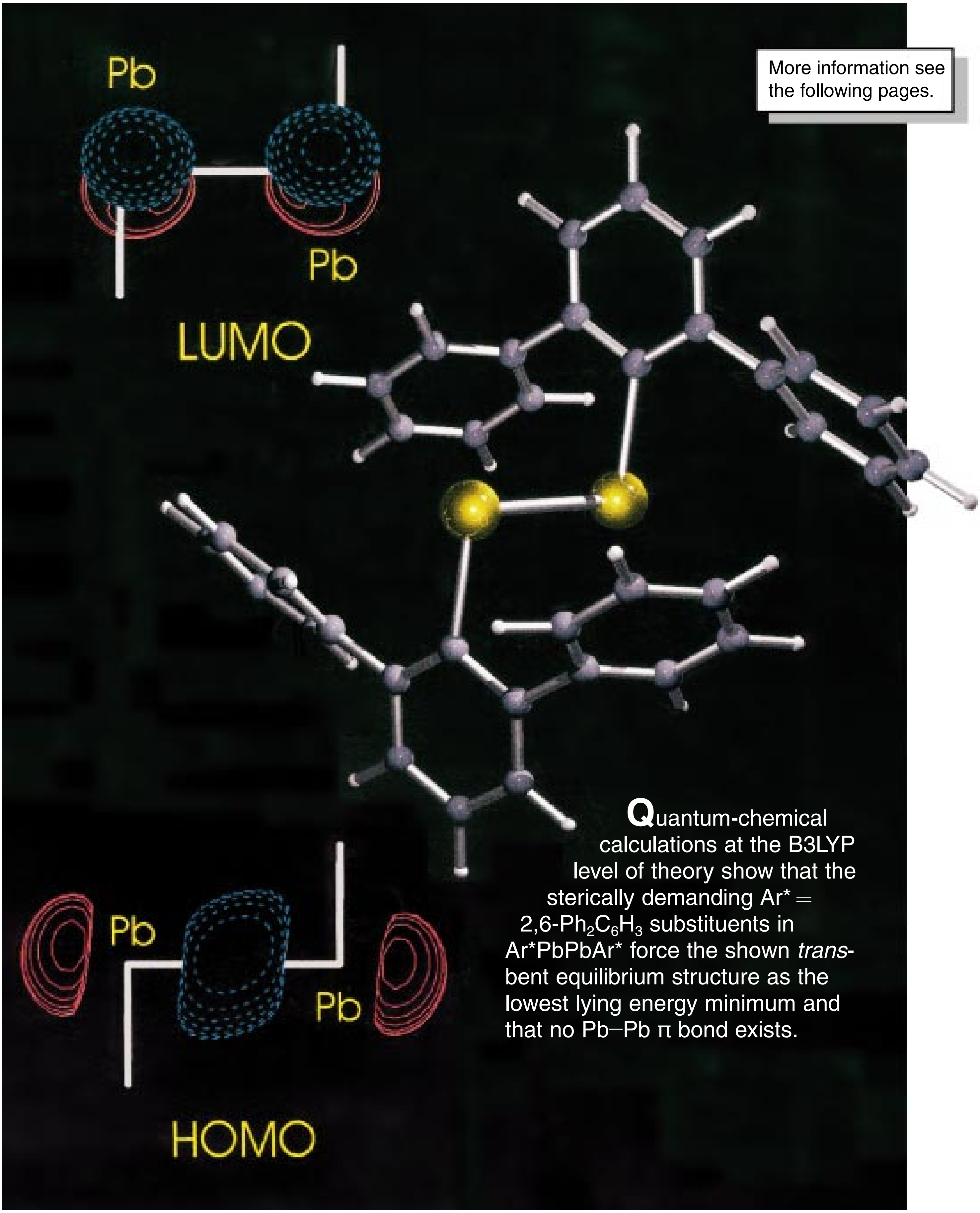
More information see the following pages.



Quantum-chemical calculations at the B3LYP level of theory show that the sterically demanding Ar* = 2,6-$Ph_2C_6H_3$ substituents in Ar*PbPbAr* force the shown *trans*-bent equilibrium structure as the lowest lying energy minimum and that no Pb–Pb π bond exists.

