

# Reactions of $H_2X=XH_2$ and $H_2X=O$ Double Bonds ( $X = Si, Ge, Sn, Pb$ ): Are 1,3-Dioxa-2,4-dimetaletanes Unusual Molecules?

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1,3-Dioxa-2,4-dimetaletanes ( $X = Si, Ge, Sn, Pb$ ) are possible products from the reaction of the  $H_2X=XH_2$  double bonds with dioxygen as well as from  $H_2X=O$  dimerization. The energies of these reactions were investigated with DFT pseudopotential calculations (using the Becke3LYP functional and DZ+P basis sets) in order to assess the relative stabilities of  $X=X$  and  $X=O$  double bonds. While ethene and formaldehyde are exceptionally stable in this context, the reactions of most of the heavier group 14 element compounds are very exothermic. The  $H_2X=O$  dimerization energy trend follows the electronegativity of  $X$ . However, the  $H_2X=XH_2$  oxygenation energy decreases down group 14 from silicon to lead, and the dioxygen reaction of the trans-bent  $Pb_2H_4$  minimum is even less favorable than that of  $H_2C=CH_2$ . Nevertheless,  $Pb=Pb$   $\pi$  bonds are not very stable. Diplumbene can dissociate easily; reaction of the resulting divalent  $PbH_2$  subunits to tetravalent lead–oxygen compounds is not very favorable. The 1,3-dioxa-2,4-dimetaletanes have short through-ring  $X\cdots X$  distances, but no evidence for an  $X\cdots X$  bond was found by natural bond orbital analysis. Instead, the intramolecular distances are due to the short and inflexible  $X-O$  bond lengths and to the electrostatic  $O\cdots O$  repulsion. In  $(H_2XO)_2$ , the hybridization not only of the group 14 elements down the group but also of the oxygen lone pairs and bond orbitals changes significantly.

## Introduction

With the exception of diplumbene derivatives,  $R_2Pb=PbR_2$ , examples of doubly bonded compounds of heavier group 14 elements all have been synthesized.<sup>1</sup> Many theoretical investigations have dealt with the nature of the double bonds in such species,<sup>2</sup> but most of the observable compounds are stabilized by bulky groups  $R$ ,<sup>3</sup> so that little is known about their reactions. Such organometallic compounds containing double  $X=X$  (and  $X=O$ ) bonds have some synthetic utility<sup>1b,4</sup> and have been postulated as intermediates.<sup>5</sup> However, an extensive experimental chemistry of these molecules has not developed, e.g. because of the rapid addition reactions across the  $X=X$  double bonds ( $X = Si, Ge, Sn$ ).<sup>6</sup> For example,  $Mes_2Si=SiMes_2$  adds water, ketones, or ethynyl groups.<sup>6</sup>

In contrast, compounds containing  $C=C$  double bonds are of essential importance in chemistry and biology.<sup>7</sup> In light of

the exceptional behavior of carbon and other “first row” elements (i.e., the  $Si-Pb$  compounds behave “normally”, while the stabilities of the  $C=C$  and  $C=O$  bonds are unique),<sup>8–11</sup> the chemistry of the heavier group 14 element double bond deserves more attention.

Reaction with dioxygen is one of the fundamental transformations of  $X=X$  bonds ( $X = Si-Sn$ ): Disilenes take up oxygen when exposed to air; cyclic 1,3-dioxa-2,4-disilenes (**1**) (Chart 1) result.<sup>4,12</sup> Similarly, the oxidation of double bonded  $Ge=Ge$  compounds under certain conditions leads to the stable cyclo-digermoxanes  $(R_2GeO)_2$  ( $R = 2,6$ -diisopropylphenyl),<sup>4,5</sup> and the preparation of first dimeric diorganotin oxide  $(R_2SnO)_2$  has been reported recently [ $R = CH(SiMe_3)_2$ ].<sup>13</sup> The catalytic oxygenation of ethylene also is one of the most important reactions of a  $R_2C=CR_2$  double bond.<sup>14</sup> But, in contrast, epoxides are the main products.

