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The 1,4-Diphosphabuta-1,3-diene Ligand for Coordination of Divalent Group 13 and 14 Elements: A Density Functional Study

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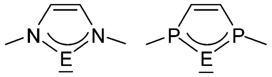
The 1,4-diphosphabuta-1,3-diene (DPB) ligand as a tool for stabilizing anionic group 13 (B, Al, Ga) and neutral group 14 (C, Si, Ge) cyclic Arduengo-type carbenes is studied by quantum chemical calculations at density functional level. Accordingly, for the former group this ligand is better suited than the corresponding 1,4-diazabuta-1,3-diene (DAB) ligand. It results in larger electron affinities for the corresponding doublet states. For the latter group the DPB ligand yields essentially smaller singlet–triplet separations than the DAB ligand. An exception is the anionic boron compound with relative low singlet stability for both the DAB and DPB ligands.

Introduction

1,4-Diazabuta-1,3-diene ligands (here abbreviated as DAB) are now well suited for the stabilization of cyclic carbenes and homologues of type I, with E = C,[1] Si,[2] and Ge.[3] Also the isoelectronic anions with E = Al[4] and Ga[5] were reported. The latter, the group 13 element homologues, were first proposed on the basis of quantum chemical calculations.[6,7] For the group 14 element species a variety of physicochemical investigations were performed[8−13] (Chart 1).

Chart 1



I II

E = $B^{(-)}$, $Al^{(-)}$, $Ga^{(-)}$, C, Si, Ge

In contrast to the plethora of experimental investigations on the so-called "Arduengo-type carbenes",[14−17] which are still in the center of interest,[18−28] the analogous compounds with a 1,4-diphosphabuta-1,3-diene ligand (here denoted as

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DPB), type II, are only scarcely known. Recently a cyclic monophosphacarbene was reported.[29] However, it is masked in a transition metal complex.

We report here on an exploration of the bonding properties of the cyclic carbenes and homologues of type II. It will be shown that the DPB ligand is very suitable for stabilization of carbene homologues with higher elements of group 13 ($E = B^{(-)}$, $Al^{(-)}$, $Ga^{(-)}$) and of group 14 (E = C, Si, Ge).

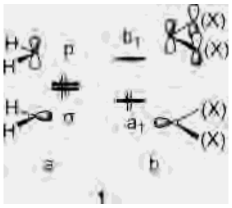
Methodology

The geometries of the various molecular structures were energy optimized at the density functional level,[30,31] utilizing Becke's three-parameter functional[32] with local and nonlocal electron correlation contributions, as given by the Lee−Yang−Parr correlation functional[33] (B3LYP). For the optimization of geometries, the 6-31++g(d,p) basis set was used throughout at all atoms (C, Si, Ge, B, Al, Ga, H).[34] This implies one set of diffuse s,p functions[35] and one set of polarization functions[36] at all atoms. Single point calculations were additionally performed with the 6-311++g(d,p) basis set[37] and with the MP4SDTQ(fc) approximation[38] for the electron correlation treatment. Zero-point vibrational energies computed with the 6-31++g(d,p) basis set were uncorrected included in the relative energies. All stationary points were verified by calculation of the corresponding Hessian matrixes. For the calculations, we used the Gaussian-98 suite of programs.[39] The electron distribution in the various molecular structures were examined with the natural bond orbital (NBO) partitioning scheme.[40]

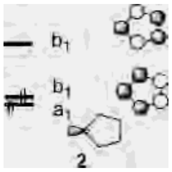
Results and Discussion

Group 13 Carbene Homologues. The stabilities of the carbene analogues are determined by (a) the singlet−triplet energy separations and (b) the electron affinities of the corresponding doublet states (E = B, Al, Ga). For small differences between both electronic states, the carbene-type structures will not be stable and their chemistry will be reminescent to biradical reactions. On the other hand, the electron affinities yield a quantitative measure about the anion stabilities. If the electron affinities are large, than the corresponding anionic systems are stable. In practice the anions are not isolated systems; they are surrounded by counterions. Hence to a first order the anion stabilities are determined by the electron affinities (of the neutral radicals) and to a second order these are also mediated by the surrounding cations (electrophilicity). In the calculations these effects are not explicitely considered. Consequently our considerations apply to computed structures in the gas phase.

