Donor–Acceptor Strategies for Stabilizing Planar Diplumbenes

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Supporting Information

ABSTRACT: Diplumbenes, R₂PbPbR₂, are more pyramidalized and trans-bent than the other group 14 analogues and feature long Pb–Pb bonds. A strategy for making these molecules locally planar at Pb, with shorter Pb–Pb separations, starts out from a realization that the Pb–Pb double bond in a hypothetical (LB)PbPb(LB) (LB = Lewis base) is made almost entirely up by 6p orbitals on the Pb atom and has lone pairs on Pb with large 6s character. Coordination of these lone pairs with Lewis acids (LA) should give an ethylene-like structure—effectively a push–pull complex, (LA)(LB)Pb=Pb(LB)(LA). However, the relativistically contracted 6s lone pair on Pb resists effective orbital interaction. To overcome this problem, we evoked in calculations electrostatic interactions between the Pb and Lewis acid ligands, by making the Pb atoms negatively charged and choosing a Lewis acid that carries positive charge. The challenge is to find realistic ligands to engineer these electron shifts. Calculations gave local minima for a diplumbene (LA)(LB)Pb=Pb(LB)(LA), with a base-stabilized borylene as the LB, and LiMe as the LA. These are predicted to be planar and have shorter Pb=Pb double bonds. For the constituent plumbylene (PbR₂) fragments of these candidates, one calculates a triplet ground state.

INTRODUCTION

We seek ways to stabilize a planar structure for substituted diplumbenes, Pb₂R₂, the Pb analogue of ethylene, by modifying the substituents, R. It is not an easy task, as we will see. Unlike ethylene (I, Scheme 1), for heavier group 14 analogues, the planar D₂h structure is no longer the equilibrium one.¹ Computations showed that, for SnH₄ and GeH₄, a trans-bent structure (2) is most stable, whereas, for SnH₄ and PbH₄, still another alternative, a trans-bridged geometry, schematically drawn in 3, takes over.⁷ The E=H=E 3-center bond in 3 can be viewed as the result of a donor–acceptor interaction between the E–H bond of one EH₂ fragment with the vacant p orbital of the other, similar to that in the heavier analogues of alkynes.² The parent molecules (EₐH₄, E = Si, Ge, Sn, Pb) are known only in matrix isolation and gas-phase studies, their structures determined by combined theory and experiment.³–⁷ Due to the high reactivity of these ethylene analogues, their isolation as crystals is possible only with bulky substituents.⁸

The disilene, germene, stannene, plumbene terminology also evokes one attractive approach to their electronic structure—they may be viewed as donor–acceptor dimer complexes of carbene analogues.⁹ The most reactive of the ethylene analogues—the diplumbenes, R₂PbPbR₂—in fact dissociate in solution to plumbylene monomers, R₂Pb.¹⁰–¹⁴ All of the diplumbenes whose crystal structures are available are stabilized by very bulky substituents, and exhibit a trans-bent geometry, unlike the simplest PbH₄ which is known only in gas phase and is suggested to have a trans-bridged structure (3) by calculations.⁵ The Pb–Pb distance in the known trans-bent diplumbenes (2.90–3.16 Å), with a formal double bond, is actually longer than the Pb–Pb single bond in diplubanes, R₂PbPbR₂ (2.84–2.97 Å).¹³,¹⁵ Diplumbenes with even longer bond lengths are known; they are perhaps better considered as plumbylene dimers.¹³ The reversal of the bond length preferences of formally single- and double-bonded Pb–Pb compounds (relative to the carbon archetype) caught our attention. As a reviewer suggested, perhaps this is not surprising, as two donor–acceptor bonds of the type thought to be at work in the trans-bent diplumbene may combine to produce a net Pb–Pb separation that is longer than a Pb–Pb single bond. We started looking for strategies to planarize the diplumbene, and in the process, perhaps shorten the Pb–Pb double bond relative to Pb–Pb single bond.

