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Donor−Acceptor Strategies for Stabilizing Planar Diplumbenes

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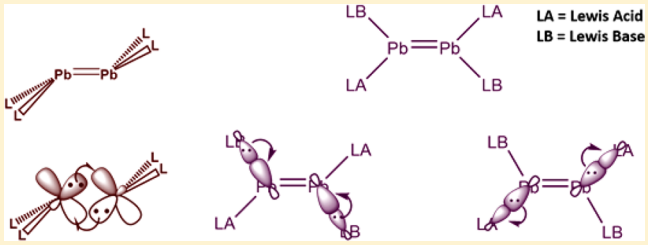
Supporting Information

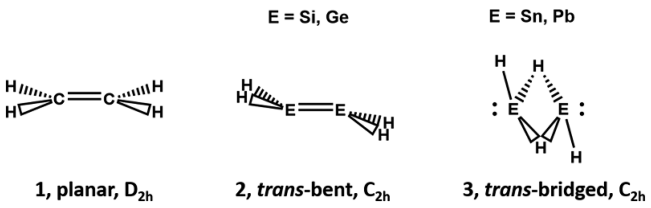
ABSTRACT: Diplumbenes, R_2PbPbR_2, are more pyramidalized and *trans*-bent than the other group 14 analogues and feature long Pb−Pb bonds. A strategy for making these molecules locally planar at Pb, with shorter Pb−Pb separations, starts out from a realization that the Pb−Pb double bond in a hypothetical (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 (PbR_2) fragments of these candidates, one calculates a triplet ground state.



INTRODUCTION

We seek ways to stabilize a planar structure for substituted diplumbene, Pb_2R_4, the Pb analogue of ethylene, by modifying the substituents, R. It is not an easy task, as we will see. Unlike ethylene (**1**, Scheme 1), for heavier group 14 analogues, the planar D_{2h} structure is no longer the equilibrium one.[1] Computations showed that, for Si_2H_4 and Ge_2H_4, a *trans*-bent structure (**2**) is most stable, whereas, for Sn_2H_4 and Pb_2H_4, still another alternative, a *trans*-bridged geometry, schematically drawn in **3**, takes over.[1] 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 EH_2 fragment with the vacant p orbital of the other, similar to that in the heavier analogues of alkynes.[2] The parent molecules (E_2H_4, 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]

Scheme 1. Equilibrium Structures for Ethylene and Its Heavier Analogues



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, R_2PbPbR_2—in fact dissociate in solution to plumbylene monomers, R_2Pb.[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 Pb_2H_4, 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 diplumbanes, R_3PbPbR_3 (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 D_{2h} structure of the ethylene analogue is a transition state, and its instability relative to the *trans*-bent

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structure increases down the group.[1] While the out-of-plane distortion is slight for disilene, it becomes more and more prominent down the group.[8] Thus, *trans*-bent equilibrium geometries of E_2H_4 are calculated to be more stable than the planar structure by 0, 2, 9, and 27 kcal/mol, respectively, for E = 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 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 diplumbene will be more difficult compared to the Si, Ge, and Sn analogues. At the same time, any strategy that can planarize a diplumbene 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 diplumbene, the most difficult case, so to speak, for our study.

Table 1. Relative Energy (RE) of the *Trans*-Bent E_2H_4 with Respect to the Planar One, for E = Si to Pb. The pyramidalization $(360 - \theta)$ in the *trans*-bent structure is also shown.[a]

	RE (*trans*-bent) (kcal/mol)	$360 - \theta$ (deg)
Si_2H_4	0	5
Ge_2H_4	−2	17
Sn_2H_4	−9	28
Pb_2H_4	−27	36

[a] 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 $(360 - \theta)$, the greater is the trans bending and the pyramidality at E.