Scheme 1



Scheme 2



The electronic situation of an acylic carbene is described by its frontier orbitals, given in **1** (Scheme 1).

They refer to a σ-[41] and p-orbital which within C_{2v} symmetry are confined to a_1 and b_1 representations.[42] For methylene both orbitals, **1a**, are in close proximity to each other and a triplet ground state results.[43] The situation is different for a stabilized carbene, such as the diaminocarbene, **1b**. The HOMO−LUMO splitting is considerable enlarged by π-conjugation of the carbon with the neighboring amino groups, and a pronounced singlet ground state is obtained.[44]

As has been shown previously,[6] the frontier orbital system for the cyclic carbene structures of type I can be viewed in an analogous manner. Confined to a planar arrangement (C_{2v} symmetry) the frontier orbital system **2** results (Scheme 2).

Since the anion stabilities of the group 13 carbene congeners depend on their electron affinities, it is necessary to examine the anions and the corresponding neutral doublet states with respect to the energy differences between these two species. The resulting relevant Slater determinants for the singlet ground state and the two doublet

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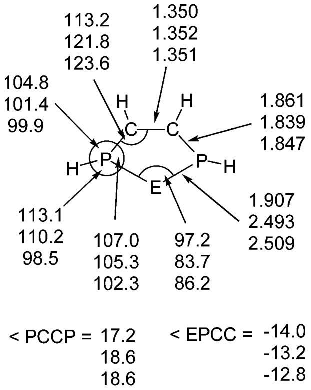


Figure 1. Equilibrium geometries (bond lengths in Å, bond and twist angles in deg) of lowest energy singlets for type II group 13 carbene homologous at the B3LYP/6-31++g(d,p) level. From top to bottom, E = $B^{(-)}$, $Al^{(-)}$, and $Ga^{(-)}$.

states are given[6] as follows:

$$\Psi(^1A_1) = |...(b_1)^2(a_1)^2>$$

$$\Psi(^2A_1) = (|...(b_1)^2(a_1)^1>$$

$$\Psi(^2B_1) = (|...(a_1)^2(b_1)^1>$$

And those for the triplet states of **2** are given by

$$\Psi(^3B_1) = |...(a_1)^1(b_1)^1>$$

$$\Psi(^3A_1) = |...(b_1)^1(b_1)^1>$$

The first of the last two ($^3B_1$) refers to the energy lowest triplet state in the classical Arduengo carbene.[45] For the case at hand the situation is more complicated. Compared with nitrogen, trigonal phosphorus possesses a much stronger tendency for pyramidalization. In other words one expects that for these states the structures are at least reduced to C_2 or C_s symmetry. The former refers to *anti*-pyramidalization and the latter to *syn*-pyramidalization of the ligands at the phosphorus atoms. We have probed all these states in question. The C_{2v} symmetrical geometries are higher energy saddle point geometries. The singlet ground states prefer C_2 symmetry, while the triplets and doublets even in most of the cases adopt in their equilibrium geometries C_1 symmetry; the substituents at the phosphorus atoms choose preferentially *anti*-pyramidalization with a slight tilting of the five-membered ring system. In any case the energy minimum of these structures were ensured by corresponding vibrational analysis.

The equilibrium geometries of the relevant singlets of the group 13 congeners are collected in Figure 1.

The anions adopt C_2 symmetry, and the phosphorus atoms are slightly pyramidalized. The sum of angles at these atoms increases in the order E = B < Al < Ga. Concomitant with the pyramidalization is the folding of the five-membered ring. We may note here that the corresponding nitrogen congeners strictly adopt C_{2v} symmetry.[6] The essential bonding features (PC and CC distances) are only slightly changed with the alteration of the chelating element E. The only essential difference is the widening of the P−C−C angle with increasing atomic size of E.