Previous computational studies have shown that, from Si to Pb, the planar D₂h structure of the ethylene analogue is a transition state, and its instability relative to the trans-bent...
structure increases down the group.\textsuperscript{5} While the out-of-plane distortion is slight for disilene, it becomes more and more prominent down the group.\textsuperscript{9} Thus, trans-bent equilibrium geometries of \( \text{E}_2\text{H}_4 \) are calculated to be more stable than the planar structure by 0, 2, 9, and 27 kcal/mol, respectively, for \( \text{E} = \text{Si, Ge, Sn, and Pb} \). The geometry follows this energetic trend—as one goes down the group, the pyramidality (measured here by the deviation of the sum of angles around \( \text{E} \) from 360°) increases (Table 1). The energies and geometrical parameters here come from PBE0/Def2-TZVPPD level calculations; details are given in the Computational Methods section at the end of the paper. Thus, planarizing diplumylene will be more difficult compared to the Si, Ge, and Sn analogues. At the same time, any strategy that can planarize a diplumylene is also likely to work for Si, Ge, and Sn analogues, whereas the reverse may not be true. This is the reason why we specifically chose diplumylene, the most difficult case, so to speak, for our study.

The reasons for trans-bending in group 14 ethylene analogues are well-studied and we do not discuss them here.\textsuperscript{9,16–18} It was shown computationally that trans-bending could be decreased by the use of electropositive substituents, such as silyl.\textsuperscript{19,20} A planar structure for digermene can be obtained by using two Li atoms and two alkyl groups as substituents, in a trans fashion.\textsuperscript{21} We found that the known ways to planarize the disilene and digermene do not work with the Sn and Pb analogues, and thus looked for an alternative strategy.

**RESULTS AND DISCUSSION**

**Tuning the Singlet–Triplet Splitting.** Building on previous work,\textsuperscript{19,20} one way to achieve our goal might be to make the constituent plumbylene, \( \text{PbR}_2 \), a triplet ground state. The relevant orbitals of the archetype, \( \text{PbH}_2 \), \( 4 \), are shown schematically and in an orbital plot in Scheme 2. The splitting of the orbitals is very large, 3.9 eV. To stabilize the triplet, we need to depress in energy the vacant \( \pi \) orbital significantly, which can be done with a \( \text{BH}_2 \) substituent. This led us to dimers \( 5 \) and \( 6 \) (Scheme 3).

Calculations did not give a planar minimum for \( 5 \), whereas, for \( 6 \), geometry optimization led to planar \( 7 \) (Figure 1) with a relatively long Pb–Pb bond (2.89 Å). The unlabelled circles here and below are hydrogen atoms. Note the delocalization of the \( \pi \) system extending to only two \( \text{BH}_2 \) groups, and the unusual geometry at the right-hand Pb (Figure 1). We do not see this interesting molecule (see further discussion in the SI; it can be viewed as a plumbylene adduct of an electron-deficient allene\textsuperscript{25}) as a diplumylene, as the \( \pi \) system is a \( 4c–2e \) one, not localized over the two Pb atoms. The Wiberg bond index for the Pb–Pb bond in \( 7 \) is 0.92, and does not give an indication of a double bond. Other typical \( \pi \) accepting substituents, such as \( \text{NO}_2, \text{CN}, \text{etc.} \), could not stabilize a planar diplumylene. Thus, we decided to look for a way other than \( \pi \) delocalization and began by analyzing the nature of bonding in ethylene analogues, \( \text{R}_2\text{EER}_2 \).

**\( \text{R}_2\text{EER}_2 \) Bonding.** Shown in Figure 2 is a plot of the most probable radius (\textit{r}_{max}) of the valence \( n \) and \( n \) \( \pi \) orbitals of group 14 elements, taken from ref 23 and the Desclaux computations.\textsuperscript{22–25} While the valence 2s and 2p of C have similar \( r_{\text{max}} \) the radii of the corresponding \( n \) and \( n \) \( \pi \) orbitals in the other elements are significantly different. The \( n \) orbitals are more contracted than \( n \) \( \pi \) orbitals for heavier elements, and the degree of contraction increases down the group. This implies that the \( n \) \( \pi \) orbitals of heavier atoms might behave like core orbitals, and hence have poor overlap with orbitals of other atoms. The overlap of \( s \) orbitals requires the heavier atoms to come very close to each other, but that in turn might cause large near-core–valence shell repulsion (repulsion between valence \( n \) \( \pi \) electrons of one atom with core \( n−1 \) \( \pi \) of the other).\textsuperscript{26,28} One anticipates that heavier atoms might prefer to exclude the \( s \) orbital from bonding, or at least reduce its participation.

