

## Theoretical Group 14 Chemistry. 4. Cyclotriplumbanes: Relativistic and Substituents Effects

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**Abstract:** We report a study on the first newly synthesized homonuclear lead ring system, the cyclotriplumbane  $\text{Pb}_3\text{R}_6$ . Its geometrical features can be best reproduced using perturbation theory (MP2) together with the Stuttgart-Dresden basis set and ECP for lead. The experimentally observed tilting of the groups R in the cyclotriplumbanes is attributed to the bonding situation: the lead–lead contacts, formed from weak interactions of plumbylene lone pairs with empty p orbitals of neighboring lead atoms, try to maximize overlap. Surprisingly and in contrast to the inert pair effect, hybridization of the former plumbylene lone pair orbitals in the cyclotriplumbane  $\text{Pb}_3\text{R}_6$  is observed, depending on the substituent. Hybrid orbitals with a 6s orbital contribution of only about 40% are found. Hydrogen atoms and methyl groups promote this effect, while for phenyl substitution the expected 6s lone pair orbital is identified as the bond-forming orbital.

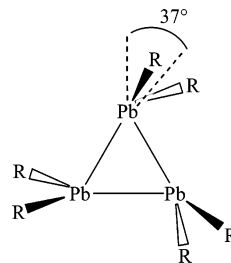
### Introduction

The chemistry of the stable heavy elements of the periodic system is not only influenced by group tendencies but also by increasingly important relativistic effects.<sup>2</sup> One of the main consequences is the energetic lowering of 6s electrons (in case of lead) whose availability for chemical bonding is therefore limited.<sup>3</sup>

While homonuclear double bonds between silicon, germanium, and tin atoms are well-known in the literature for some time,<sup>4</sup> it has been possible only a few years ago to isolate the first representative of diplumbenes, compounds with a short  $\text{Pb}=\text{Pb}$  double bonds.<sup>5</sup> However, these bonds with distances of 2.90–3.05 Å are longer than those of a typical  $\text{Pb}-\text{Pb}$  single bond, for instance in hexaphenyl-diplumbane with 2.844 Å.<sup>6</sup> In agreement with theoretical calculations on the parent compound  $\text{H}_2\text{Pb}=\text{PbH}_2$ ,<sup>7–9</sup> the experimental bond lengths and the pronounced trans-bending of the substituents from the  $\text{Pb}-\text{Pb}$  vector indicate that the double bond in diplumbenes is formed by dual donor–acceptor interactions of the occupied 6s<sup>2</sup> orbitals with the empty 6p orbitals of the neighboring lead atom.

Recently, we were able to obtain cyclotriplumbane **1** as

the first homocyclic compound formed from lead atoms.<sup>10</sup> Lead–lead distances of averaged 3.18 Å together with a substituent twisting of 37° out of their ideal positions indicate that bonding in the three-membered ring is dominated by donor–acceptor interactions and not by overlapping sp-hybridized orbitals. However, the structural parameters of **1** are only in limited accordance with an early theoretical study on the parent system  $\text{Pb}_3\text{H}_6$ .<sup>11</sup> Despite the sterically undemanding hydrogen atoms, a longer  $\text{Pb}-\text{Pb}$  distance of 3.231 Å and trans-bent angles of 51° were determined. The employment of the outdated Hartree–Fock level of theory, a relatively small basis set for the geometry optimizations, and the restriction to hydrogen as substituent does not allow reliable conclusions.



**1**, R = 2,4,6- $\text{Et}_3\text{C}_6\text{H}_2$

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We think it is timely to obtain more information on the interplay of relativistic effects and substituent influence and have therefore embarked on such a study on cyclotriplumbane with different substituents and report herein the results.

