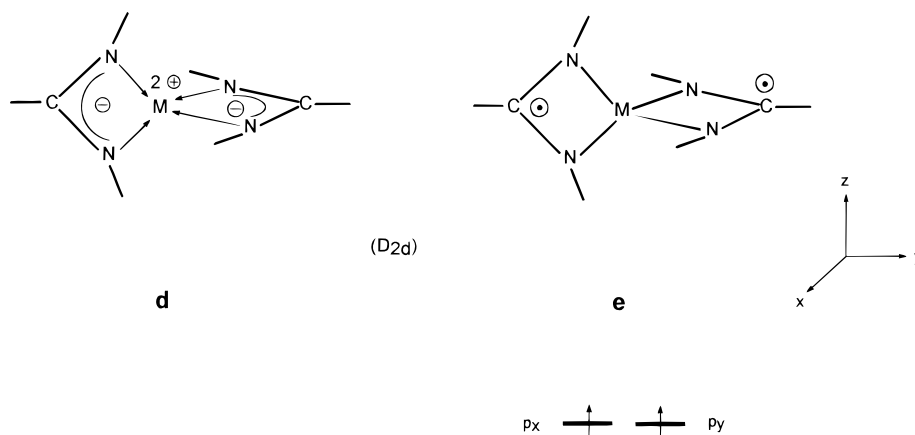
We have further investigated the possible tetrahedral ( $D_{2d}$ ) structures with MCSCF calculations. According to the qualitative model (see section a), these adopt open shell geometries. The structure **e** (with two amidinate ligands,  $D_{2d}$  symmetry imposed) prefers for the whole variety of  $M = \text{Si}$ ,  $\text{Ge}$ ,  $\text{Sn}$ ,  $\text{Pb}$  a triplet ground state ( $^3B_1$ ), almost similar in energy to the corresponding singlet states ( $^1A_1$ ) ( $\Delta E \leq -0.5$  kcal/mol, at the CAS(2,2) MCSCF level with CI correction at the given MCSCF wave functions). More details of the MCSCF calculations are given in the Appendix.

Hence, likely candidates for the achievement of tetrahedral structure or distortion of the trigonal bipyramid in the direction of tetrahedral conformations are as follows (Scheme 10).

(26) Program Molden written by Schaftenaar, G.: [www.caos.kun.nl/~schaft/molden/molden.html](http://www.caos.kun.nl/~schaft/molden/molden.html).

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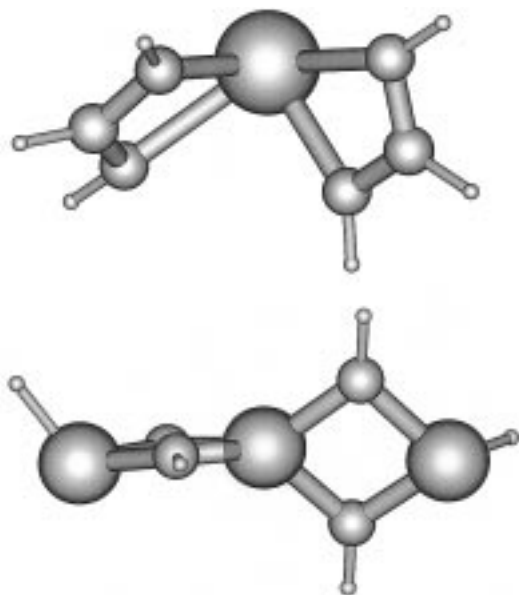
## Scheme 9