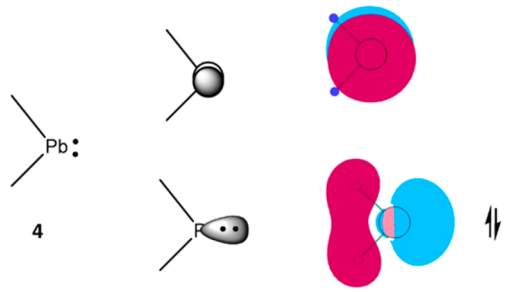
The reasons for *trans*-bending in group 14 ethylene analogues are well-studied and we do not discuss them here.[9,16−18] It was shown computationally that *trans*-bending could be decreased by the use of electropositive substituents, such as silyl.[19,20] A planar structure for digermene can be obtained by using two Li atoms and two alkyl groups as substituents, in a *trans* fashion.[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

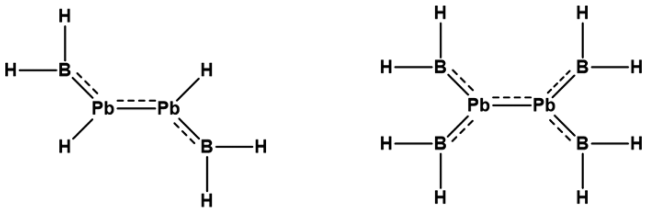
Tuning the Singlet−Triplet Splitting. Building on previous work,[1,9] one way to achieve our goal might be to make the constituent plumbylene, PbR_2, a triplet ground state. The relevant orbitals of the archetype, PbH_2, **4**, are shown schematically and in an orbital plot in Scheme 2. The splitting of the orbitals is very large, 3.9 eV. To stabilize the triplet, we need to depress in energy the vacant p orbital significantly, which can be done with a 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 unlabeled circles here and below are hydrogen atoms. Note the delocalization of the π system extending to only two 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^{2+}) as a diplumbene, as the π 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 π accepting substituents, such as NO_2, CN, etc., could not stabilize a planar diplumbene. Thus, we decided to look for a way other than π delocalization and began by analyzing the nature of bonding in ethylene analogues, R_2EER_2.

Scheme 2. Frontier Orbitals of Plumbylene



Scheme 3. Diplumbenes, with BH_2 Substituents



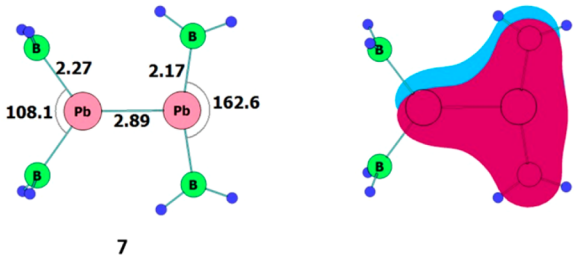


Figure 1. Optimized geometry of the BH_2-substituted diplumbene, **6**, and its π MO.

R_2EER_2 Bonding. Shown in Figure 2 is a plot of the most probable radius (r_{max}) of the valence *n*s and *n*p orbitals of group 14 elements, taken from ref 23 and the Desclaux computations.[22−25] While the valence 2s and 2p of C have similar r_{max}, the radii of the corresponding *n*s and *n*p orbitals in the other elements are significantly different. The *n*s orbitals are more contracted than *n*p orbitals for heavier elements, and the degree of contraction increases down the group. This implies that the *n*s 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*p electrons of one atom with core $(n - 1)$p of the other).[26,18] 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*-bent, and *trans*-bridged structures of E_2H_4, obtained from a Natural Bond Orbital (NBO) analysis.[27] Notice that the NBO

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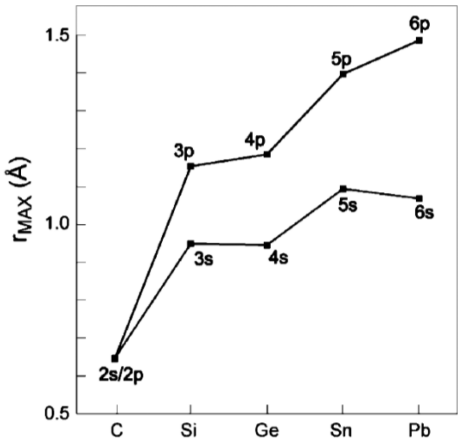