Turning a Transition State into a Minimum—The Nature of the Bonding in Diplumbylene Compounds RPbPbR (R = H, Ar)[**]

Yu Chen, Michael Hartmann, Michael Diedenhofen, and Gernot Frenking*

Much progress has been made recently in the synthesis of molecules with multiple bonds between heavier main group elements.[1] Numerous compounds in particular of the Group 14 elements with the formula $R_2E{=}ER_2$ (E = Si–Pb; R = bulky alkyl groups) have been prepared and their geometries characterized by X-ray structure analysis.[2] The structures and bonding of the heavier analogues $R_2E{=}ER_2$ differ strongly from those of the olefins $R_2C{=}CR_2$. The former species have a skeleton with a nonplanar geometry and the E=E bonding is rather weak, which is evident from the fact that many compounds dissociate in solution.[3] Much less is known about the heavier Group 14 analogues of alkynes REER. Theoretical studies predicted that the energetically lowest lying structures of Si_2H_2 and Ge_2H_2 are very different from the linear equilibrium geometry of acetylene (Figure 1).[4]

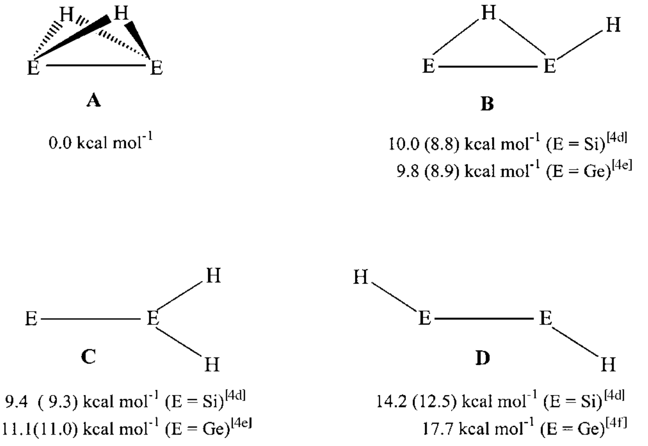


Figure 1. Theoretically predicted energy minima on the E_2H_2 (E = Si, Ge) potential energy surface.

The doubly bridged form **A** is calculated as the global minimum on the potential energy surface (PES) of Si_2H_2 and Ge_2H_2. The singly bridged isomer **B** and the vinylidene form **C** are 9–11 kcal mol^{-1} higher in energy than **A**. The *trans*-bent form **D**, which resembles most closely the geometry of acetylene, is the highest lying isomer of Si_2H_2 and Ge_2H_2. The linear forms HSi≡SiH and HGe≡GeH are no minima but high-lying saddle points on the PES. They are about 40 kcal mol^{-1} higher in energy than **A**.[4] Gas-phase spectroscopic investigations of Si_2H_2 have been reported which also suggest that the most stable isomers have the bridged geometries **A** and **B**.[6] Until recently these were the only experimental studies about the heavier Group 14 analogues of alkynes. The doubly bridged form **A** has been calculated for Pb_2H_2 but the other isomers have not been investigated.[5]

The recent report by Power and co-workers[7] about the synthesis and X-ray structure determination of 2,6-$Trip_2C_6H_3$PbPb-2,6-$Trip_2C_6H_3$ (Trip = 2,4,6-*i*$Pr_3C_6H_2$) (**1Ar**) is a breakthrough in the chemistry of heavier Group 14 analogues of alkynes. The isolation of a stable compound with the formula RPbPbR is not only a great success experimentally, the unusual geometry of **1Ar** (Figure 2a) indicates that the bonding of the molecule is different from the E–E bonding in the species **A**–**D** (Figure 1). The rather long Pb–Pb interatomic distance in **1Ar** (3.188 Å) and the small C-Pb-Pb angle (94.26°) led the authors to suggest that the molecule has only a Pb–Pb single bond.[7] They proposed that the 6p(π) atomic orbitals at the lead atoms are empty and that the Pb–Pb and Pb–C bonds are formed from the remaining two valence p(σ) orbitals of each Pb atom without significant hybridization with the 6s orbital. The latter orbital accomodates a lone pair of electrons which is found at each Pb. Thus the lead atoms have an electron sextet in the valence shell (Figure 2b).

