On the Bonding Properties of Diphosphanylmethanide Complexes with the Group-14 Elements Silicon, Germanium, Tin, and Lead in Their Divalent Oxidation States

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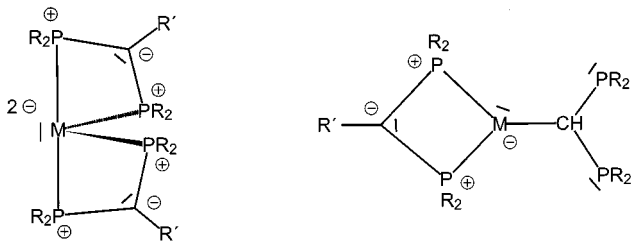
The mono- and bidentate chelation of the main-group elements silicon, germanium, tin, and lead through the phosphorus atoms of the diphosphanylmethanide ligand has been studied by means of quantum chemical methods. In accord with experimental investigations, the species are found to adopt a ψ-tbp conformation of high flexibility. The various distortional modes causing the axial and equatorial positions to become equivalent have also been investigated. In addition, the bonding situations in the electronically related bis(diamino)- and the higher element homologue bis(diarsanyl)methanide ligand systems have been studied. The bonding situation in the hitherto experimentally unknown bis(diamino)methanide ligands is predicted to be similar to that in bis(amidinate) complexes. An analysis of the electron distributions (natural bond orbital population analysis) in these compounds reveals that the central main-group element is positively charged and weakly chelated by the surrounding ligands.

Introduction

Divalent silicon compounds are currently of interest due to their high potential in new synthetic routes. Archetypal compounds in this field are $(C_5Me_5)Si$ with η^5-bonded ligands (silicocene)[1] and the intramolecular donor-stabilized diphosphanylmethanide complexes **1** (M = Si).[2] For the higher element homologues with M = Ge[3] and Sn,[4] corresponding compounds have also been characterized experimentally. Besides the connectivity seen in **1**, chelation of the main-group element can also occur in three-fold coordinated compounds such as **2** (Scheme 1).



M = Si, Ge, Sn
R = phenyl
R´= SiMe3

1 **2**

Scheme 1

Species of this kind are known for M = Ge, Sn, and Pb.[5] Recently, a diphosphanylmethanide complex was reported with phosphorus as the central main-group element.[6] For the Group-14 elements, chelation has been well documented in the amidinate chemistry of these species, which has been extensively investigated for tin and lead[7–10] as well as for germanium.[11] For silicon, bidentate amidinate chelation could be deduced on the basis of NMR investigations.[12] A first quantum chemical interpretation of the various structural alternatives in amidinate chemistry has recently been presented.[13]

The extremely rich chemistry in this field prompted us to investigate diphosphanylmethanide structures containing a Group-14 element (Si, Ge, Sn, Pb) as the central atom by quantum chemical methods. We report here the results of ab initio calculations on the chelated main-group elements in their divalent oxidation states, utilizing relativistic effective core potentials for the description of the higher main-group elements. In particular, we have analyzed the following aspects of the complexes: (a) bis(diphosphanyl)methanide chelation, and (b) the likelihoods of various geometrical arrangements at the central atom, i.e. trigonal-pyramidal (C_2) or planar (D_{2h}) environments. From experimental investigations it is known that these structures preferentially adopt pseudo-trigonal-bipyramidal (Ψ-tbp) geometries, which can easily be distorted. In solution, the structures undergo geometrical rearrangements that may be observed as dynamic processes by NMR spectroscopy.[4][5] All these aspects have been analyzed by means of quantum chemical calculations. Details of the quantum chemical methodology are given in the Appendix.

Results and Discussion

(a) The Ligand Field of the p-Block Elements

We begin our analysis with a discussion of some qualitative aspects. The formation of diphosphanylmethanide complexes can be considered in terms of the coordination of a