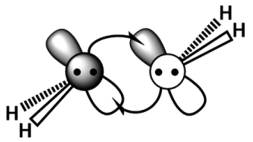
Figure 2. Variation of the most probable radius of the valence *ns* and *np* orbitals of group 14 atoms.[22,23] Reproduced from reference 23, with permission from Royal Society of Chemistry.

analysis of *trans*-bent Pb_2H_4 does not show any formal Pb−Pb bond orbital, but instead features a lone pair on each Pb with large s character ($sp^{0.18}$) 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 Pb_2H_4 to two PbH_2 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 Sn_2H_4 and Pb_2H_4 (*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.

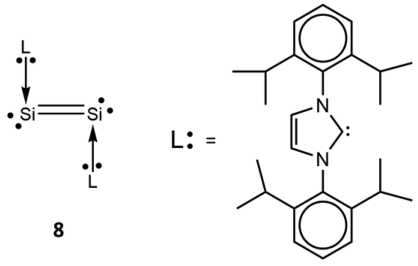
Lewis Base and Acid Coordination as the Strategy. Prompted by the above analysis, we started looking for a group

Scheme 4. Donor−Acceptor Interaction in *Trans*-Bent Diplumbene



14 E═E double-bonded system where the σ bonds would be made up mainly by the p orbitals. We did find one: compound **8**, which was synthesized by Robinson and co-workers, is a Si═Si double-bonded system, where each Si retains a lone pair (Scheme 5).[28] The approximately 90° C−Si−Si angle and the

Scheme 5. Si−Si Double-Bonded System, Stabilized with N-Heterocyclic Carbenes



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 $Pb_2(LB)_2$ (**9**, Scheme 6), where the N-Heterocyclic Carbene (NHC) is replaced by a general Lewis base, LB (LB = CO, PR_3, H^-, CH_3^-, etc.). In order to get an ethylene analogue RR′Pb═PbRR′ 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

Table 2. Nature of the Hybrid Orbitals on E Atom, in E_2H_4 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 Analogues, the Relative Energy (RE) with Respect to the Planar Structure is Also Shown[a]

E	E−H	E−E (σ)	E−E (π)	E−H−E	LP	360 − θ (deg)	RE
C_2H_4	$sp^{2.34}$	$sp^{1.47}$	p				
Si_2H_4-planar	$sp^{2.13}$	$sp^{1.73}$	p				0
Si_2H_4-*trans*-bent	$sp^{2.19}$	$sp^{1.78}$	$sp^{50.68}$			5	0
Si_2H_4-*trans*-bridged	$sp^{6.32}$			$sp^{15.34}$	$sp^{0.34}$		20
Ge_2H_4-planar	$sp^{2.09}$	$sp^{1.83}$	p				0
Ge_2H_4-*trans*-bent	$sp^{2.39}$	$sp^{2.01}$	$sp^{11.63}$			17	−2
Ge_2H_4-*trans*-bridged	$sp^{7.92}$			$sp^{20.86}$	$sp^{0.25}$		6
Sn_2H_4-planar	$sp^{2.03}$	$sp^{1.93}$	p				0
Sn_2H_4-*trans*-bent	$sp^{2.59}$	$sp^{2.31}$	$sp^{5.97}$			28	−9
Sn_2H_4-*trans*-bridged	$sp^{9.23}$			$sp^{24.12}$	$sp^{0.21}$		−18
Pb_2H_4-planar	$sp^{1.94}$	$sp^{2.11}$	p				0
Pb_2H_4-*trans*-bent	$sp^{12.28}$				$sp^{0.18}$	36	−27
Pb_2H_4-*trans*-bridged	$sp^{13.34}$			$sp^{35.69}$	$sp^{0.14}$		−48

[a] 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.