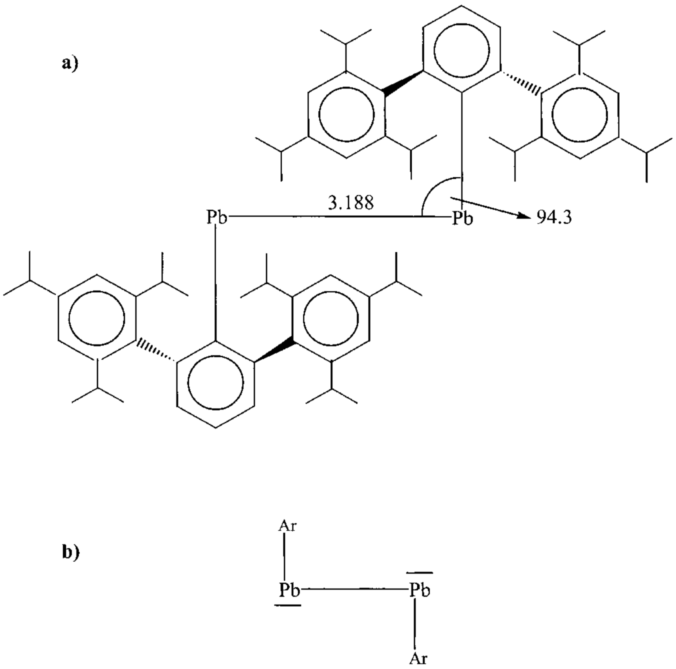


Figure 2. a) Graphical representation of the molecule 2,6-$Trip_2C_6H_3$PbPb-2,6-$Trip_2C_6H_3$ (Trip = 2,4,6-*i*$Pr_3C_6H_2$) (**1Ar**); the experimental Pb–Pb bond length [Å] and C-Pb-Pb bond angle [°] are taken from reference [7]. b) Proposed bonding for **1Ar**.

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The above-mentioned suggestion about the bonding in **1Ar** was made using Pauling's proposed correlation between bond angle and hybridization.[8] However, it has been shown by Kutzelnigg[9] that the correlation is not valid for heavier elements. The bonding shown in Figure 2b does not agree with the *trans*-bent structure **D** which has an out-of-plane π bond. To investigate the bonding in **1Ar** with quantum-chemical methods we carried out denisty functional theory (DFT) and ab initio calculations[10] of the parent system Pb_2H_2 (**1H**) and the phenyl-substituted species Pb_2Ph_2 (**1Ph**). We also calculated the equilibrium structure and bonding of the model compound Ar*PbPbAr* (**1Ar***) (Ar* = 2,6-$Ph_2C_6H_3$).

The calculated structures of **1H** are shown in Figure 3. The doubly bridged form **1H(A)** is the theoretically predicted global minimum on the Pb_2H_2 PES. The calculated geometry is very similar to the theoretical structure which was reported by Han et al. using a relativistic Hartree–Fock method.[5] The singly bridged form **1H(B)** is 15.6 kcal mol^{-1} higher in energy than **1H(A)**. However, **1H(B)** is not an energy minimum at the B3LYP level of theory.[15] Calculation of the vibrational frequencies showed that **1H(B)** has one imaginary frequency and thus, is a transition state. The only other energy minimum form on the Pb_2H_2 singlet PES[16] is the vinylidene analogue **1H(C)**. This isomer is 18.1 kcal mol^{-1} higher in energy than **1H(A)** (Figure 3).