Table 2 lists the hybridization of the E atom in planar, trans-, and trans-bridged structures of \( \text{E}_2\text{H}_4 \), obtained from a Natural Bond Orbital (NBO) analysis.\textsuperscript{27} Notice that the NBO

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**Table 1. Relative Energy (RE) of the Trans-Bent \( \text{E}_2\text{H}_4 \) with Respect to the Planar One, for \( \text{E} = \text{Si to Pb} \). The pyramidization \((360° − \theta)\) in the trans-bent structure is also shown.\textsuperscript{24}**

<table>
<thead>
<tr>
<th>( \text{E}_2\text{H}_4 )</th>
<th>RE (trans-bent) (kcal/mol)</th>
<th>( 360° − \theta ) (deg)</th>
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<tr>
<td>( \text{Si}_2\text{H}_4 )</td>
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<td>( \text{Ge}_2\text{H}_4 )</td>
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<td>17</td>
</tr>
<tr>
<td>( \text{Sn}_2\text{H}_4 )</td>
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<td>28</td>
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<tr>
<td>( \text{Pb}_2\text{H}_4 )</td>
<td>−27</td>
<td>36</td>
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</table>

\( \theta \) is the sum of H–E–H and E–E–H angles around an E atom in the trans-bent structure—the larger the value of \((360° − \theta)\), the greater is the trans bending and the pyramidality at E.

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**Scheme 2. Frontier Orbitals of Plumbylene**

**Scheme 3. Diplumenenes, with \( \text{BH}_2 \) Substituents**

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**Figure 1.** Optimized geometry of the \( \text{BH}_2 \)-substituted diplumylene, \( 6 \), and its \( \pi \) MO.
analysis of trans-bent Pb₂H₄ does not show any formal Pb–Pb bond orbital, but instead features a lone pair on each Pb with large s character (sp0.18) as shown in Scheme 4. The occupancy of these heavily s lone pairs is relatively low (1.74), due to a donor–acceptor interaction between them and the p orbital on the neighboring Pb, illustrated in Scheme 4. The NBO second-order donor–acceptor stabilization energy for each of these interactions is 47 kcal/mol. Note that this stabilizing interaction is not a measure of the Pb–Pb bond energy, as the total interaction energy has other repulsive contributions. The calculated free energy of dissociation of trans-bent Pb₂H₄ to two PbH₂ fragments is not large: 5 kcal/mol.

As is evident from Table 2, the degree of trans bending and the p character of the σ bonds increase as one goes down the group. Interestingly, the global minima for Sn₂H₄ and Pb₂H₄ (trans-bridged, 3) have all the bonds (E–H σ bond and E–H–E 3-center bond) formed mainly by p orbitals at Pb. Thus, the nonplanar distortion in heavier analogues of ethylene could be seen as a mechanism to increase the p character of the relevant σ bonds. We will use this fact.

**Lewis Base and Acid Coordination as the Strategy.**

Prompted by the above analysis, we started looking for a group that e cient orbital interaction with the lone pairs on Pb atoms would be Pb₂(LB)₂ ( Scheme 6 ), where the N-Heterocyclic Carbene (NHC) is replaced by a general Lewis base, LB (LB = CO, PR₃, H⁻, CH₃⁻, etc.). In order to get an ethylene analogue RR’PbPb’R’ from 9, one could imagine the coordination of two Lewis acids (LA) that would interact with the lone pairs on Pb, as in structure 10. The problem is that efficient orbital interaction with the lone pairs on Pb atoms long Si–Si bond length of 2.23 Å (the Si–Si double bond length in disilenes is typically 2.14 Å) suggest that the bonding (both σ and π) is constructed mainly by p orbitals. The paper by the Robinson group also reports large s character of the lone pair and large p character of the Si–Si σ bond, based on an NBO analysis.

A hypothetical Pb=Pb double-bonded structure analogous to 8 would be Pb₂(LB)₂ ( Scheme 5 ), where the N-Heterocyclic Carbene (NHC) is replaced by a general Lewis base, LB (LB = CO, PR₃, H⁻, CH₃⁻, etc.). In order to get an ethylene analogue RR’PbPb’R’ from 9, one could imagine the coordination of two Lewis acids (LA) that would interact with the lone pairs on Pb, as in structure 10. The problem is that efficient orbital interaction with the lone pairs on Pb atoms long Si–Si bond length of 2.23 Å (the Si–Si double bond length in disilenes is typically 2.14 Å) suggest that the bonding (both σ and π) is constructed mainly by p orbitals. The paper by the Robinson group also reports large s character of the lone pair and large p character of the Si–Si σ bond, based on an NBO analysis.