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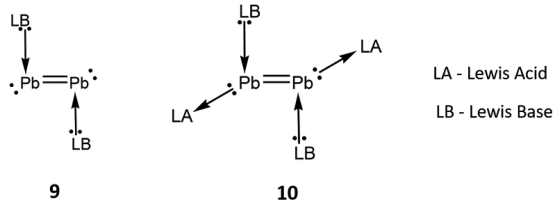
Scheme 6. Hypothetical Construction of a Planar Diplumbene



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 $BeMe_2$ and LiMe as possible LAs, and CH_3^- as an LB.

The calculated structure of **9** is shown in **11**, with CH_3^- 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]

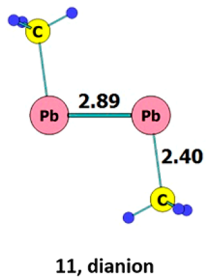


Figure 3. Calculated structure of hypothetical, dianionic Pb–Pb double-bonded system.

Coordination of two LiMe groups to **11** gave structure **12** (Figure 4), and coordination of two $BeMe_2$ 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 $Pb_2Me_2^{2-}$ (**11**) shows that there is a

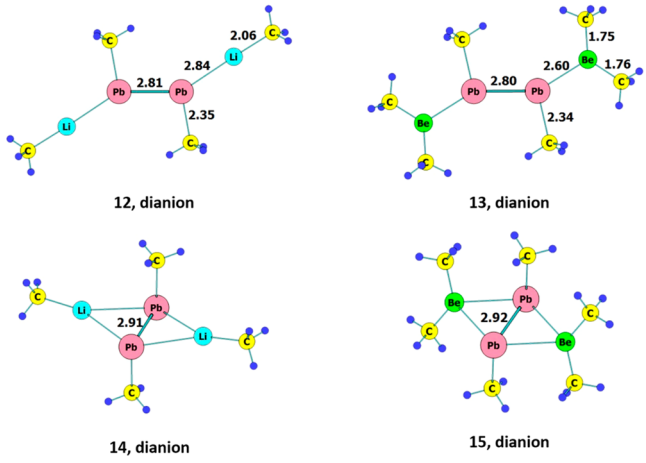


Figure 4. Calculated structures of the dianionic, planar diplumbenes (**12**, **13**) and the corresponding bridged isomers (**14**, **15**).

significant shortening of the Pb–Pb bond on coordination with LiMe and $BeMe_2$. Competing bridged structures, **14** and **15**, were found, analogous to structure **3** for the prototype Pb_2H_4. 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 Pb_2H_6 (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

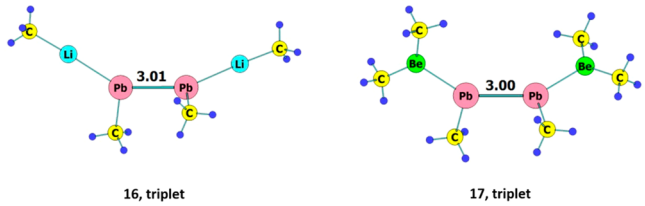


Figure 5. Calculated triplet-state geometries (**16** and **17**) of the diplumbenes **12** and **13**.

~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 C_2H_4. The energy difference between the C_2H_4 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) + Pb_2). We found that the free energy of this reaction is 7 and −39 kcal/mol, respectively, for **12** and **13**. The BeR_2 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 the essential molecules below shows no great effect on the bonding. The natural resonance theory analysis[31,32] 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.

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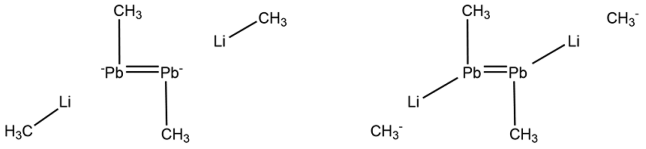
Scheme 7. Leading Resonance Structures of 12 Obtained by Natural Resonance Theory Analysis, with the Respective Weights Shown in Parentheses

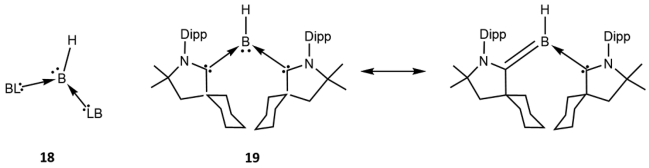


12a (53%) 12b (27%)