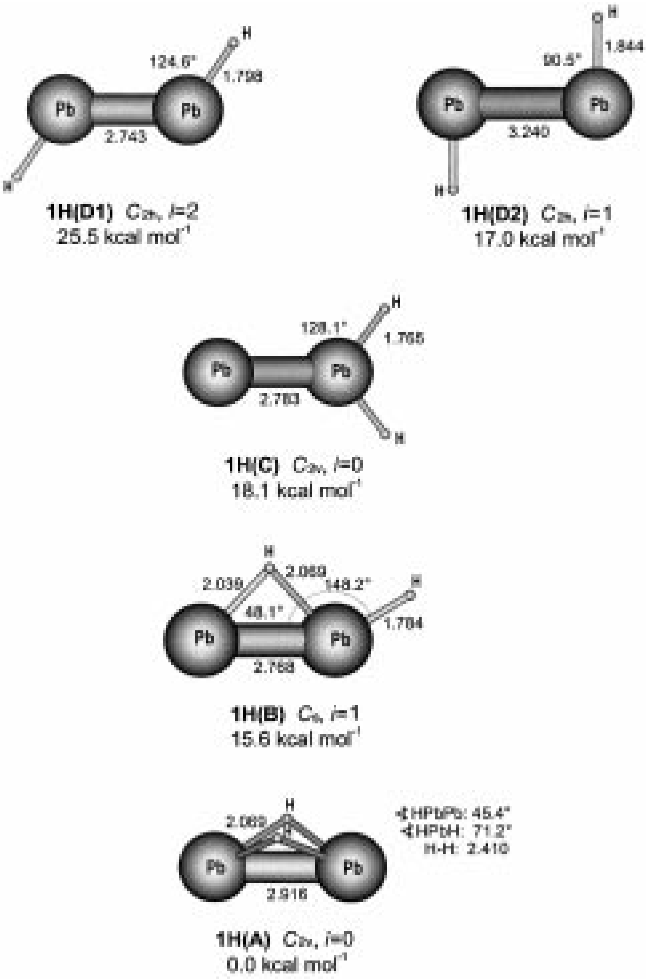


Figure 3. Calculated stationary points on the Pb_2H_2 singlet PES at the B3LYP level with information on the number of imaginary frequencies (*i*) and relative energies. Bond lengths in Å and bond angles in degrees.

We searched for *trans*-bent forms of Pb_2H_2 by using theoretical methods. Geometry optimizations with the constraint of planar symmetry yielded two structures **1H(D1)** and the energetically lower lying form **1H(D2)** (Figure 3). The former species is the lead analogue of the structure **D** which was found as a high-lying energy minimum on the Si_2H_2 and Ge_2H_2 PES.[4] The H-Pb-Pb bond angle (124.6°) of **1H(D1)** is similar to the values which have been reported for the **D** forms of Si_2H_2 and Ge_2H_2. Inspection of the calculated orbitals showed that **1H(D1)** has an occupied Pb–Pb π orbital as HOMO (Figure 4a). The second *trans*-bent form **1H(D2)** has a significantly longer Pb–Pb distance (3.240 Å) than **1H(D1)** (2.743 Å) and a smaller H-Pb-Pb bond angle (90.5°). Analysis of the electronic structure of **1H(D2)** showed that the HOMO is a σ orbital which can be described as a lone-pair orbital, while the Pb–Pb π orbital is the LUMO (Figure 4b). Thus, HOMO and LUMO of **1H(D1)** and **1H(D2)** are exchanged and the former species can be considered as the first excited singlet state of **1H(D2)** with the same symmetry (^1A_g). The lower energy of **1H(D2)** can be explained with the electronic structure of PbH in the doublet electronic ground state and with the doublet → quartet excitation energy. Figure 5 shows that the dimerization of PbH in the $^2\Pi$ ground state via coupling of the unpaired electrons directly leads to **1H(D2)**, while the $^4\Sigma^-$ excited state of PbH is the reference state for the higher lying π-bonded form **1H(D1)**. The calculations suggest that **1H(D1)** is higher in energy than **1H(D2)** because the $^2\Pi \rightarrow {}^4\Sigma^-$ excitation energy of PbH is larger than the energy gain of the Pb–Pb π bond in the former isomer. Calculations at the B3LYP level show that the