Table 2. Nature of the Hybrid Orbitals on E Atom, in E₂H₄ from an NBO Analysis. E–H–E and LP Refer to the Three-Center E–H–E Bonding Orbitals and Lone Pair on E, Respectively. For the Heavier Analogue, the Relative Energy (RE) with Respect to the Planar Structure is Also Shown

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<td>sp¹,4</td>
<td>sp⁰,4</td>
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</table>

θ is the sum of H–E–H and E–E–H angles around an E atom in the trans-bent structure—the larger the value of (360 – θ), the greater is the trans-bending and the pyramidality at E.
is likely to be difficult, as these have great 6s character (similar to 8) and lie low in energy. We imagine that the Pb–LA interaction should then be mainly electrostatic. This means that Pb in 9 should carry some negative charge (not easy to engineer for such an electropositive atom) and LA preferably bears a positive charge at the coordinating atom. On the basis of this reasoning, we began with BeMe₂ and LiMe as possible LAs, and CH₃⁻ as an LB.

The calculated structure of 9 is shown in 11, with CH₃⁻ as LB (Figure 3). Dianions analogous to 11 are known for Sn and Ge, with bulkier substituents, instead of the methyl group.²⁹ The geometry of 11 is similar to the Pb analogue of acetylene.³⁰

Figure 3. Calculated structure of hypothetical, dianionic Pb–Pb double-bonded system.

Coordination of two LiMe groups to 11 gave structure 12 (Figure 4), and coordination of two BeMe₂ gave structure 13. These are calculated to be local minima. While structure 12 is planar, structure 13 is slightly nonplanar, with a Be–Pb–Pb–Me dihedral angle of 8°. Comparison of 12 and 13 with the calculated structure of Pb₂Me₂⁻ (11) shows that there is a significant shortening of the Pb–Pb bond on coordination with LiMe and BeMe₂. Competing bridged structures, 14 and 15, were found, analogous to structure 3 for the prototype Pb₂H₄. These structures can be thought of as the outcome of the interaction of the Lewis acid (LA) with the π system. Structure 12 is isoenergetic to 14, and structure 13 is more stable than 15 by 5 kcal/mol. The Pb–Pb bonds in 12 and 13 are shorter than that calculated for Pb₂H₄ (2.86 Å). Dianions 12–15 are calculated to be shallow minima, with several small frequencies below 100 cm⁻¹.

A Potential Triplet State. The HOMO–LUMO gaps calculated for 12 and 13 are 1.9 and 2.2 eV, respectively—not large, hinting at the possibility of low energy triplet structures. The calculated triplet structures, 16 and 17 (Figure 5), lie only ~10 kcal/mol above 12 and 13. In fact, this energy difference between the singlet and triplet structures is a measure of the strength of the π bond, as that π bond is broken in 16 and 17, due to the population of the π* orbital. Notice the twisted geometry of 16 and 17, similar to the triplet excited state geometry of C₂H₄. The energy difference between the C₂H₄ ground state and its triplet state with a broken π bond is 58 kcal/mol, calculated at the same level of theory. It is evident that the C–C π bond is more than 5 times stronger than Pb–Pb π, as measured by this criterion. The Li–Pb–Pb–Li and C–Pb–Pb–C dihedral angles for 16 are 62° and 88°, respectively (these dihedral angles are 180° in 12). Similarly, the Be–Pb–Pb–Be and C–Pb–Pb–C dihedral angles for 17 are 43° and 92° (those dihedral angles are 177° and 180°, respectively, in 13).