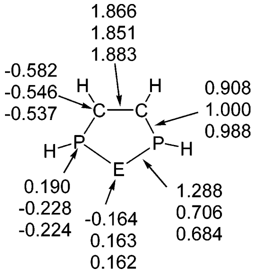
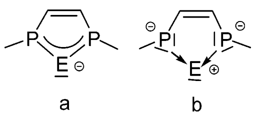


Figure 2. NBO analysis, natural charges, and Wiberg bond indices (values obtained in the NAO basis) for type II group 13 carbene homologues in their energy lowest singlet states.

Chart 2



3

Further information on bonding is given by the results of the NBO population analysis, as shown in Figure 2.

For the first homologue in this series, E = B, negative charge is accumulated at E with concomitant strengthening of the PB bonds. The situation is different for the higher homologues of E. The chelating atoms become more positive, and the EP bonds are weaker than a single bond. However the trends are less pronounced than in the corresponding DAB derivatives.[6] In other words in terms of canonical structures, these carbene homologues can also be written by the limiting structures, **3a** versus **3b** (Chart 2).

The former, **3a**, refers to a classical carbene structure with a partial π-delocalization within the ring system. The latter, **3b**, refers to a donor−acceptor complex in which the element E in a formal +I oxidation state is doubly coordinated by a dinegative DPB ligand. While these alternatives present extreme bonding cases, the calculations reveal an intermediate situation.

One could imagine that the bonding situation in the type II structures are similar to those in the type I compounds. Albeit one proposes a stronger covalency of a PE bond than a NE bond, due to the larger electronegativity of nitrogen versus phosphorus. The following considerations will show that there are essential differences between both type of ligands. For this purpose it is necessary to inspect the energy contributions which determine the stabilities of these species. Electron affinities and the singlet−triplet energy differences of the group 13 congeners are collected in Table 1.

The electron affinities and hence the anion stabilities are larger for the DPB than for the DAB ligands (values in parentheses). On the contrary the DPB ligand exerts a smaller singlet−triplet separation than the DAB ligand.[6] This indicates that the type II ligand is more favorable in stabilizing the higher element homologues of E than the type I ligand. We note that systematic experimental studies on the type II ligand are lacking.

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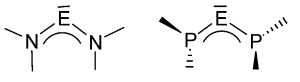
Table 1. Electron Affinities (EA) (in kcal/mol) and Singlet−Triplet Energy Separations (ST, in kcal/mol) for Structures of Type II (E = B$^{(-)}$, Al$^{(-)}$, Ga$^{(-)}$)

atom E			basis I[a]	basis I/ZPE[b]	basis II[c]	MP4[d]
B	$^{2}\mathrm{A}\ (C_2) \rightarrow {}^{1}\mathrm{A}\ (C_2)$	EA	27.2 (7.0)	28.3	28.0	24.6 (3.3)
	$^{1}\mathrm{A}\ (C_2) \rightarrow {}^{3}\mathrm{A}\ (C_1)$	ST	11.8 (20.2)	11.5	12.0	12.7 (23.1)
Al	$^{2}\mathrm{A}\ (C_1) \rightarrow {}^{1}\mathrm{A}\ (C_2)$	EA	42.5 (32.5)	43.9	43.0	36.7 (34.5)
	$^{1}\mathrm{A}\ (C_2) \rightarrow {}^{3}\mathrm{A}\ (C_2)$	ST	50.8 (41.3)	49.5	50.5	55.6 (45.3)
Ga	$^{2}\mathrm{A}\ (C_1) \rightarrow {}^{1}\mathrm{A}\ (C_2)$	EA	44.0 (27.0)	44.5	45.2	39.2 (39.3)
	$^{1}\mathrm{A}\ (C_2) \rightarrow {}^{3}\mathrm{B}\ (C_2)$	ST	47.5 (52.0)	45.8	47.8	69.3

[a] B3LYP/6-31++g(d,p). [b] Method *a* plus zero-point vibrational energy correction (unscaled). [c] B3LYP/6-311++g(d,p)//B3LYP/6-31++g(d,p). [d] MP4SDTQ(fc)/6-31++g(d,p)//B3LYP/6-31++g(d,p).