**Table 3.** Equilibrium Geometries (Bond Lengths in Å, Bond Angles in deg) of Substituted Bisamidinate Complexes and Homologues, with M = Si

ligand	R(N)	R(C)	MN <sub>ax</sub>	Mn <sub>eq</sub>	∠N <sub>ax</sub> MN <sub>ax</sub>	∠N <sub>eq</sub> MN <sub>eq</sub>
C <sup>a</sup>	H	H	1.994; 3.108	1.980; 1.796	142.9	100.2
C	F	H	2.263; 2.093	1.903; 1.939	131.3	97.7
C	CH <sub>3</sub>	H	2.206; 2.183	1.875; 1.881	142.4	102.5
C	SiH <sub>3</sub>	H	2.194; 2.181	1.898; 1.895	144.0	100.9
C	H	NH <sub>2</sub>	2.542; 2.039	1.849; 1.902	137.3	100.2
C	H	CN	2.140; 2.171	1.878; 1.873	139.9	101.0
D <sup>b</sup>	H	H	1.764; 1.764	1.761; 1.761	125.8	127.1
E <sup>c</sup>	H	H	1.742; 1.723	1.749; 1.761	134.0	123.9

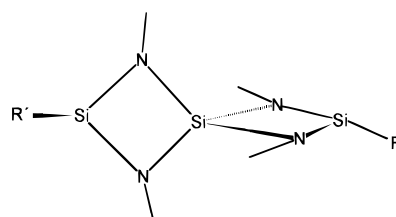
<sup>a</sup> C = HNCHNH<sup>-</sup>. <sup>b</sup> D = HNSiHNH<sup>-</sup>. <sup>c</sup> E = HNP<sub>2</sub>NH<sup>-</sup>.



**Figure 6.** MOLDEN plots of equilibrium geometries for bisamidinate complexes with silicon (top) and of bis-silaamidinate complexes with silicon (bottom).

It requires the presence of an allylic ligand with a weak  $\pi$ -system and substituents R' with a strong ability to stabilize a radical, e.g., phenyl, naphthyl, etc. The verification of this concept remains a challenge to the experimental chemist. We note that these considerations were evaluated for the case of M = Si. We expect that general tendencies for the formation of tetrahedral structures also hold for the higher element homologues with M = Ge, Sn, and Pb, but to less extent. It is, however, encumbered by the tendency to increase the stereochemical activity of the nonbonding s-orbital at M in the order

## Scheme 10



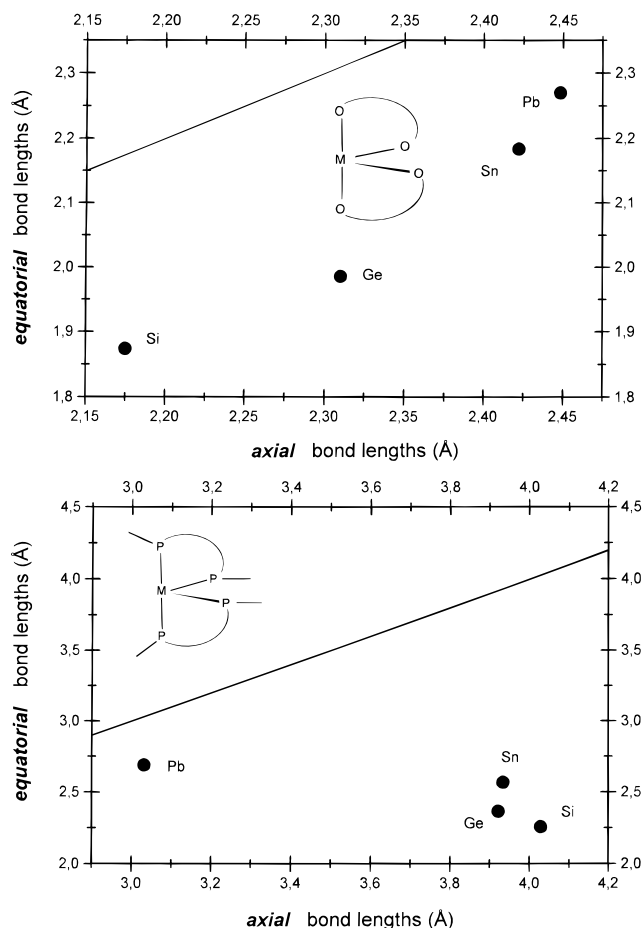
Si < Ge < Sn < Pb. This trend is manifested in the corresponding stabilities of MCl<sub>4</sub> structures to fragment into MCl<sub>2</sub> and Cl<sub>2</sub>.<sup>23</sup>