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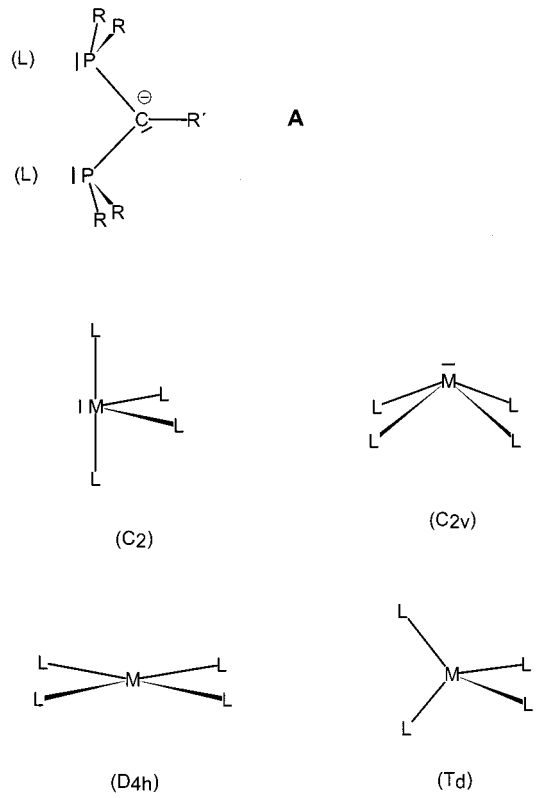
central element M (Si, Ge, Sn, etc.) in a ligand field[14] that is spanned by the diphosphanylmethanide ligands **A** (Scheme 2).

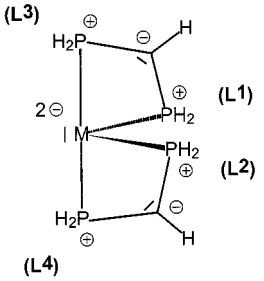


Scheme 2

The ligand **A** refers to two two-electron donors (denoted here as L). In other words, each two-electron donor is confined to a non-bonding lone pair at the (terminal) phosphorus atoms and each phosphorus atom of the diphosphanylmethanide ligand supplies two electrons to the central atom M. Various a priori possible conformations can be drawn. In each of them, the ligand exerts a ligand field[14] on the central atom. The orbital splitting for the different geometrical arrangements can be deduced from symmetry considerations, as has been shown previously for coordination of a central atom M with amidinato ligands.[13] In the C_2 and C_{2v} conformations, a non-bonding lone-pair orbital is operative at the central element M. The latter differs from the former geometry in that all M−L bonds are equivalent. It can be considered as the transition state geometry for interchange of the equatorial and axial bond positions in the dynamic rearrangement.[3] Possible planar (D_{4h}) or tetrahedral (T_d) conformations are not observed experimentally, and are thus not included in our considerations. For the corresponding amidinate complexes, the latter tetrahedral structure incorporates four strong bonds between the central atom M and the ligands, and can be assigned to a structure with a high degree of open-shell character.[13] For a more exhaustive discussion on the action of the ligand field on the orbitals of the central element M, the reader might like to refer to a recent report.[13]

(b) Bidentate Chelation

In this section, we report the numerical results obtained for the parent bis(diphosphanyl)methanide structures **B** (R = H). We first studied their equilibrium geometries with the main-group element M being varied by descending the group Si, Ge, Sn, and Pb. As ligands L^i (i = 1 to 4), the diamino- (L^i = N), diphosphanyl- (L^i = P), and diarsanylmethanide (L^i = As) components were chosen (Scheme 3). Experimentally, only the case of L^i = P is known, so our calculations make predictions for a variety of structures of experimentally unknown homologues. In all calculations we replaced the substituents at L^i and at the carbon atoms by hydrogen atoms. In the actual experimental situation the bis(diphosphanyl)methanide complexes are kinetically protected by bulky substituents (aryl, alkyl) at the chelating phosphorus atoms. Hence, our present calculations cannot account for these steric effects, but should accurately reflect the trends in bonding. The relevant equilibrium bonding parameters (bond lengths in Å, bond angles in degrees), obtained by energy optimizations of the equilibrium structures, are collected in Table 1.



Scheme 3

The most stable structure is found to be the ψ-tbp geometry, in accord with experiment. Two ligands L^1 and L^2 occupy equatorial while the other two L^3 and L^4 occupy axial positions. All of the equilibrium geometries could be ascertained by corresponding vibrational analyses. As expected, the equatorial bonds are invariably shorter than the axial ones. This is a common feature of the trigonal-bipyramid surrounding a central main-group element.[15] The actual equilibrium geometry of the ψ-tbp complex is determined by the electronegativity of the chelating axial and equatorial atoms (groups). We may discuss this for the case M = Si, L^i = N (diaminomethanide ligand), for which corresponding experimental structures are unknown. Here, the two axial bonds are equivalent in length, hence this molecule strictly adopts C_2 symmetry. On the other hand, replacement of N by P (diphosphanylmethanide ligand) makes the two axial bonds asymmetrical. The trend increases in the order (L^4/L^3, N = 1.0, P 1.35, As 1.41). However, with increasing atomic size of the central element M (Si < Ge < Sn < Pb), the asymmetry of the axial bonds becomes less marked. In fact, for M = Sn the two axial bonds in the ψ-tbp geometries are invariably symmetrical. The effects on the equatorial bonds are almost negligible so