To get a neutral Pb−Pb double-bonded structure, we have to replace CH_3^- 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 CH_3^- by typical Lewis bases, such as PH_3, 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.[33−35] However, borylenes like BR, BNR_2, 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

Scheme 8. Base-Stabilized Borylenes—A General Representation (18) and an Experimental Example (19)

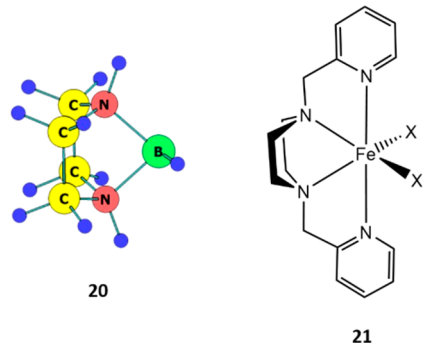


18 19

boron-centered bases is a very recent development.[36−39] 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.[36−39]

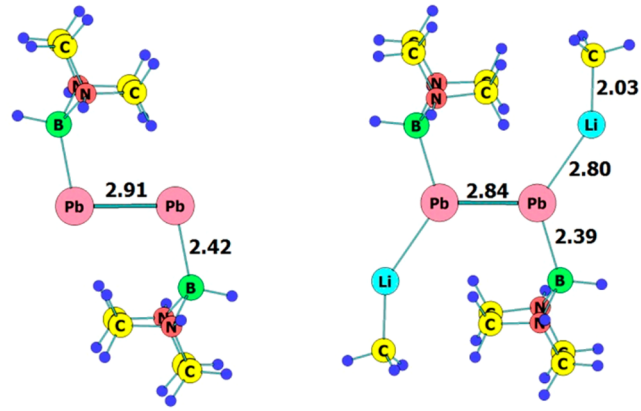
Since **19** is too bulky to use for our purpose, and also because the lone pair on B in **19** is delocalized in the CAAC ligand and hence less available for further interaction, we searched for alternatives, based on the same strategy (borylene, BR, with two electron-pair donors attached to B). After several trials, we found that a piperazine-stabilized borylene (PSB), **20** (Figure 6), suited our purposes. Structure **20** is computed to be a local minimum, with no low frequencies (<100 cm^{-1}). Piperazine complexes with transition metals are known (**21**, Figure 6).[40] 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 $Pb_2(PSB)_2$ (**22**, Figure 7), which emerged as a minimum, with a charge of −0.47 on Pb. As



20 21

Figure 6. Piperazine complexes with borylene and transition metal fragment.



22 23

Figure 7. Calculated structures of **22** and **23**, which are systems **9** and **10** with **20** as LB and LiMe as LA.

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.

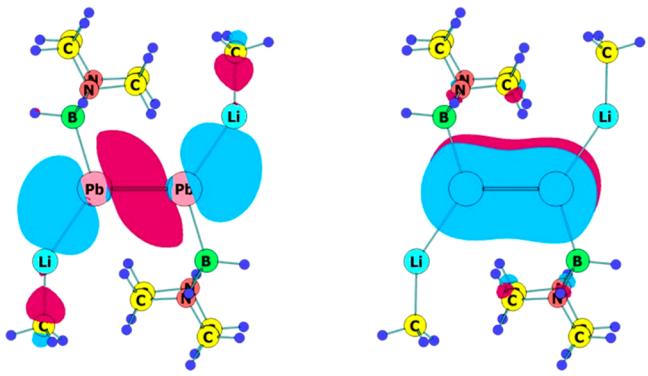


Figure 8. Pb−Pb σ and π orbitals of **23**.