## Computational Details

In the present study all calculations at the Hartree–Fock (HF),<sup>12</sup> density functional theory (DFT, employing the hybrid functional B3LYP),<sup>13,14</sup> many-body perturbation theory methods (second-order Møller–Plesset (MP2),<sup>15,16</sup> and coupled-cluster theory including single, double, and triple excitations (CCSD(T))<sup>17–19</sup> were performed with Gaussian 98,<sup>20</sup> together with Pople's 6-31G(d)<sup>21–23</sup> basis set for C and H and the Stuttgart/Dresden (SDD) basis set and effective core potentials (ECP)<sup>24,25</sup> for Pb (denoted as "I"). For comparison, calculations with the LANL2DZ<sup>26</sup> basis set and pseudopotential for Pb ("II") and a triple- $\zeta$  ("TZ") base (cc-pVTZ-PP for lead<sup>27</sup> and 6-311G(2d,2p)<sup>28,29</sup> for other atoms) were also performed. Both the SDD and the LANL2DZ basis sets employed for lead are of double- $\zeta$  quality, but the former basis set is generally considered superior over the latter because polarization functions are included. The CCSD(T) calculations used the relatively small basis set I and the triple- $\zeta$  ("TZ") base. The nature of all optimized structures was confirmed as minima or transition state by calculating harmonic frequencies. Population analyses were performed with NBO<sup>30,31</sup> as implemented in Gaussian 98 and atoms-in-molecules investigations<sup>32,33</sup> with AIM2000<sup>34</sup> employing the MP2 wave function.

## Results and Discussion

In a first step,  $\text{Pb}_3\text{R}_6$  with  $\text{R}=\text{H}$ , Me, and phenyl were optimized at various levels of theory (see below and Table 1 for details). At the Hartree–Fock level of theory, Pb–Pb bond lengths are largely overestimated independent of the employed basis set/ECP for lead, compared to either the experimental data or coupled-cluster calculations which serve as reference data for the smaller groups where no experimental data are available. Hartree–Fock is not a sufficient level of theory to describe the geometry of cyclotriplumbanes! The general trend is an elongation of the Pb–Pb bond distances when increasing the steric demand of the substituents. DFT calculations with B3LYP differ only slightly from the MP2 results for  $\text{R} = \text{H}$ , but larger substituents result in a Pb–Pb bond length overestimation: for instance, in hexaphenylcyclotriplumbane, the distances are calculated to be 0.1 Å longer compared to the MP2 data. The latter calculations give the shortest Pb–Pb distances for  $\text{R} = \text{Ph}$  (3.216 Å) and the best agreement with the experimental result which surprisingly shows even shorter contacts despite bulkier groups (3.185 Å). The comparison between SDD and LANL2DZ shows that both basis sets give similar results. In combination with perturbation theory, SDD gives slightly shorter distances, while the other two approaches yield shorter contacts with LANL2DZ. However, SDD is generally considered to be superior due to the inclusion of polarization functions and is therefore to be preferred.

Although both theory and basis set should be systematically better than the other levels of theory, the "TZ" basis

**Table 1.** Selected Geometrical Properties of  $\text{Pb}_3\text{R}_6$  and **1** with Different Theoretical Methods Respectively from Experimental Results<sup>a</sup>

structure	method	Pb–Pb bond length	trans-bent angle
$\text{Pb}_3\text{H}_6$	HF/I	3.270 Å	49.9°
	HF/II	3.269 Å	50.8°
	B3LYP/I	3.165 Å	50.9°
	B3LYP/II	3.142 Å	51.7°
	MP2/I	3.132 Å	50.3°
	MP2/II	3.140 Å	51.6°
	MP2/TZ	2.972 Å	51.1°
	CCSD(T)/I	3.161 Å	51.4°
	CCSD(T)/TZ	3.026 Å	51.1°
$\text{Pb}_3(\text{CH}_3)_6$	HF/I	3.336 Å	44.5°
	HF/II	3.352 Å	45.1°
	B3LYP/I	3.215 Å	43.5°
	B3LYP/II	3.182 Å	42.6°
	MP2/I	3.161 Å	43.8°
	MP2/II	3.192 Å	44.2°
	MP2/TZ	2.986 Å	44.8°
$\text{Pb}_3\text{Ph}_6$	HF/I	3.579 Å	49.2°
	B3LYP/I	3.310 Å	47.1°
	MP2/I	3.216 Å	50.2°
$\text{Pb}_3(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_6$	B3LYP/I	3.364 Å	35.0°
	B3LYP/I	3.185 Å	31.2°
		(constrained)	
<b>1</b>	exptl	3.185 Å	37°