Such  $(H_2XO)_2$  rings (**1**) also result from head-to-tail dimerization of the corresponding aldehydes congeners,  $H_2X=O$ . Cyclic polysiloxanes (e.g., **2**) are well-known,<sup>6</sup> and the highly reactive diorganogermanones  $R_2Ge=O$  also polymerize into cyclogermanones  $(R_2GeO)_n$  ( $n = 2-4$ ).<sup>5</sup> We have shown that the reactivity of  $X=O$  groups should increase down the group,<sup>9</sup>

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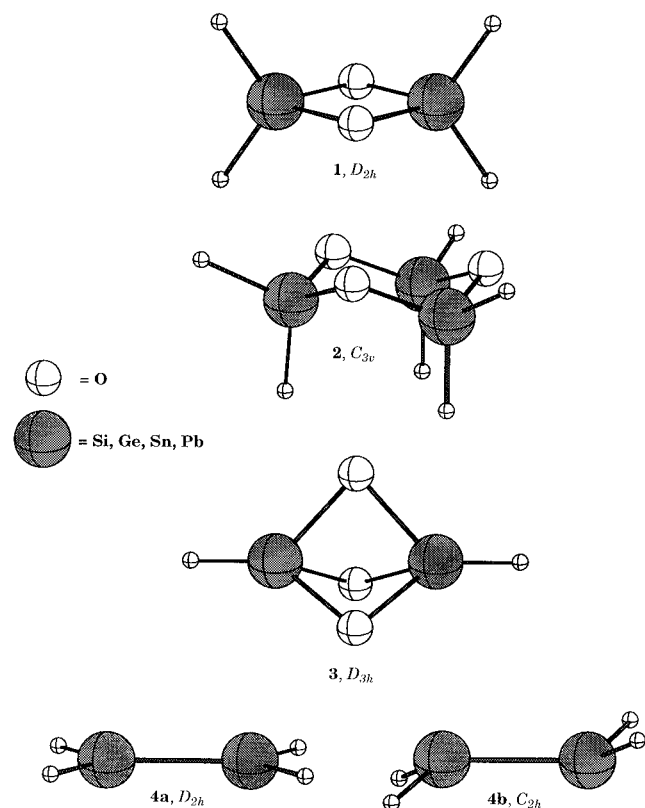
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Chart 1



and neither monomeric stanane  $R_2Sn=O$  or plumbane  $R_2Pb=O$  derivatives are known.

Some of the  $(H_2XO)_2$  structures (**1**) also have been studied theoretically. Kudo and Nagase found that the dimerization of dihydrosilanone proceeds without a barrier by a nonconcerted mechanism.<sup>15</sup> The geometry of the four-membered ring dimerization product is unusual: The nonbonding  $Si\cdots Si$  distance is very small.<sup>16</sup> However, small  $^{29}Si\cdots^{29}Si$  coupling constants of an unsymmetrically substituted 1,3-dioxa-2,4-disilane revealed that no  $\sigma$  bond occurs between the silicon atoms.<sup>17</sup> Grev and Schaefer attributed the short  $Si\cdots Si$  contact in cyclic disiloxanes to the existence of an “unsupported  $\pi$  bond” between the silicon atoms.<sup>18</sup>

Similarly short  $X\cdots X$  distances were found in 2,4,5-trioxa-1,3-dimetallabicyclo[1.1.1]pentanes  $X_2O_3H_2$  (**3**,  $X = Si-Pb$ ).<sup>19</sup> Nagase and Kudo described the nature of such close approaches as “phantom bonds”, since no covalent interaction between the X atoms should occur. The  $(H_2XO)_2$  (**1**) and  $X_2O_3H_2$  molecules (**3**) are regarded as donor–acceptor complexes of central  $X_2H_4$  or  $X_2H_2$  units with two or three surrounding oxygen substituents.<sup>18–20</sup> Electropositive substituents (instead of oxygen) donate electron density into the  $\pi^*$  orbitals of the central  $X_2H_2$  or  $X_2H_4$  groups. Furthermore, the X atoms are electron rich. Both effects elongate the central  $X\cdots X$  distance. According to

this model, the lone pairs of oxygen substituents around  $X_2H_2$  and  $X_2H_4$  are not effective as good  $\pi$  donors for the “ $X_2H_{2/4}$ ”  $\pi^*$  orbitals.<sup>18–20</sup> In addition, due to the higher electronegativity of O the electrostatic repulsion between the X atoms is reduced. Hence, the central  $X\cdots X$  distance is very short in **1** and **3**.