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 Pb_2H_6 (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**,

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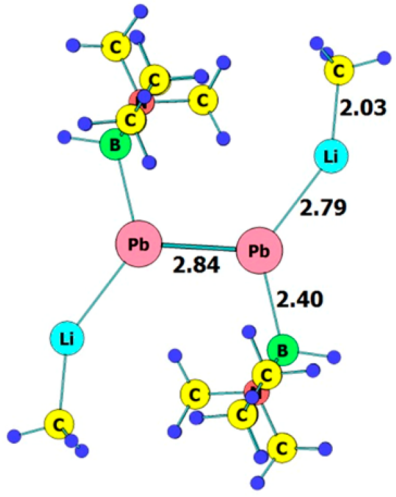
as shown in **24** (Figure 9), which is also a planar minimum. Coordination of another Lewis base, e.g., pyridine, to Li is



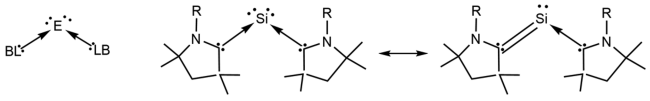
24

Figure 9. Calculated structure of the *N*-ethyl-substituted derivative of **23**, molecule **24**.

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).[41,42] Atom E in **25** has two lone pairs—one σ-type lone pair,

Scheme 9. Silicon Analogue of Carbone

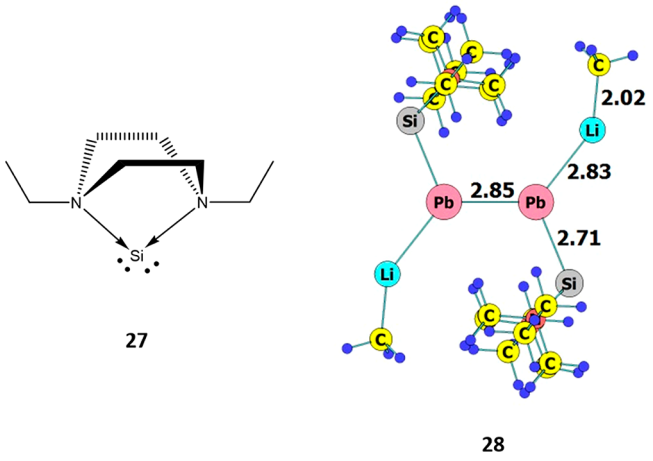


25 26

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.[43,44] An example for this kind of system known experimentally, with CAACs as the LB, is shown in **26**.[41]

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 borylenes, in stabilizing the planar diplumbenes.

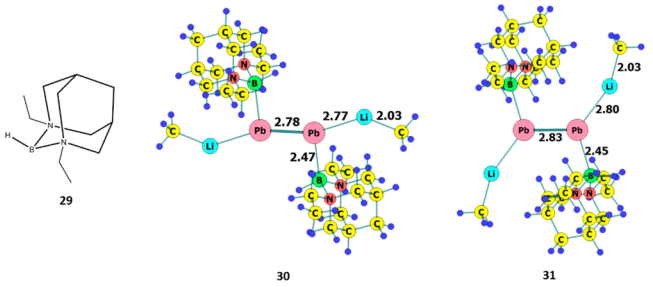
Structure **20** is not the only base-coordinated borylene that can stabilize a planar diplumbene. A bispidine-stabilized borylene (BSB), as shown in **29**, and similar molecules might also serve the same purpose. Note that, unlike **20**, structure **29** benefits from the favorable chair confirmation of the 6-



27 28

Figure 10. Calculated structure of **28**, with **27** as LB and LiMe as LA.

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.

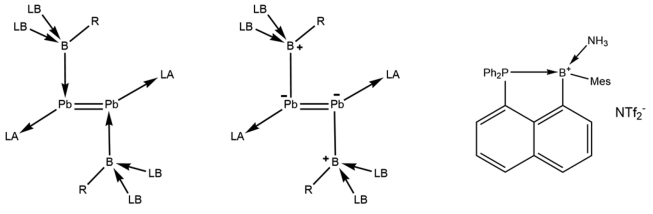


29 30 31

Figure 11. Bispidine-stabilized borylene (**29**), and the calculated structures of two conformations of planar diplumbenes **30** and **31**, with **29** as LB.