<sup>a</sup> Basis set for C and H is 6-31G(d), basis set and ECP for Pb is I: SDD and II: LANL2DZ.

set in combination with perturbation and coupled cluster theory yields bond lengths that are significantly shorter (about 3.0 Å) than all other calculated and experimental data. One should therefore use these results with care as weak lead–lead interactions are rare and may be overestimated in this basis set. Also, these "TZ" calculations are very sensitive to the proper choice of the ECP. For instance use of the SDD ECP gives distances of 3.26 Å, much too long.

The twisting of the substituents is estimated to be about 50° for  $\text{R} = \text{H}$  and Ph, while it is slightly smaller with the sterically more demanding methyl group ( $\sim 44^\circ$ ). There is a discrepancy to the experimental value of 37° which is observed with the much larger 2,4,6- $\text{Et}_3\text{C}_6\text{H}_2$  substituent. B3LYP optimization (MP2 is not feasible) of  $\text{Pb}_3(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_6$  results in a reduction of the trans-bent angles to 35°, now in excellent agreement with the experiment, indicating that a phenyl group is by no means an adequate geometry model for the bulky triethylphenyl substituent!<sup>1,35</sup> To summarize, the MP2/I calculations give the best agreement with the experimental structure with B3LYP, and in particular HF methods show significant deficiencies in the prediction of Pb–Pb distances.

The reported structures with long lead–lead distances and our population analyses clearly indicate that these "bonds" are not classical single bonds but rather weak interactions between three plumblylene units. To obtain information on how weak these contacts really are, bond dissociation energies are determined. However, one has to keep in mind that these values include the release of ring strain of the three-

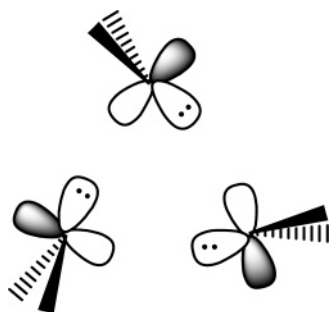
**Table 2.** Bond Dissociation Energies (kJ/mol) for the Reaction  $\text{Pb}_3\text{R}_6 \rightarrow 3 \text{PbR}_2$  at Different Levels of Theory

structure	B3LYP/I	MP2/I	CCSD(T)/I	CCSD(T)/TZ
$\text{Pb}_3\text{H}_6$	129.7	133.8	121.6	185.4
$\text{Pb}_3\text{Me}_6$	114.1	132.8		
$\text{Pb}_3\text{Ph}_6$	73.1	150.7		

**Table 3.** Bond Dissociation Energies (kJ/mol) for the Reaction  $\text{E}_3\text{H}_6 \rightarrow 3 \text{EH}_2$  at the Perturbation Theory Level

structure	MP2/I
$\text{C}_3\text{H}_6^a$	1151 <sup>b</sup>
$\text{Si}_3\text{H}_6$	582 <sup>b</sup>
$\text{Ge}_3\text{H}_6$	555 <sup>b</sup>
$\text{Sn}_3\text{H}_6$	449
$\text{Pb}_3\text{H}_6$	134