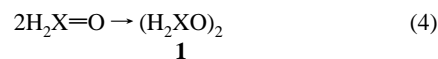
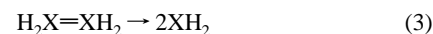
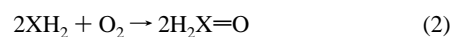
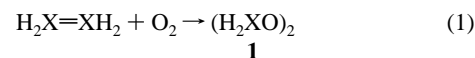
However, Gordon et al. pointed out that the short  $X\cdots X$  through ring distances could be due simply to geometric constraints (i.e., the oxygen atoms are quite small).<sup>21</sup> When two metal atoms are connected by two (1,3-dioxa-2,4-dimetallatanes, **1**) or three oxygen atoms (2,4,5-trioxa-1,3-dimetallabicyclo[1.1.1]pentanes, **3**), the heavy elements must approach each other closely. Due to these different explanations of the short central distances in the  $(H_2XO)_2$  rings (**1**) and the not yet convincing description of the  $X\cdots X$  interaction, the nature of the bonding in these species is of interest.

We now present an examination of the thermodynamics of the reaction of  $X=X$  bonds with dioxygen, of  $X=X$  bond decomposition, and of the dimerization of  $X=O$  species. This provides data regarding the relative stabilities of the double-bonded species. We also analyze the bonding in “simple” group 14  $H_2X=XH_2$  (**4a,b**) and  $(H_2XO)_2$  (**1**) systems: Are unusual explanations necessary for a correct description of these compounds?

### Computational Details

All compounds were optimized with the GAUSSIAN94 program<sup>22</sup> employing the hybrid Becke3LYP functional.<sup>23</sup> Vibrational frequency calculations gave zero-point energies (ZPE) and the number of imaginary frequencies.<sup>24</sup> In order to obtain results of the same quality for the whole set of compounds, we replaced the core electrons of all group 14 elements and of oxygen by the (quasi-) relativistic pseudopotentials of Stoll et al.<sup>25,26</sup> The corresponding DZ+P basis sets were used for the valence orbitals. For compounds containing lead, additional calculations were performed with a nonrelativistic Pb-pseudopotential (“n-Pb”).<sup>27</sup> The 6-31++G\*\* basis set was used for hydrogen. Reed and Weinhold’s NBO analysis gave natural atomic charges, bond orders, and orbital hybridizations.<sup>28</sup>

Energies were computed for the oxygenation (1, 2), decomposition (3), and dimerization (4) reactions:



The B3LYP total energies of the various species studied are listed in Table 1, together with the zero point vibrational energies (ZPE).

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**Table 1.** Becke3LYP Energies and Zero Point Energies (ZPE) (–au and kcal/mol)<sup>a)</sup>