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.[45] Note that the B in **34** is coordinated to two Lewis bases

Scheme 10. A General Representation of the Designed Diplumbenes, Shown with Dative Bonds (32) and Zwitterionic Form (33), and the Comparison with the Known Tetracoordinate Borenium Ion, 34



32 33 34

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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 ($360 - \theta = 2.5°$ around one of the Pb atoms), as shown in atomic detail, in **36**.

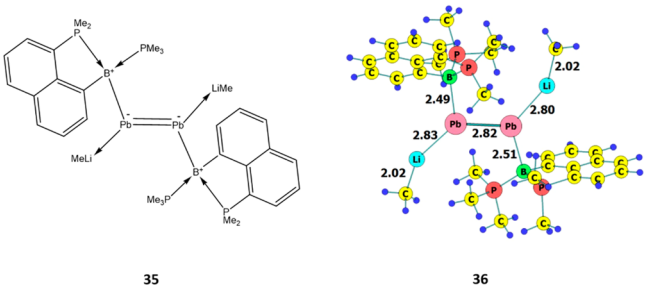


Figure 12. A planar diplumbene designed, and its calculated structure.

The Diplumbenes Designed. Table 3 lists the Pb−Pb bond lengths of the planar diplumbenes we have designed, the

Table 3. Comparison of the Pb−Pb Bond Lengths (in Å) of the Designed Planar Diplumbenes with That of Pb_2H_6 and *Trans*-Bent-Pb_2H_4, Calculated at PBE0/Def2-TZVP Level of Theory

	24	**30**	**31**	**36**	Pb_2H_4 (*trans*-bent)	Pb_2H_6
Pb−Pb bond length	2.84	2.78	2.83	2.82	2.89	2.86

diplumbane Pb_2H_6, and a *trans*-bent Pb_2H_4 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 Pb_2H_4 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 Pb_2H_6, 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 plumbylene fragment, Pb(LiMe)(Borylene), is a ground state triplet. For the plumbylene fragments of **24**, **30**, **31**, and **36**, the triplet is more stable than singlet by 9, 13, 12, and 2 kcal/mol, respectively.

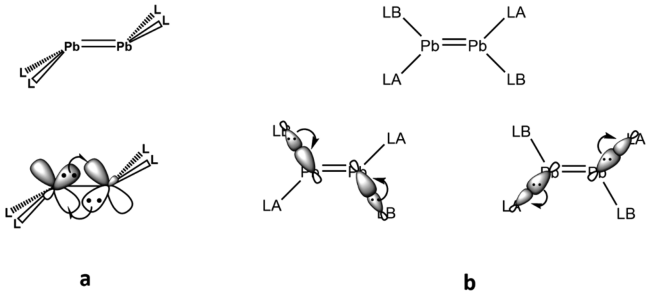
The free energies of dissociation of the systems **24**, **30**, **31**, and **36** to two LiMe and (LB)Pb═Pb(LB) are 35, 36, 37, and 25 kcal/mol, respectively (corresponding to the cleavage of two Pb−Li bonds). On the other hand, the free energy of dissociation into two triplet plumbylene fragments (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 (Pb_2H_4) is more stable than the *trans*-bent form,[1,5] all the experimentally isolated diplumbenes have the *trans*-bent structure.[10−14] 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



bent structure is a dative bond between the lone pair on Pb in one PbH_2 fragment with the vacant p orbital on the other.[9] 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.[46] 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.[47]

CONCLUSION

In an alternative perspective on bonding in the heavier analogues of ethylene, R_2EER_2, the nonplanar distortion of these molecules may be viewed as a mechanism to decrease the s orbital participation in bonding. This is likely a consequence of the relativistic contraction of s orbitals, and their consequent core-like behavior. To stabilize a planar diplumbene, a substitution strategy of a push−pull type is suggested and

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probed computationally. Lewis bases of a special type, base-stabilized borylenes, 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 both 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.[49−58] For discussion, we use computations at the PBE0/Def2-TZVPPD level unless otherwise specified.[59,60] 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 involve 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 BH_2-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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