Tuning Lewis Base/Acid Ligand Character. Notice that the Pb–Li bond length in 12, 2.84 Å, is close to the sum of their covalent bond radii (2.81 Å), whereas the Pb–Be bond length in 13, 2.60 Å, is longer than the sum of covalent radii (2.37 Å). As a reviewer suggested, we checked the thermodynamic stability of 10 towards direct bonding between LA and LB (10 → 2 (LA–LB) + Pb₂). We found that the free energy of this reaction is 7 and −39 kcal/mol, respectively, for 12 and 13. The BeR₂ ligand is clearly not a good one for realistic implementation of the strategy; we think that LiMe is the Lewis acid best suited for stabilizing planar diplumbene. In all the subsequent stabilization strategies, we will be using only LiMe as the LA. We do this with full awareness that there is likely to be Lewis base coordination of the relatively exposed Li ion. Detailed studies with one pyridine coordinating to Li for all the subsequent stabilization strategies, we will be using only LiMe as the LA. We do this with full awareness that there is likely to be Lewis base coordination of the relatively exposed Li ion. Detailed studies with one pyridine coordinating to Li for these molecules below shows no great effect on the bonding. The natural resonance theory analysis confirmed our idea that the Pb–Li bond in 12 is mainly ionic, with a natural bond order of 0.38, out of which 0.32 is the ionic contribution. The leading NBO resonance structures are shown in Scheme 7, where 12a contributes 53% and 12b contributes 27%. The Pb–C bonds are 50% ionic and 50% covalent.
To get a neutral Pb–Pb double-bonded structure, we have to replace CH₃ in 12 by a neutral Lewis base. At the same time, we need to choose that LB such that Pb in structure 9 continues to be significantly negative. The calculated natural charge on Pb in 11 is −0.42. We calculated the neutral analogues of 11, obtained by replacing CH₃ by typical Lewis bases, such as PH₃, CO, and NHC; these gave charges of −0.12, 0.14, and −0.19, respectively, on Pb. Yet, none of these led to a RR′Pb=PbRR′ planar geometry similar to 12. Thus, we started searching for a neutral, but electropositive, LB; the first base that came to mind is borylene for which transition metal complexes are known. The bonding in these compounds was subjected to a detailed theoretical analysis. However, borylenes like BR, BNR₂, and BF as LB gave structures where the B atom bridges the Pb atoms and the Pb–Pb bond elongates significantly. Following numerous computational trials, we were led to base-stabilized borylenes (BH or BR stabilized by Lewis bases), quite aware that these might be highly reactive.

Borylenes as Lewis Bases. The availability of base-stabilized borylenes (molecules of type 18, Scheme 8) as boron-centered bases is a very recent development. In 18, two LBs formally donate electrons for two bonds with B, while one electron of B is used for the BH bond; the two remaining electrons of B can then be retained as a lone pair. The actual system synthesized is shown in 19, where CAAC (Cyclic Alkyl Amino Carbene) was used as the LB.

Since 19 is too bulky to use for our purpose, and also because the lone pair on B in 19 is delocalized in the CAAC ligand and hence less available for further interaction, we searched for alternatives, based on the same strategy (borylene, BR, with two electron-pair donors attached to B). After several trials, we found that a piperazine-stabilized borylene (PSB), 20 (Figure 6), suited our purposes. Structure 20 was computed to be a local minimum, with no low frequencies (<100 cm⁻¹). Piperazine complexes with transition metals are known (21, Figure 6). Given the fact that transition metal ions may be seen as Lewis acids, similar to borylene, our choice seems reasonable, though hitherto unknown experimentally.

We proceeded to calculate Pb₂(PSB)₂ (22, Figure 7), which emerged as a minimum, with a charge of −0.47 on Pb. As expected, 22 gave a planar structure on coordination with LiMe (23). The Pb–Pb σ and π orbitals of 23 are shown in Figure 8.

Note that the σ bond is formed by nearly pure p. The HOMO–LUMO gap in 23 is 2.4 eV. Again, the coordination of LiMe to 22 to give 23 decreased the Pb–Pb bond length and made it shorter than the single bond in Pb₂H₆ (2.86 Å). The N–H bond in 23 is likely to be very reactive. So let us move to a more realistic example where an alkyl group replaces the H in the N–H bond (similar to stabilization strategies for N-heterocyclic carbenes). From this point on, we use a smaller basis set, Def2-TZVP, as the systems involve large number of atoms. We calculated the N-ethyl-substituted derivative of 23,
as shown in 24 (Figure 9), which is also a planar minimum. Coordination of another Lewis base, e.g., pyridine, to Li is found to increase the Pb–Li distance to 2.97 Å, but still gives a planar minimum, and free energy change associated with this is 0 kcal/mol. Results of the computation on a different conformation of 24 are discussed in the SI.