Table 1. Equilibrium geometries of complexes **1** (bond lengths in Å; bond angles in degrees)

M	L^i	Symmetry	M−L^1	M−L^2	M−L^3	M−L^4	∠ L^1ML^2	∠ L^3ML^4
Si	N	C_2	1.956	1.956	2.165	2.165	96.0	142.0
	P	C_1	2.331	2.338	2.401	3.245	93.5	138.2
	As	C_1	2.435	2.459	2.502	3.514	90.6	135.2
Ge	N	C_2	2.079	2.079	2.284	2.284	94.8	137.8
	P	C_2	2.432	2.432	2.749	2.749	92.8	140.9
	As	C_1	2.525	2.548	2.664	3.200	89.6	139.3
Sn	N	C_2	2.301	2.301	2.417	2.417	89.9	130.4
	P	C_2	2.639	2.639	2.900	2.900	90.5	132.7
	As	C_2	2.731	2.731	3.008	3.008	87.8	133.8
Pb	N[a]	C_2	2.420	2.420	2.462	3.462	85.1	131.8
	P	C_2	2.691	2.691	2.929	2.929	90.6	131.6
	As	C_2	2.776	2.776	3.021	3.021	89.1	134.1

[a] Unstable (transition state) structure, rearranges to **d**.

that these have similar lengths in all cases. We note that for M = Pb and L^i = N the corresponding structure **B** is not stable on the electronic hypersurface, but further rearranges to its isomer **d** (vide infra) without having to surmount an energy barrier.

It is of interest to inspect the population analyses (NBO) of the resulting equilibrium geometries. These are presented in Table 2.

Table 2. Wiberg bond indices and NBO charges of complexes **1**

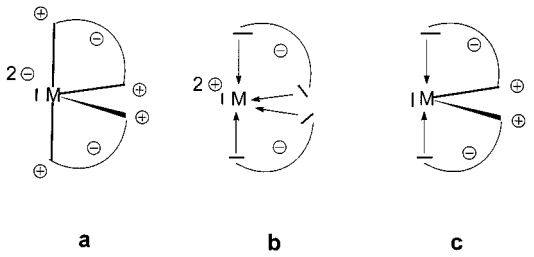
M	L^i	M−L^1	M−L^2	M−L^3	M−L^4	q(M)
Si	N	0.37	0.37	0.24	0.24	1.28
	P	0.84	0.80	0.72	0.10	0.24
	As	0.86	0.80	0.75	0.06	0.22
Ge	N	0.32	0.32	0.20	0.20	1.36
	P	0.77	0.77	0.40	0.40	0.39
	As	0.81	0.78	0.60	0.17	0.36
Sn	N	0.21	0.21	0.17	0.16	1.48
	P	0.66	0.66	0.37	0.37	0.64
	As	0.67	0.67	0.36	0.36	0.64
Pb	N	0.16	0.16	0.15	0.15	1.51
	P	0.63	0.63	0.34	0.34	0.73
	As	0.63	0.63	0.33	0.33	0.74

In general, the Wiberg bond indices for the axial bonds are smaller than those for the equatorial bonds. Nevertheless, for L^i = N, M = Si both the equatorial and the axial bonds are even weaker than a half bond. Replacing the ligands L^i by more electropositive elements (P, As) increases the strengths of the equatorial bonds, but makes the axial bonds more asymmetrical. As a further consequence, one axial bond becomes much stronger than the other (e.g. M = Si, L^i = P). As will be shown below by energetic considerations (vide infra), the overall energy differences resulting from the increased strength of one axial bond and the simultaneous weakening of the other are fairly small. With the higher element homologues as the central atom, M = Ge > Sn > Pb, the trend towards asymmetry of the two axial bonds is diminished.