|   | C                        | Si           | Ge           | Sn           | n-Pb <sup>b</sup> | Pb           |
|---|--------------------------|--------------|--------------|--------------|-------------------|--------------|
| H <sub>2</sub> X=XH <sub>2</sub> ( <i>D</i> <sub>2h</sub> Symmetry) ( <b>4a</b> ) |                          |              |              |              |                   |              |
| B3LYP   | 13.730 76(0)             | 10.115 55(1) | 9.979 78(1)  | 9.115 77(1)  | 8.625 17(1)       | 9.183 55(1)  |
| ZPE   | 31.99                    | 19.42        | 17.76        | 15.46        | 14.46             | 14.91        |
| H <sub>2</sub> X=XH <sub>2</sub> ( <i>C</i> <sub>2h</sub> Symmetry) ( <b>4b</b> ) |                          |              |              |              |                   |              |
| B3LYP   |                          | 10.117 66(0) | 9.990 67(0)  | 9.132 56(0)  | 8.636 80(0)       | 9.221 60(0)  |
| ZPE   |                          | 19.56        | 17.47        | 15.06        | 14.33             | 13.82        |
| H <sub>2</sub> X=O <sup>c</sup>   |                          |              |              |              |                   |              |
| B3LYP   | 22.907 17(0)             | 21.129 43(0) | 21.016 52(0) | 20.563 51(0) | 20.311 39(0)      | 20.575 05(0) |
| ZPE   | 16.73                    | 11.59        | 10.11        | 8.74         | 8.18              | 8.03         |
| cyclo-(H <sub>2</sub> XO) <sub>2</sub> ( <b>1</b> )                               |                          |              |              |              |                   |              |
| B3LYP   | 45.805 26(0)             | 42.420 67(0) | 42.169 32(0) | 41.284 63(0) | 40.793 66(0)      | 41.273 85(0) |
| ZPE   | 39.56                    | 27.81        | 24.04        | 20.89        | 19.50             | 19.22        |
| H <sub>2</sub> X  |                          |              |              |              |                   |              |
| B3LYP   | 6.729 51(0) <sup>d</sup> | 5.012 35(0)  | 4.965 90(0)  | 4.545 81(0)  | 4.296 54(0)       | 4.600 38(0)  |
| ZPE   | 10.84                    | 7.29         | 6.61         | 5.92         | 5.69              | 5.60         |
| O <sub>2</sub>  | triplet                  | singlet      |              |              |                   |              |
| B3LYP   | 31.985 51(0)             | 31.924 04(0) |              |              |                   |              |
| ZPE   | 2.35                     | 2.34         |              |              |                   |              |

<sup>a</sup> Number of imaginary frequencies in parentheses (0, minimum; 1, transition structure). <sup>b</sup> Computed with a nonrelativistic Pb pseudopotential. <sup>c</sup> From ref 9. <sup>d</sup> <sup>3</sup>CH<sub>2</sub>.