Chart 3



4 **5**

Group 14 Carbene Homologues. Next we discuss the group 14 carbene homologues. A great deal of information is already gained by a comparison of the diamino- versus diphosphinocarbene with the corresponding silylene derivatives. The diaminocarbene, **4** (E = C), possesses a rather large singlet−triplet energy separation (50.7,[46] 58.5,[47] 52.1[48] kcal/mol, estimated from the calculations) (Chart 3).

A similar magnitude is obtained for the diaminosilylene, **4** (E = Si). We obtained for this species a singlet−triplet energy splitting of 56.1 kcal/mol (B3LYP/6-31++g(d,p), with zero-point vibrational energy correction). The situation is different for the symmetrically substituted phosphinocarbenes.[48] For **5** (E = C) the singlet−triplet gap is comparably small; it amounts to 8.4 kcal/mol. It is now well established that stable phosphinocarbenes are only accessible by a corresponding push−pull substitution[13c,49] at the divalent carbene center. At the given quantum chemical level (B3LYP/6-31++g(d,p)), we obtain for the hitherto unknown diphosphinosilylene derivative, **5** (E = Si), a singlet−triplet separation of 21.1 kcal/mol (with ZPE correction). Hence, this indicates that the phosphino substituent is more effective in stabilizing a singlet ground state in a silylene than in a carbene. It must be noted here that parent silylene adopts a singlet ground state and parent methylene a triplet ground state.[50]

The equilibrium geometries of the group 14 carbene homologues of type II are summarized in Figure 3, and the corresponding results of the population analysis, in Figure 4.

The relevant energy quantities which determine the stabilities of these species are here the singlet−triplet separations. They are collected in Table 2.

The equilibrium parameters may be compared with those for the group 13 elements. They are very much alike. With increasing atomic size of the element E the angle P−C−C tends to widen. All the structures possess twisted five-membered ring systems. The group 14 carbene homologous throughout adopt the structure **3a**, as substantiated by the population analyses. In other words these refer more to classical carbene structures rather than the group 13 homologues. For E = C negative charge is accumulated at carbon and this species also possesses the strongest E−P Wiberg bond indices. However, also the higher element homologues with E = Si and Ge indicate a bond order of at least one. Taken together this emphasizes the carbene character, as summarized in the canonical structure **3a**.

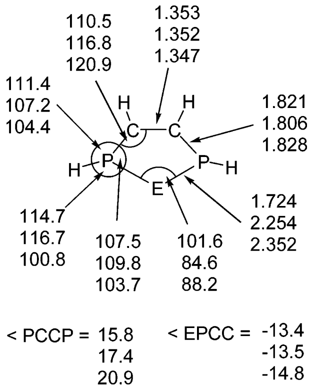


Figure 3. Equilibrium geometries (bond lengths in Å, bond and twist angles in deg) of lowest energy singlets for type II group 14 carbene homologous at the B3LYP/6-31++g(d,p) level. From top to bottom, E = C, Si, and Ge.

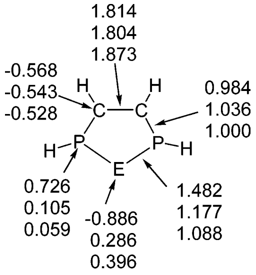


Figure 4. NBO analysis, natural charges, and Wiberg bond indices (values obtained in the NAO basis) of type II group 14 carbene homologues in their energy lowest singlet states.