It is notable that the axial bonds of the diphosphanylmethanide structures can easily become asymmetrical. Thus, one axial bond lengthens while the other shortens, and the energy difference between these forms and the highly symmetrical structure (C_2 symmetry) is fairly small. In order to further support this argument we have performed calculations at a higher level for the case M = Si, L^i = P. The two stationary points, with either C_2 symmetry (transition state structure) or C_1 symmetry (equilibrium structure) were taken into consideration. At the MP2 level, we obtained the following energy differences (in kJ/mol) as a function of the basis sets: (a) 6-31g** level 3.9, (b) 6-31+g** 5.1, (c) 6-311+g** 3.6. Thus, at higher computational levels our findings compare extremely well with the results obtained with the effective core potential basis sets. In other words, the more refined calculations are supportive of the present discussion. In the actual experiment, however, the structures are substituted by bulky substituents, which exert a steric hindrance. Hence, the subtle energy differences revealed by the quantum chemical theory for the unsubstituted cases can be neglected in comparison with the steric effects exerted by the substituents. The calculations also predict that the trend towards decreased symmetry should increase with decreasing positive charge at the central main-group element, e.g. for M = Si, in the order N < P < As.

We have also analyzed the extent of a bonding interaction between the negatively charged methanide carbon atoms and the central atom M. Overall, the Wiberg bond indices, i.e. the bond orders, are negligible (≤ 0.05) for the cases M = Si to Pb. Of interest is the charge at the central atom M. For L^i = N (diaminomethanide ligand) this amounts to ca. +1.3 to +1.5, while for the higher element homologues L^i = P, As it is much less (ca. +0.2 to +0.7). Such a description also holds true for the related amidinate complexes.[13] On the basis of the charge densities and the Wiberg bond indices, one can view the bonding situation in the complexes in terms of the three canonical structures **a** to **c** (Scheme 4).

In **a**, the central element M is tetravalent but additionally bears a lone pair orbital. Thus, this canonical structure formally refers to a 10-electron configuration at M. In comparison, in the canonical structure **b** the central atom M is chelated by four two-electron donating groups. In this structure, M is assigned a formal charge of +2. Finally, we may add a third canonical structure **c**. It is characterized by equatorial single bonds and two axial bonds fixed by a



Scheme 4

donor−acceptor interaction with the central atom. According to the population analyses, the various complexes can be divided into two categories: (a) In cases where the donating atoms are strongly electronegative (e.g. with the diaminomethanide ligand), the resulting compounds are best described by canonical structure **b**. In these cases, the Wiberg bond indices indicate a bond order of less than a half for the equatorial *and* axial bonds. However, the latter bonds are invariably stronger than the former ones. (b) On the other hand, in the case of L^i = P, As (diphosphanyl-, diarsanylmethanide ligands) the equatorial and, to a much lesser extent, the axial bonds become stronger. This supports the predominance of canonical structure **c** for the overall bonding description. Interestingly, for the structures with asymmetrical bonds, the shorter axial bond becomes much stronger, while the longer axial bond is weakened (e.g. M = Si, L^i = P).

Besides the ψ-tbp conformations with symmetrical (C_2 symmetry) or asymmetrical (C_1) axial bonds, we also explored structures in which the axial and equatorial bonds in the complexes were of equal length. This refers to the case of C_{2v} symmetry and represents the transition state for pseudorotation, i.e. the positional interchange of the equatorial and axial bonds. We will not present here the details of the equilibrium structures, but all geometries refer to transition states established from the corresponding vibrational analyses. They are in accordance with one imaginary vibration in these C_{2v} geometries. A summary of the energies of the ψ-tbp geometries and their corresponding C_{2v} geometries is also given in Table 3.

Table 3. Relative energies (in kJ/mol) for complexes **1**

M	L^i	$E(C_1)$	$E(C_2)$	$E(C_{2v})$
Si	N	0.0	0.0	21.9
	P	0.0	3.8	34.0
	As	0.0	6.1	41.7
Ge	N	−	0.0	15.0
	P	−	0.0	33.6
	As	0.0	0.6	38.1
Sn	N	−	0.0	6.2
	P	−	0.0	15.7
	As	−	0.0	20.0
Pb	N	−	0.0	9.6
	P	−	0.0	11.9
	As	−	0.0	15.0

The numerical data indicate that the energy differences between the two conformations are fairly small. The values decrease in the order M = Si > Ge > Sn > Pb and with increasing electronegativity of the chelating atoms, N < P < As. In the same order, canonical structure **b** comes to the fore.

These results allow a clear-cut assignment of the various mechanisms for the dynamic rearrangement of the bis(diphosphanyl)methanides. It has been noted that these species undergo exchange of the equatorial and axial phosphorus atoms and even more facile exchange of the axial and *exo*-phosphanyl groups.[3] The mechanism for the latter process is outlined in Scheme 5.