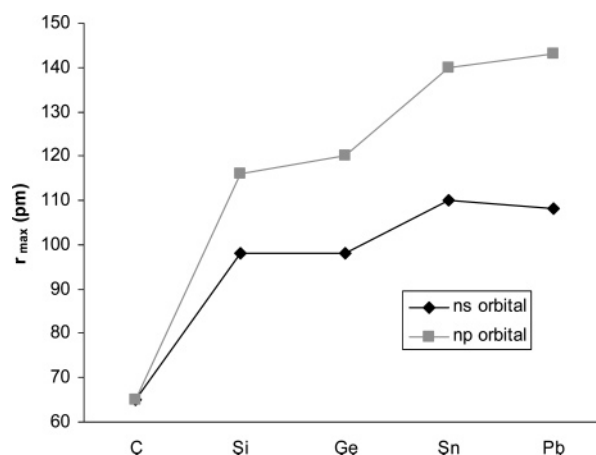
<sup>a</sup>  $\text{CH}_2$  calculated as triplet. <sup>b</sup> The 6-31G(d) basis set was used for the central atom.

**Figure 1.** Schematic interactions of the lead–lead bonds in cyclotriplumbanes (reproduced from ref 11).

membered rings as well and therefore do not directly correspond to the energy of three single bonds.

One can clearly see from Table 2 that independent of the employed level of theory, the bond dissociation energy for cyclotriplumbanes is almost constant at 45 kJ/mol per bond/interaction. The exceptions are the DFT-optimized hexaphenylcyclotriplumbane with too long and hence too weak Pb–Pb contacts and the CCSD(T)/TZ-derived values with too short and hence too strong Pb–Pb bonds. The comparison with the lighter homologues confirms the weak nature of the lead–lead interactions: a C–C bond is almost nine times stronger and even cyclotristannane possesses three times stronger bonds (Table 3).

To explain why the substituents are twisted out of their “ideal” positions one has to look on the orientation of the orbitals forming the Pb–Pb contacts in cyclotriplumbane. Plumbylenes usually exist in a singlet state with the lone pair formed predominantly from the 6s orbital. This is confirmed by NBO calculations of different MP2-optimized  $\text{PbR}_2$  structures (contribution of more than 85%, independent of R). As expected for a singlet carbene analogue, the lone pair and the unoccupied p orbital are about orthogonal to each other ( $92^\circ$  in  $\text{PbH}_2$  and  $\text{Pb}(\text{CH}_3)_2$  and  $95^\circ$  in the phenyl-substituted plumbylene). To maximize overlap between doubly occupied  $6s^2$  and empty 6p plumbylene orbitals in cyclotriplumbane, the  $\text{PbR}_2$  units have to arrange in a tilted manner as shown in Figure 1. This kind of bonding bears a similarity to the double bonds formed by heavier homologues

**Figure 2.** The calculated sizes of the valence *ns* and *np* orbitals of group 14 elements.<sup>36</sup>

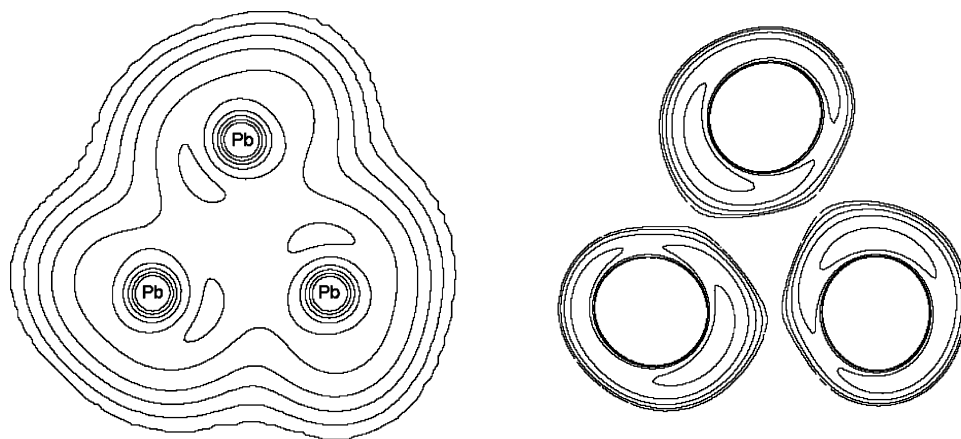
of group 14 elements where also the same interactions and trans-bent angles exist. The smaller trans-bent angles in **1** and in  $\text{Pb}_3(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_6$  result from the interplay between maximum overlap and the increased steric demand of the substituents.