**Table 2.** B3LYP Optimized Geometries (Å and deg)<sup>a)</sup>

| X                           | H <sub>2</sub> X=O <sup>b</sup>                  |                        | cyclo-(H <sub>2</sub> XO) <sub>2</sub> ( <b>1</b> ) |                        |   |                  |  |  |  |
|-----------------------------|--|------------------------|---|------------------------|---|------------------|--|--|--|
|                             | <i>d</i> <sub>XO</sub>                           | <i>d</i> <sub>XH</sub> | <i>d</i> <sub>XO</sub>                              | <i>d</i> <sub>XH</sub> | ∠XOX  | ∠HXH             | <i>d</i> <sub>O...O</sub> <sup>c</sup> | <i>d</i> <sub>X...X</sub> <sup>c</sup> | cyclo-(H <sub>2</sub> X–O) <sub>3</sub> <sup>b,d</sup> |
| C                           | 1.202  | 1.109                  | 1.430   | 1.098                  | 87.3  | 111.3            | 2.070                                  | 1.973                                  | 1.411  |
| Si                          | 1.529  | 1.482                  | 1.695   | 1.476                  | 90.3  | 111.5            | 2.378                                  | 2.415                                  | 1.659  |
| Ge                          | 1.657  | 1.546                  | 1.848   | 1.538                  | 92.4  | 114.1            | 2.557                                  | 2.668                                  | 1.808  |
| Sn                          | 1.854  | 1.718                  | 2.027   | 1.710                  | 95.3  | 113.8            | 2.732                                  | 2.995                                  | 1.984  |
| n-Pb                        | 1.943  | 1.813                  | 2.103   | 1.807                  | 97.5  | 112.9            | 2.772                                  | 3.163                                  | 2.056  |
| Pb                          | 1.927  | 1.755                  | 2.118   | 1.740                  | 96.3  | 117.1            | 2.826                                  | 3.156                                  | 2.077  |
| φ∠HXO: 121.5–124.5°         |  |                        |   |                        |   |                  |  |  |  |
| X                           | H <sub>2</sub> X=XH <sub>2</sub> ( <b>4a,b</b> ) |                        |   |                        |   | H <sub>2</sub> X |  |  |  |
|                             | <i>d</i> <sub>XX</sub>                           | <i>d</i> <sub>XH</sub> | ∠HXH  | <i>e</i>               | H <sub>3</sub> X–XH <sub>3</sub> <sup>d</sup> | X                | <i>d</i> <sub>XH</sub>                 | ∠HXH                                   |  |
| C <i>D</i> <sub>2h</sub>    | 1.335  | 1.087                  | 116.6   |                        | 1.533   | C <sup>f</sup>   | 1.115                                  | 101.4                                  |  |
| Si <i>D</i> <sub>2h</sub>   | 2.141  | 1.475                  | 115.8   |                        | 2.354   | Si               | 1.529                                  | 91.3                                   |  |
| Si <i>C</i> <sub>2h</sub>   | 2.184  | 1.483                  | 111.0   | 34.1                   |   |                  |  |  |  |
| Ge <i>D</i> <sub>2h</sub>   | 2.258  | 1.530                  | 116.0   |                        | 2.479   | Ge               | 1.609                                  | 90.7                                   |  |
| Ge <i>C</i> <sub>2h</sub>   | 2.362  | 1.557                  | 105.9   | 46.3                   |   |                  |  |  |  |
| Sn <i>D</i> <sub>2h</sub>   | 2.583  | 1.699                  | 115.3   |                        | 2.827   | Sn               | 1.784                                  | 90.6                                   |  |
| Sn <i>C</i> <sub>2h</sub>   | 2.748  | 1.737                  | 102.9   | 50.4                   |   |                  |  |  |  |
| n-Pb <i>D</i> <sub>2h</sub> | 2.784  | 1.795                  | 114.5   |                        | 3.038   | n-Pb             | 1.870                                  | 90.9                                   |  |
| n-Pb <i>C</i> <sub>2h</sub> | 2.932  | 1.824                  | 103.9   | 48.1                   |   |                  |  |  |  |
| Pb <i>D</i> <sub>2h</sub>   | 2.640  | 1.725                  | 116.7   |                        | 2.891   | Pb               | 1.836                                  | 90.8                                   |  |
| Pb <i>C</i> <sub>2h</sub>   | 2.926  | 1.795                  | 98.9  | 53.1                   |   |                  |  |  |  |

<sup>a</sup> See Figure 1 and Computational Details. n-Pb: lead computed with a nonrelativistic pseudopotential. <sup>b</sup> From ref 9. <sup>c</sup> Through-ring distance. <sup>d</sup> The cyclo-(H<sub>2</sub>XO)<sub>3</sub> X–O and X<sub>2</sub>H<sub>6</sub> X–X distances (at the same level of theory) are given for comparison. <sup>e</sup> XH<sub>2</sub> out of plane bending angle. <sup>f</sup> <sup>3</sup>CH<sub>2</sub>.

The B3LYP/DZ+P optimized geometries are given in Table 2. Table 3 summarizes the reaction energies. We have employed triplet oxygen in evaluating these equations, even though the products are singlets. Since (<sup>1</sup>Σ) singlet O<sub>2</sub> is higher in energy than (<sup>3</sup>Σ) triplet O<sub>2</sub> by 38.58 kcal/mol at our level of theory (B3LYP/DZ+P, exp. 37 kcal/mol), all calculated reaction energies are about 38.6 kcal/mol more exothermic, when singlet instead of triplet oxygen is employed (Table 3).

## Results and Discussion

**General Considerations.** As expected from previous work,<sup>2</sup> the planar *D*<sub>2h</sub> H<sub>2</sub>X=XH<sub>2</sub> structures (**4a**, X = Si–Pb) have one imaginary frequency, while trans-bent structures (**4b**) are minima. The bending of the ethene congeners can be explained

in terms of a π–σ\* mixing model:<sup>2b</sup> Valence s orbital contributions of X to the “π” bond are possible (the symmetry descriptions “σ” and “π” are no longer valid in the bent structures); the π bond is not formed only by X valence p orbitals (Figure 1a).