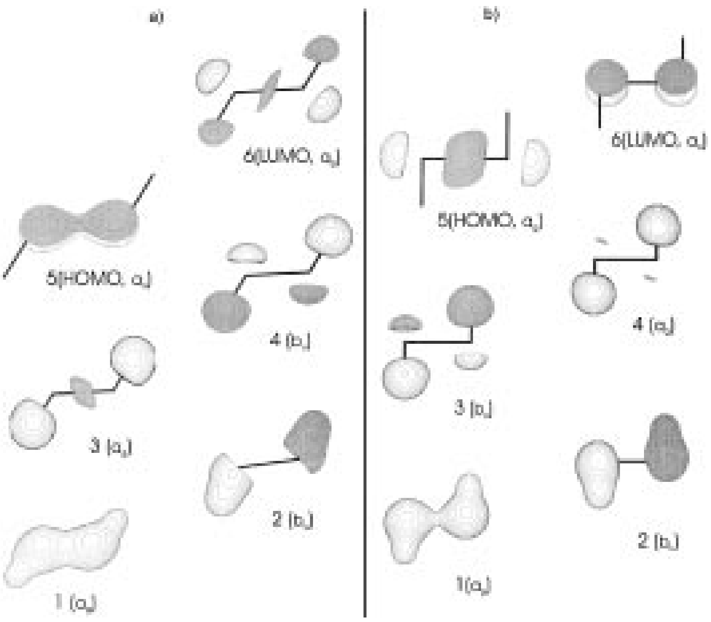
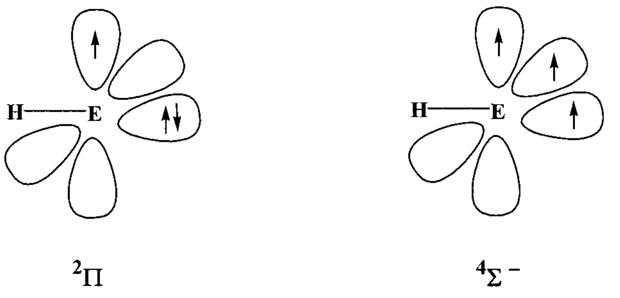


Figure 4. Plot of the valence orbitals of **1H(D1)** (a) and **1H(D2)** (b).



0.0 kcal mol^{-1}

exp.	B3LYP
16.7	20.7 kcal mol^{-1} (E=C)
36.4[a]	43.1 kcal mol^{-1} (E=Si)
47.8	49.2 kcal mol^{-1} (E=Ge)
44.5	46.6 kcal mol^{-1} (E=Sn)
50.3	54.6 kcal mol^{-1} (E=Pb)

Figure 5. Schematic represenation of the $^2\Pi$ electronic ground state and $^4\Sigma^-$ excited state of EH (E = C – Pb). Calculated $^2\Pi \rightarrow {}^4\Sigma^-$ excitation energies at the B3LYP level. Experimental values were taken from ref. [19]. [a] The full configuration interaction estimate of SiH was taken from ref. [20].

$^2\Pi \rightarrow {}^4\Sigma^-$ excitation energy of PbH is the highest among the Group 14 hydrides EH (Figure 5). Furthermore, the π-bond energy decreases for heavier atoms of the same group.[9] The calculated excitation energies of EH are supported by the experimental values and high-level ab initio data which are also shown in Figure 5. The good agreement between theory and experiment indicates that the theoretical values should be quite reliable.

The calculated Pb–Pb distance and the H-Pb-Pb angle of **1H(D2)** agree very well with the experimental values of **1Ar**.[7] However, **1H(D2)** is a high-lying transition state and not an energy minimum on the Pb_2H_2 PES. We investigated the question of whether the relative energies of structures **A** and **D** might be reversed for the phenyl-substituted system Pb_2Ph_2 (**1Ph**). Figure 6 shows the calculated geometry of **1Ph(A)**. The DFT calculations predict an unsymmetrical bridging of the lead atoms by the phenyl substituents, while the MP2 method gives a symmetrical structure with Pb–C distance of 2.579 Å. The Pb–C bond lengths at the B3LYP level are 2.467 and 2.780 Å. The calculations suggest that the isomer **1Ph(A)** is the global minimum on the Pb_2Ph_2 potential energy surface. The *trans*-bent forms **1Ph(D1)** and **1Ph(D2)** are 10.0 and 8.0 kcal mol^{-1} higher in energy than **1Ph(A)**.