The predominance of singlet carbene analogues can be contributed to the relativistic contraction of the 6s electrons.<sup>2,3</sup> It is known that with the increasing atomic number the difference in the radial extensions of the s and p orbitals of group 14 elements also increases (Figure 2).<sup>36</sup> The splitting of *np* orbitals due to spin–orbit coupling is not taken into account in the figure because although the resulting  $\text{Pb } p_{1/2}$  and the  $p_{3/2}$  orbitals differ in size, they are still significantly larger than the 6s orbital.<sup>2</sup> The described radii difference renders hybridization of s and p orbitals highly unfavorable with the higher homologues (“inert pair effect”). Another study suggests a dependency of size of the orbital radii and hence the hybridization on the metal partial charge.<sup>37</sup>

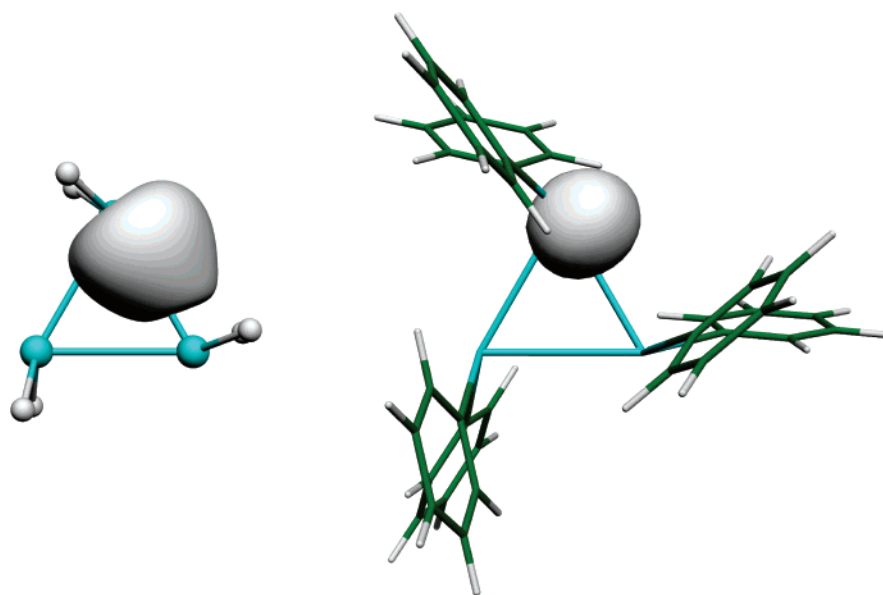
From the literature it is known that the trans-bent angle in double bond systems can be correlated with the singlet–triplet splitting of the corresponding carbene analogues.<sup>38</sup> A large gap corresponds to a large displacement angle. We calculated the singlet–triplet gaps of the according plumbylenes and found that the gap rises from 132 kJ/mol for  $\text{PbH}_2$  to 171 kJ/mol for  $\text{PbPh}_2$ . The trans-bent angles however do not follow this trend but decrease from hydrogen to methyl and rise again to phenyl. Therefore, the energy gap cannot be correlated with the trans-bent angle in case of the cyclic structures.

Atoms-in molecule population analysis performed on cyclotriplumbanes confirm the nature of interactions between the lead atoms. Relevant bond- and ring-critical points could be located, thereby describing the weak donor–acceptor interactions as bonding. Contour plots of the electron density and the Laplacian of the electronic charge density (charge concentrations,  $\nabla^2\rho(r) < 0$ ) reveal areas of increased electron density where the donor orbitals are located but do not show significant differences for the employed substituents; Figure 3 illustrates the situation in  $\text{Pb}_3\text{H}_6$ .

As mentioned above, our NBO analyses of the cyclotriplumbanes show that the lead–lead bonds are formed by weak interactions between an occupied orbital and an empty



**Figure 3.** Contour plots of the electron density  $\rho$  (left) and the Laplacian of the electronic charge density  $\nabla^2\rho(r)$  (right) of cyclotriplumbane.