Other candidates for electropositive Lewis bases are the heavier analogues of carbones represented by 25 (Scheme 9). Atom E in 25 has two lone pairs—one σ-type lone pair, and a π-type lone pair occupying a p orbital. While the σ lone pair, being more core-like, may be less reactive, the π lone pair would render it strongly basic. Frenking et al. have provided a detailed and incisive exploration of the tetrylones and shown that the protonation of the heavier tetrylones occurs at the π lone pair. An example for this kind of system known experimentally, with CAACs as the LB, is shown in 26.

Motivated by the preceding discussion, we moved from CAAC and used piperazine as the donor. The silylone base so formed (27, Figure 10), could stabilize a planar diplumbene, as shown in 28. However, the geometry optimization of the extended conformation, obtained by rotating the silylone fragment by 180°, gave a structure, which is lower in energy by 25 kcal/mol, and does not retain the ethylene-like geometry. Thus, it seems that the heavier analogues of carbones are not as good as base-stabilized borylones, in stabilizing the planar diplumbenes.

Structure 20 is not the only base-coordinated borylene that can stabilize a planar diplumbene. A bispidine-stabilized borylene (BSB), as shown in 29, and similar molecules might also serve the same purpose. Note that, unlike 20, structure 29 benefits from the favorable chair confirmation of the 6-membered rings. The calculated structures of the planar diplumbene, with 29 as LB, are shown in 30 and 31, which correspond to the extended and folded conformations, respectively. Structure 31 is more stable than 30 by 7 kcal/mol (see Figure 11). We also calculated a bridged isomer, which is isoenergetic to 31. The HOMO–LUMO gaps of 30 and 31 are 2.4 and 2.5 eV, respectively.

A Connection to Tetracoordinate Borenium Cations. The borylene-substituted planar diplumbenes studied here can be represented by the general formulation shown in 32 (Scheme 10). Alternatively, one could write a charge-separated structure, 33. One can then see the similarity between 33 and compound 34, where the cation is a tetracoordinate borenium ion. Note that the B in 34 is coordinated to two Lewis bases.
as in 33. The difference between 34 and 33 is that, in the former, an external counteranion is used, whereas, in 33, the external anion is not required, as Pb carries the negative charge. One can think of a planar diplumbene, with a tetracoordinate borenium ion (similar to that in 34) as a substituent, as shown in 35 (Figure 12). Structure 35 was calculated to be a nearly planar local minimum (360° − θ = 2.5° around one of the Pb atoms), as shown in atomic detail, in 36.

![Figure 12: A planar diplumbene designed, and its calculated structure.](image)

**The Diplumbenes Designed.** Table 3 lists the Pb–Pb bond lengths of the planar diplumbenes we have designed, the diplumbane PbH₄ and a trans-bent Pb₂H₆ at the PBE0/Def2-TZVP level. Calculations were done also at other levels such as B3LYP, M06-2X, BP86, and BP86-ZORA (see the SI). The Pb–Pb double bonds in all the designed diplumbenes are shorter than that in trans-bent Pb₂H₆ at all levels of theory applied. However, only for structure 30 is the Pb–Pb double bond shorter than the Pb–Pb single bond in Pb₂H₆, consistently at all levels of theory. For structures 24, 30, 31, and 36, the free energy changes associated with direct bonding (i.e., extrusion) between the borylene-donor and LiMe acceptor are 66, 61, 68, and 24 kcal/mol, respectively, which indicates that such direct bonding is not likely.

Consistent with common views of the reasons for assuming a planar ethylene-analogue geometry, for all of these molecules, the borylene fragment, Pb(LiMe)(Borylene), is a ground state triplet. For the borylene fragments of 24, 30, 31, and 36, the triplet is more stable than singlet by 9, 13, 12, and 2 kcal/mol, respectively.

The free energies of dissociation of the systems 24, 30, 31, and 36 to two LiMe and (LB)Pb==Pb(LB) are 35, 36, 37, and 25 kcal/mol, respectively (corresponding to the cleavage of two Pb–Li bonds). On the other hand, the free energy of dissociation into two triplet borylene fragments (corresponds to the cleavage of Pb–Pb bond) is 33, 27, 33, and 31 kcal/mol, respectively, for 24, 30, 31, and 36. Due to the weak nature of the Pb–Li bonding, we expect these structures might be isolated only in the solid state, not in solution, as in the case with the known diplumbenes.

**The Drawbacks of Our Design.** Though carefully planned, with step-by-step analogy to existing compounds, the molecules we suggest are nevertheless complex, and with that complexity come “escape channels”, reactivities we did not anticipate.