Inspection of the orbital structure showed that the Pb–Pb bonding of **1Ph(D1)** and **1Ph(D2)** is the same as in **1H(D1)** and **1H(D2)**, that is the former has a Pb–Pb π bond, while the latter has a lone pair of electrons at each lead atom. Note that **1Ph(D2)** is only 2.0 kcal mol^{-1} lower in energy than **1Ph(D1)**, while **1H(D2)** is 8.5 kcal mol^{-1} more stable than **1H(D1)**.[17] The phenyl-substituted structures **1Ph(D1)** and **1Ph(D2)** are like the parent compounds **1H(D1)** and **1H(D2)** not minima on the PES. The calculations give one imaginary frequency for **1Ph(D2)** and two imaginary frequencies for **1Ph(D1)**. Thus, the experimentally observed stability of **1Ar** cannot be explained with electronic effects of the aryl substituents.

We finally calculated the model compound **1Ar*** which has bulky substituents (Ar* = 2,6-$Ph_2C_6H_3$) bonded to the lead atoms. The geometry optimization of a structure in which the Ar* groups are in a bridging position like in **1Ph(A)** failed because of steric repulsion between the large substituents. The calculations rather yielded the *trans*-bent form **1Ar*(D2)** (Figure 7). Calculation of the Hessian matrix showed that, unlike **1Ph(D2)**, **1Ar*(D2)** is an energy minimum. The orbital analysis revealed that there is no Pb–Pb π bond in **1Ar*(D2)**. The calculated Pb–Pb bond length (3.213 Å) and the C-Pb-Pb angle (91.2°) are very similar to the experimental data of **1Ar** (Figure 2a). They are also similar to the calculated values of **1H(D2)** and **1Ph(D2)**. However, the latter structures are transition states and not energy minima. It follows that the steric effect of the large aryl substituents Ar* not only stabilizes the *trans*-bent form **D2** relative to the other isomeric forms **A** – **C** energetically, it also contributes to **D2** becoming

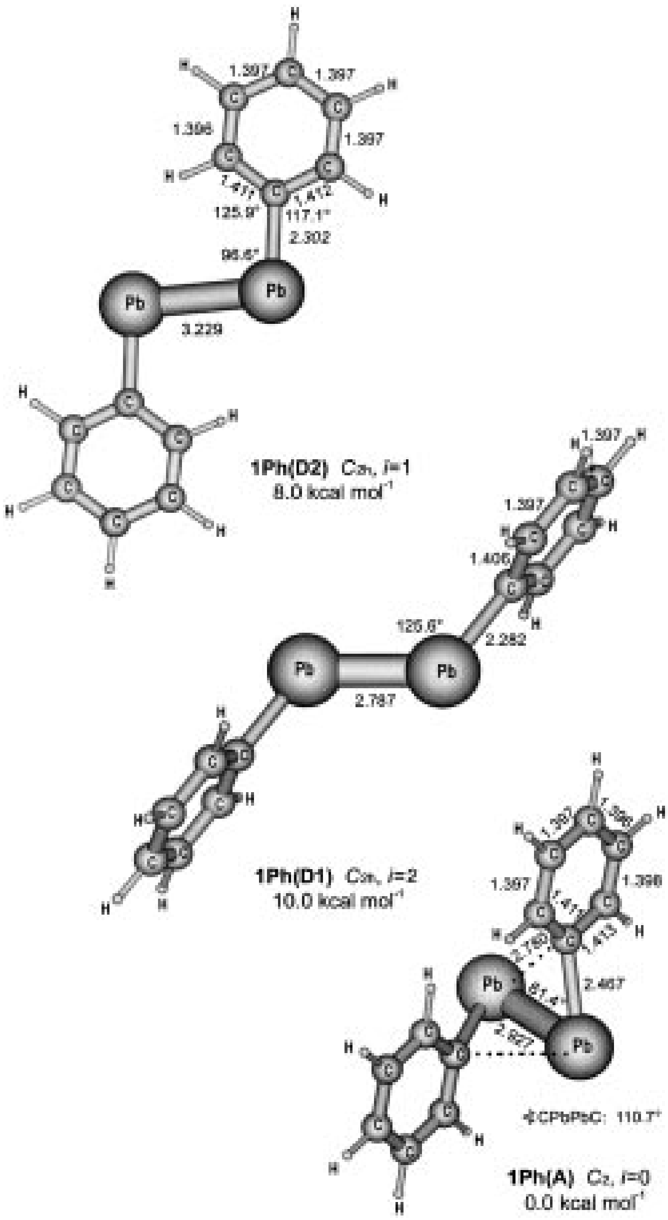


Figure 6. Calculated stationary points on the Pb_2Ph_2 singlet PES at the B3LYP level with information on the number of imaginary frequencies (*i*) and relative energies. Bond lengths in Å and bond angles in degrees.