Table 2. Singlet−Triplet Energy Separations (in kcal/mol) for Structures of Type II (E = C to Ge)

atom E		basis I[a]	basis I/ZPE[b]	basis II[c]	MP4[d]
C	$^{1}\mathrm{A}\ (C_2) \rightarrow {}^{3}\mathrm{B}\ (C_2)$	18.6	18.3 (79.3;[e,f] 80.0[g])	19.3	21.2
Si	$^{1}\mathrm{A}\ (C_2) \rightarrow {}^{3}\mathrm{A}\ (C_1)$	34.3	34.2 (85.9[e,h])	34.0	35.8
Ge	$^{1}\mathrm{A}\ (C_2) \rightarrow {}^{3}\mathrm{A}\ (C_1)$	37.7	36.8 (52.8[e,h])	35.6	43.3

[a] B3LYP/6-31++g(d,p). [b] Method *a* plus zero-point vibrational energy correction (unscaled). [c] B3LYP/6-311++g(d,p)//B3LYP/6-31++g(d,p). [d] MP4SDTQ(fc)/6-31++g(d,p)//B3LYP/6-31++g(d,p). [e] Values for the corresponding diaza (type I) derivatives (B3LYP/6-31++g(d,p)). [f] Reference 52. [g] Reference 49. [h] Basis I/ZPE level; unpublished results.

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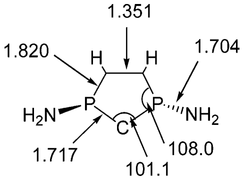

Figure 5. Equilibrium geometries (bond lengths in Å, bond and twist angles in deg) of P-amino-substituted type II species (singlet) at the B3LYP/6-31++g(d,p) level.

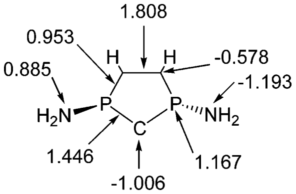

Figure 6. NBO analysis, natural charges, and Wiberg bond indices (values obtained in the NAO basis) of P-amino-substituted type II species (singlet).

It is known that amino groups at phosphorus increase the ylide character of the neighboring carbon atoms. It is the consequence of the tendency of phosphorus to suffer from *orbital nonhybridization.*[51] Hence it is expected that amino substituents at phosphorus strengthen the bonds toward the neighboring divalent element centers. We have probed this effect for the carbon case (Figures 5 and 6).

The PC bond to the divalent carbon is slightly shortened as compared with the parent compound (Figure 3), and the negative charge is enhanced.

For the energy considerations of the group 14 carbene homologues we restricted to an analysis of singlet−triplet separations (Table 2). As already reported for the heterocyclic diphosphinocarbene the gap between both relevant electronic states is fairly small. It considerably enlarges for E = Si and Ge. However for the cyclic structures and in comparison with the type I Arduengo carbenes, they result still lower in magnitude. For the latter (E = C) a singlet−triplet separation of 79 kcal/mol has been calculated.[52] For completeness for the other type I congeners they were also calculated (see Table 2). In other words the hitherto experimentally unknown type II species should be valuable targets for experimental verification. Our present considerations do not include the phosphorus analogues (group 15) with E = $P^{(+)}$. Also our analysis does not deal with the stannylene and plumbylene analogues; the type I species were experimentally investigated by the Lappert group.[53−55] A skillful discussion on the corresponding type I carbene has been given recently by Gudat et al.[56] They are very stable entities. Hence it is to be expected that the phosphorus analogues of type II behave similarly.

Summary

In this study we examined the action of a phosphino group on stabilization in the Arduengo-type cyclic carbene structures constituted from the group 13 and group 14 homologues. Hitherto in detail only the cyclic congeners with amino functions neighboring the carbene center are known. Our study reveals some essential different bonding features in comparison to the Arduengo carbenes of type I. They can be summarized as follows:

(1) Phosphorus is less electronegative than nitrogen. Consequently the resulting bonds toward E in general gain more covalent bonding contributions than the type I carbene homologues. This is an essential character of the hitherto experimentally unknown group 13 species.

(2) The phosphino group in the type II species is better suited to stabilize a singlet ground state for the higher element homologues of group 13 as compared with the structures of type I. On the basis of the quantum chemical calculations, these higher element homologous should possess strongly pronounced singlet ground states.

(3) Amino substituents at the phosphorus (type II species) induce an increase of negative charge at the element E, as probed for E = C.

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