One axial bond is readily extended, while the other is strengthened. This is followed by a facile rotation about the P−C bond (I) and subsequent ring-closure (II). Along this reaction coordinate, the phosphanyl groups undergo positional interchange. Considering the presented results, such a process is easy to understand. While one axial bond is stretched, the other is shortened and the overall energy expense for such a process is fairly small.

There is another point that needs to be considered here. It has been reported that certain bis(diphosphanyl)methanide structures undergo irreversible reaction of the ψ-tbp geometry[4] to give a structure in which one diphosphanylmethanide ligand is linked through an M−C bond (structure **d**, Scheme 6).

In order to gain an insight into the stability of the latter geometry, we have calculated the energy balances for various cases (different M, L^i and R′, R = H) (Table 4).

In all cases, the structures **d** are found to be more stable than the ψ-tbp structures. Furthermore, the investigations indicate that with various substituents R the energy balances between the two structures are not significantly affected. This indicates that silyl or phosphanyl groups[16] at the carbon atom in structure **d** do not exert strongly stabilizing effects on the ψ-tbp geometries.

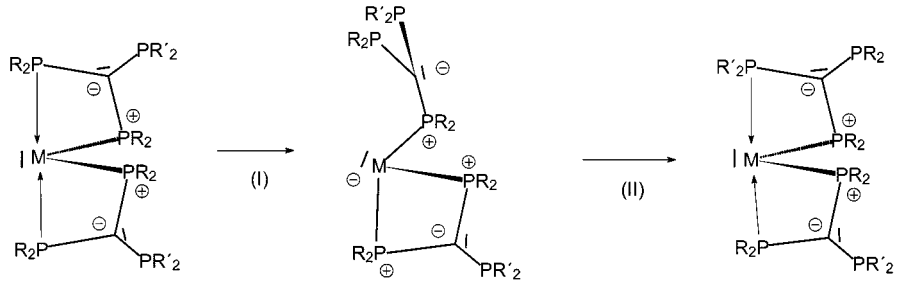
Conclusions

The results of our investigation can be summarized as follows:

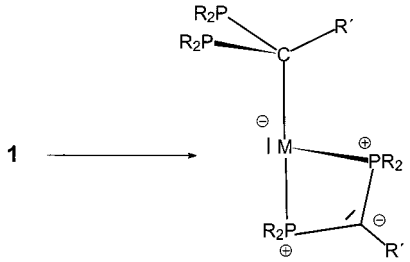
1. The bis(diphosphanyl)methanide complexes with Group-14 central elements have been studied by quantum chemical methods at an effective core potential level. They have been found to be capable of facile pseudorotation over a C_{2v} symmetrical structure. The energy barrier for the degenerate rearrangement decreases in the order Si > Ge > Sn > Pb. Rearrangement is also facilitated with increasing difference in electronegativity between the central and chelating atoms, As > P > N.

2. The structures with the diphosphanylmethanide and diarsanylmethanide ligands are best described as having equatorial single bonds and weak axial bonds, which can distort to form asymmetrical trigonal bipyramids. This explains the experimentally observed facile rearrangement of these species.

3. A "true" chelation, i.e. the formation of partial bonds between the central atom M and the ligands is observed only for the case L^i = N, i.e. the hitherto experimentally



Scheme 5



d

Scheme 6

Table 4. Energy differences (in kJ/mol) between ψ-tbp and geometries **d**

M	L^i	X = H	SiH_3	PH_2
Si	N	168.3	–	–
	P	131.5	109.7	107.1
Ge	N	157.5	–	–
	P	116.5	–	–
Sn	N	124.1	–	–
	P	97.5	–	–
Pb	N	76.4	–	–
	P	96.4	–	–

unknown diaminomethanide ligand. In this case, an extremely facile exchange of the equatorial and axial ligating atoms can be expected.

4. Structures in which one diphosphanylmethanide ligand is linked through an M−C bond are considerably lower in energy and the energy differences are found to be almost independent of the substituents R′ attached to the carbon atoms.

Experimental Section

All quantum chemical calculations were carried out at the MP2 level of theory using the Gamess set of programs.[17] The relativistically corrected effective core potential basis sets were taken from Stevens, Basch, and Krauss,[18] with a double-ζ basis set expansion for the valence space. All heavy atoms were augmented by a single set of polarization functions, as provided by Schmidt et al.[19] The energy optimizations of structures were performed at the MP2 level utilizing analytically determined nuclear coordinate gradients.[20] The force constants for the ECP(d) calculations were derived by the method of numerical differences. The population analyses at the given computational level were performed according to the Weinhold−Reed partitioning scheme.[21]

Acknowledgments

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