**e. Phosphidinato and Oxydinato Ligand.** Hitherto ligands were tested in which the central main group element M is surrounded by nitrogen atoms, as part of the amidinato ligands. For this case the MN bonds are extremely polar and possess only a small covalent bonding character. It is of interest to have knowledge about the operation of ligands with more or less electronegative terminal positions (than nitrogen), e.g., [OCHO]<sup>-</sup> and [HPCHPH]<sup>-</sup>. We have evaluated the equilibrium geometries of both types of ligands for the whole series M = Si, Ge, Sn, Pb. Experimental information on these ligands and their complexation behavior has not been recorded. For the former type of ligand ([OCHO]<sup>-</sup>) the  $\Psi$ -tpb conformation is adopted with two equal axial bonds (C<sub>2</sub> symmetry), as proven by corresponding vibrational analysis. For the latter ([HPCHPH]<sup>-</sup>) for M = Si the structure (C<sub>2</sub> symmetry) rearranges without activation energy to a planar all-trans conformation; in other words the axial bonds become extremely long as compared with the equatorial bonds.

A plot of axial versus equatorial bond lengths for the complete series of M is illustrated in Figure 7.

The solid line in the drawing refers to the bonding situation of equal axial and equatorial bonds; that is, the case of C<sub>2v</sub> geometries (structure **b** in Scheme 8) would be achieved. This extreme situation is not obtained but best approached for complexation of M with the ligands [OCHO]<sup>-</sup> and for M = Pb with [HPCHPH]<sup>-</sup>.

**f. Chlorine adducts.** For completeness we also included in our considerations structures within the formal +IV oxidation state of the central atom M (Si, Ge, Sn, Pb) since hitherto we considered only structures with the central atom M in its formal divalent state. In the experiment<sup>9</sup> two chlorines are added to the precursor compounds of the divalent bisamidinate complexes. A priori these can occupy (a) one axial and one equatorial position (structure I) or (b) simultaneously two axial



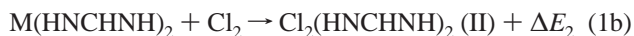
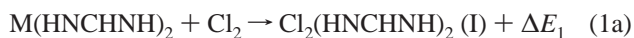
**Figure 7.** Axial versus equatorial bond lengths (in Å) in complexes with the ligands [OCHO]<sup>-</sup> (top) and [HPCHPH]<sup>-</sup> (bottom), for M = Si, Ge, Sn, and Pb (at the MP2/ECP-31G\* level). Solid lines indicate a bonding situation with equal equatorial and axial bond lengths.

**Table 4.** Energy Balances (in kcal/mol) for Reactions 1a,b, at the MP2/ECP-31G\* Level plus Zero-Point Vibrational Energy Corrections

M	reaction	$\Delta E$	$N^a$
Si	1a	-118.7	0
	1b	-107.0	2
Ge	1a	-85.1	0
	1b	-73.3	2
Sn	1a	-88.1	0
	1b	-77.3	2
Pb	1a	-66.8	0
	1b	-56.6	2

<sup>a</sup> N = number of imaginary vibrations.

positions (structure II). In the experiment only the former type of geometrical isomer has been found. Both types of structures were evaluated with the ab initio calculations. The energy balances for the reactions (1a,b) give a quantitative measure of the stabilities of the chlorine adducts.