The mainly electrostatic nature of the Pb–Li bond would make it less directional. Thus, Li may stay in-plane or out-of-plane depending on the charge and steric environment, and hence not every base-stabilized borylene can stabilize a planar diplumbene. The planar diplumbenes we calculate have energetically competitive trans-bridged structures. Again, the charge and steric environment may decide their relative stability. In our design, the focus is to prevent the trans-bending, not trans-bridging. At this point, we have to highlight the fact that, even though computationally the trans-bridge structure of the parent diplumbene (Pb₂H₄) is more stable than the trans-bent form, all the experimentally isolated diplumbenes have the trans-bent structure. This might be due to steric protection, though other, still to be investigated, factors of interest to us may be at work. We hope that, even with the competing bridged structures, by proper tuning of the steric environment, it might be possible to attain experimentally a relatively kinetically stable planar diplumbene.

**Relation to the Donor–Acceptor Model.** An interesting relationship of our design strategy for planar diplumbene to the donor–acceptor model of diplumbene bonding is shown in Scheme 11. Central to the donor–acceptor model of the trans-

![Scheme 11. (a) Diplumbene as Donor–Acceptor Complex of Plumbylene Fragments; (b) Diplumbene as a Push–Pull Complex](image)

bent structure is a dative bond between the lone pair on Pb in one PbH₂ fragment with the vacant p orbital on the other. In our design, we “redirect” the donor–acceptor interaction so that it now becomes in between Pb and the substituents (from LB to Pb, from Pb to LA), thus effectively designing what could be called a push–pull complex. The donor–acceptor strategy is not a new thing in the chemistry of heavier alkene analogues. Rivard et al. have shown that heavier group 14 hydrides can be trapped by complexing them with donor and acceptor substituents.

**CONCLUSION**

In an alternative perspective on bonding in the heavier analogues of ethylene, R₂EER₂, the nonplanar distortion of these molecules may be viewed as a mechanism to decrease the σ orbital participation in bonding. This is likely a consequence of the relativistic contraction of σ orbitals, and their consequent core-like behavior. To stabilize a planar diplumbene, a substitution strategy of a push–pull type is suggested and
probed computationally. Lewis bases of a special type, base-
stabilized borylene, play an essential part in our strategy, as do
weak Lewis acids, with positive charge on the acceptor atom,
such as LiMe. Our ligand design to put this strategy into effect
stays close to the known ligands, yet modifies them in what we
think are realistic ways. The molecules described can be
prototypes for the possible planar diplumbenes; no doubt,
experimentalists will find better ligands. The ones we chose, as
realistic as they can be, serve as a proof of principle for the
underlying orbital and donor–acceptor strategy.

**COMPUTATIONAL METHODS**

Computations were carried out using the Gaussian 09 program with
each DFT and wave function methods.48 The employed levels of
theory include MP2, B2PLYP, B3LYP, M06-2X, PBE0, and BP86; the
results with the various methods are qualitatively similar.49

The employed levels of theory include MP2, B2PLYP, B3LYP, M06-2X, PBE0, and BP86; the
results with the various methods are qualitatively similar.48

For discussion, we use computations at the PBE0/Def2-TZVPPD level
unless otherwise specified.50 Results from other levels are given in the
Supporting Information (SI). Calculations at the MP2 and
B2PLYP levels were carried out with a smaller basis set: 6-31++g(d,p)
for lighter elements, and LANL2DZdp for Pb.59, 60 As the calculations
involving Pb, we also carried out relativistic calculations with the zeroth
order regular approximation (ZORA), using the ORCA program.61–64
Relativistic calculations were done using the BP86 functional and using the
segmented all-electron relativistically contracted (SARC) basis set
for Pb, and Def2-TZVP basis set for other elements.65 The relative
energy values include the zero point energies, and the free energy
values include thermal corrections corresponding to 298.15 K.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the
ACS Publications website at DOI: 10.1021/acs.organomet.7b00733.

Comparison of Pb–Pb bond lengths from calculations at
different levels of theory, conformations of structure
24, effect of pyridine coordination to Li in structure
24, a bridged isomer for the planar diplumbenes, 30 and 31,
and bonding in BH2-substituted diplumbenes (PDF)
Coordinates and energies of the calculated structures
(PDF)

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Notes

The authors declare no competing financial interest.

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