**Figure 4.** Influence of substitution on hybridization of bond-forming orbital: a lead  $sp$  hybrid orbital in  $Pb_3H_6$  (left) and an almost pure  $s$  orbital in  $Pb_3Ph_6$  (right). The spherical form of the latter indicates the absence of a  $p$  contribution.

$p$  orbital of a neighboring Pb atom with the occupied orbital being the former lone pair of the plumblylene unit. Interestingly, there are differences in the composition of these occupied orbitals in the trimeric structure which depend on the substituent R. The  $s$  orbital contribution in the plumblylenes is above 85%, it is more or less the same for hexaphenylcyclotriplumbane (81%), resulting in doubly occupied, almost pure  $s$  orbitals. However, the smaller hydrogen atoms and the methyl group lead to a reduction of the  $s/p$  ratio in the cyclotriplumbanes, hence hybridization of the “inert”  $6s$  and  $6p$  orbitals takes place: the formerly pure  $s$  lone pair possesses now only around 40%  $s$  character, and the Pb–Pb bond-forming occupied orbitals are now formally between  $sp$  and  $sp^2$  hybrid orbitals (Table 4). Figure 4 illustrates the different occupied orbitals. This is somewhat surprising considering the textbook knowledge of the inert pair effect where no hybridization should take place.

Analysis of the frontier orbitals (Table 4) does not give further indication why the phenyl-substituted cyclotriplumbane hybridizes and the other two do not. The relevant

**Table 4.** NLMO Analysis of Hybridization and Frontier Orbital Energies (in a.u.) in Cyclotriplumbanes and Plumblylenes

species	Pb–R $s/p$ ratio	“lone pair” $s/p$ ratio <sup>a</sup>	HOMO/LUMO	H/L gap
$PbH_2$	8/92	85/15	−0.318/0.002	0.320
$Pb_3H_6$	29/71	43/57	−0.308/0.005	0.313
$Pb(CH_3)_2$	6/94	88/12	−0.288/0.022	0.310
$Pb_3(CH_3)_6$	31/69	38/62	−0.269/0.035	0.304
$PbPh_2$	7/93	87/13	−0.302/0.013	0.315
$Pb_3Ph_6$	9/91	81/19	−0.279/0.008	0.287

<sup>a</sup>  $s/p$  contributions in % of the former lone pair, forming the Pb–Pb bond in the trimer.

plumblylene orbitals have very similar shapes, and the only notable feature is the lowering of the HOMO/LUMO gap in  $Pb_3Ph_6$ .

## Conclusions

It is of utmost importance to employ a reasonably high level of theory together with a reliable basis set/ECP combination



in order to reproduce both geometry and bonding situation of plumblylenes and the trimeric cyclotriplumbane  $\text{Pb}_3\text{R}_6$ . Substitution has a pronounced influence on the geometry, so that MP2 calculations are necessary to get the required good agreement with the experimental structure. Also, phenyl groups are not adequate for the reproduction of the trans-bent angles in **1**. The bulkier trimethylphenyl substituents give the correct tilting of the groups R in the cyclotriplumbanes which is attributed to the bonding situation: the lead–lead contacts are formed from weak interactions of plumblylene lone pairs with empty p orbitals of neighboring lead atoms, and in order to maximize overlap, the plumblylene units have to twist from their “ideal” positions. The trans-bending cannot be correlated with the singlet–triplet splitting as in double bond systems.

Another striking observation is the hybridization of the former lone pair orbitals in the cyclotriplumbane  $\text{Pb}_3\text{R}_6$ . Depending on the substituent, hybrid orbitals with a 6s orbital contribution of only about 40% are found. Hydrogen atoms and methyl groups promote this effect, in contrast to the inert pair effect, while for phenyl substitution the expected 6s lone pair orbital is identified as the bond-forming orbital.

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