Overall they possess strongly exothermic reaction balances (Table 4). Noticeable is the exothermicity for the reactions. They increase in the order Pb < Sn < Ge < Si, in accord with the tendency to prefer tetravalency in the same order of the group IV elements. According to the calculations, only the structures

with one chlorine in an axial and the other in the equatorial position of the bipyramid are stable (structure I,  $C_2$  symmetry). Overall these structures possess positive vibrational frequencies. The isomers with the two chlorine occupying the two axial positions are less stable and in accordance with vibrational analysis prove to be unstable structures (with regard to further geometrical rearrangement) on the corresponding electronic hypersurfaces. The energy balances for reactions 1a,b in the order Pb < Sn < Ge < Si become increasingly more exothermic. Since the chlorine compounds are in general taken as the precursors for the formation of the bisamidinate complexes with the oxidation state +II, the calculations indicate that it is more difficult to prepare these for silicon rather than for lead. This is supported by the experiment.<sup>9</sup> Hitherto bisamidinate complexes are only known up to germanium as the central atom. In other words the tetravalent species with the formal oxidation state +IV result in the same order more stable than the divalent species with the formal oxidation state +II.

## Conclusions

The results of our investigations can be summarized as follows.

(1) Bis(amidinate) complexes adopt distorted pseudo-trigonal bipyramids which can easily undergo pseudorotation over a  $C_{2v}$  symmetrical structure. The energy barrier for the degenerate rearrangement decreases in the order Si > Ge > Sn > Pb.

(2) A corresponding planar structure with  $D_{2h}$  symmetry is essentially higher in energy. It becomes more facile in the opposite order.

(3) A tetrahedral structure in which the nonbonding lone pair orbital at the central atom partakes in bonding was tested for M = Si. It should become important if weaker  $\pi$ -allylic systems (in the ligands) are present. For the  $D_{2d}$  symmetrical geometry a biradical is to be expected which becomes closed shell upon reduction to  $C_2$  symmetry.

Our considerations were evaluated mainly for amidinate ligands and their valence isoelectronic homologues. Whether these considerations also apply to other p-block main group elements, surrounded by other types of ligands, such as the bis-(diphosphinomethanide) ligand<sup>28</sup> has to be investigated by further quantum chemical calculations. These are in progress in our laboratory.

## Theoretical Section

**a. Methodology.** The qualitative considerations were deduced from EH calculations.<sup>29</sup> All of the quantum chemical calculations were carried out with the Gamess set of programs.<sup>30</sup> The relativistic corrected effective core potential basis sets were taken from Stevens, Basch, and Krauss<sup>31</sup> with a double- $\zeta$  basis set expansion for the valence space. All heavy atoms were augmented by a single set of polarization

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functions, as provided by Schmidt et al.<sup>32</sup> The energy optimizations of structures were conducted by analytically determined nuclear coordinate gradients.<sup>33</sup> The force constants for the ECP(d) calculations were performed by the method of numerical differences. The population analysis at the given computational level was conducted according to the Weinhold–Reed partitioning scheme.<sup>34</sup>

**b. MCSCF Calculations.** Energy lowest singlet ( $^1A_1$ ) and triplet states ( $^3B_1$ ) for M = Si, Ge, Sn, and Pb were determined by optimization at  $D_2$  symmetry constraints. The computed structures refer to the canonical structure **e**. Vibrational analysis identifies the corresponding geometries as second-order saddle points. The equilibrium bonding

parameters, i.e., bond lengths and bond angles, for the energy lowest triplet and singlet states are almost identical. Also the energies that result after CI corrections (single and double excitations included) differ only slightly in energy (less than 1 kcal/mol in favor of the triplet state). Thus there is only a weak electronic coupling between the unpaired electrons. This indicates that the canonical structure **e** refers to a (covalent) biradical. Details of the MCSCF calculations, i.e., equilibrium geometries, etc., are available on request.

**Acknowledgment.** This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Computer time has been generously allocated by the Rechenzentrum der Universität Aachen, the HLRZ Jülich, and the computer center at the University at Bielefeld.

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