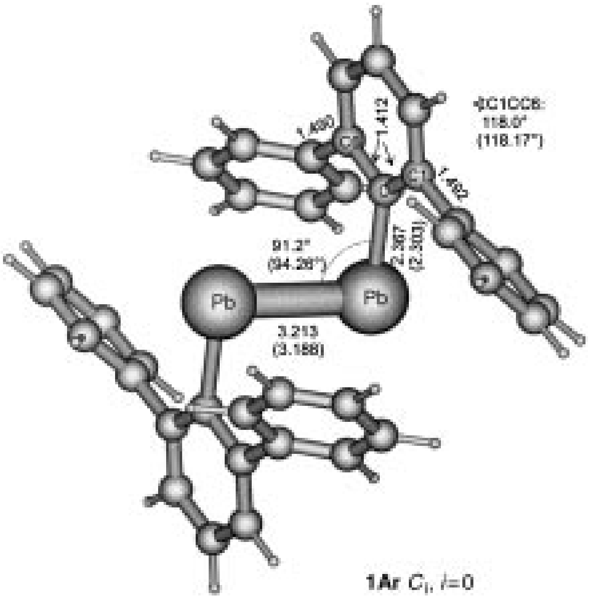


Figure 7. Calculated geometry of **1Ar*(D2)** at the B3LYP level. Bond lengths in Å and bond angles in degrees. Experimental values of **1Ar** are given in parentheses.

an energy minimum rather than a transition state. The lower energy of the six-valence-electron form **D2** compared with **D1** is an electronic effect which is already found in the parent system **1H(D)**.

The results presented here indicate that the lighter homologues of **1Ar** with E = Si – Sn might also be isolated. Recent experimental work has shown that the compound $Si_2(2,6\text{-}Mes_2C_6H_3)_2$ (Mes = 2,4,6-$Me_3C_6H_2$) is probably formed as an intermediate.[18] Our calculations suggest that $Si_2(2,6\text{-}Mes_2C_6H_3)_2$ should rather display bonding like that in **D1**, because the energetically lowest *trans*-bent form of Si_2H_2 has a π bond.[21] We are currently investigating the structure and bonding of E_2R_2 (E = Si – Sn; R = H, Ar).

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[10] The geometries have been optimized at the B3LYP level[11] using a quasi-relativistic ECP[12] with a (31/31/1) valence basis set for Pb and 6-31G(d) basis sets for C and H (6-31G(d,p) in the case of Pb_2H_2). The vibrational frequencies of the optimized structures were calculated with second analytical derivatives. Calculations of the Pb_2H_2 and Pb_2Ph_2 isomers have also been carried out at the MP2 level.[13] Because the results at the MP2 and B3LYP levels are very similar we give only the B3LYP data. MP2 values are only reported when larger deviations from the B3LYP results were observed. The calculations were carried out with the program package Gaussian 98.[14]

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[15] The MP2 calculations predict that **1H(B)** is an energy minimum which is 15.9 kcal mol^{-1} higher lying than **1H(A)**.

[16] Calculations of Pb_2H_2 in the triplet state gave structures which are higher in energy than **1H(A)**.

[17] The smaller energy difference between **1Ph(D1)** and **1Ph(D2)** seems to be related to the repulsion between the π electrons of the phenyl substituents and the Pb–Pb π electrons (in **1Ph(D1)**) or Pb lone pairs of electrons (in **1Ph(D2)**). Note that the phenyl rings in **1Ph(D1)** are rotated by 90° out of the molecular plane which means that there is no conjugation between the phenyl π electrons and the Pb–Pb π bond. The planar form of **1Ph(D1)** is an even higher order saddle point (i = 3) which is 4.3 kcal mol^{-1} higher in energy than the structure which is shown in Figure 6. The phenyl rings of **1Ph(D2)** are in the molecular plane. The equilibrium structure in which the phenyl rings of **1Ph(D2)** are rotated by 90° is 8.2 kcal mol^{-1} higher in energy than the planar form.

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