The bending results in considerable elongation of the X=X distances of the *C*<sub>2h</sub> structures (**4b**) relative to the double bonds in the planar *D*<sub>2h</sub> conformers, **4a** (from 0.04 Å for X = Si to 0.19 Å for X = Pb, Table 2). The elongated Sn=Sn and Pb=Pb double bonds are close to the Sn–Sn and Pb–Pb single bond distances [Sn, 2.748 (*C*<sub>2h</sub>) and 2.827 (Sn<sub>2</sub>H<sub>6</sub>); Pb, 2.926 (*C*<sub>2h</sub>) and 2.891 (Pb<sub>2</sub>H<sub>6</sub>)].

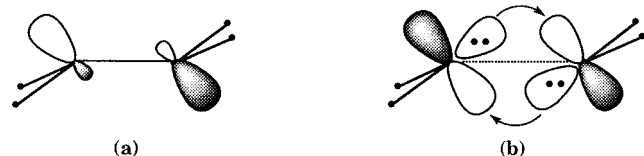
Our computed X=X/X–X bond lengths (Table 2) as well as the H<sub>2</sub>X=XH<sub>2</sub> dissociation energies (Table 3) follow the pattern of the available experimental values (Tables 4), which are, of course, based on substituted derivatives. Because of the relatively small positive dissociation energies (H<sub>2</sub>X=XH<sub>2</sub> →

(28) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (c) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

**Table 3.** B3LYP Reaction Energies (kcal/mol)<sup>a</sup>

| X                 | H <sub>2</sub> X=XH <sub>2</sub> + O <sub>2</sub> →<br>cyclo-(H <sub>2</sub> XO) <sub>2</sub> <sup>b,c</sup> | 2H <sub>2</sub> X + O <sub>2</sub> →<br>2H <sub>2</sub> X=O <sup>c</sup> | H <sub>2</sub> X=XH <sub>2</sub> →<br>2H <sub>2</sub> X <sup>b</sup> | 2H <sub>2</sub> X=O →<br>cyclo-(H <sub>2</sub> XO) <sub>2</sub> |
|-------------------|--|--|--|---|
| C                 | -50.60   | -222.62  | 160.21 <sup>d</sup>  | 11.79   |
| Si                | -193.32  | -149.78  | 53.35  | -96.88  |
| Ge                | -116.96  | -67.97   | 32.69  | -81.69  |
| Sn                | -101.01  | -28.02   | 22.47  | -95.49  |
| n-Pb <sup>e</sup> | -104.69  | -25.10   | 24.48  | -104.08   |
| Pb                | -38.81   | 25.21  | 10.46  | -74.49  |

<sup>a</sup> All energies include ZPE; see Computational Details. <sup>b</sup> Calculated with the C<sub>2h</sub> minimum structures of the Si, Ge, Sn, n-Pb, and Pb compounds (planarization barriers: 1.18, 6.54, 10.13, 7.17, and 22.79 kcal/mol, respectively). <sup>c</sup> Reactions with singlet oxygen are 38.6 kcal/mol more exothermic. <sup>d</sup> Calculation with triplet CH<sub>2</sub>; compare ref 31. <sup>e</sup> n-Pb: lead computed with a nonrelativistic pseudopotential.

**Figure 1.** MO schemas of the trans-bent M<sub>2</sub>H<sub>4</sub> structures: (a) distortion due to  $\pi$ - $\sigma^*$  mixing of the planar structure (i.e., metal valence s orbitals contribute to the “ $\pi$ ” bond); (b) donor-acceptor complex of two MH<sub>2</sub> fragments.**Table 4.** Experimental Bond Lengths (in Å) and Dissociation energies (kcal/mol) of Double-Bonded X=X and Single-Bonded X-X Species<sup>a</sup>

| X  | bond length |       | dissociation energies |     |
|----|-------------|-------|-----------------------|-----|
|    | X=X         | X-X   | X=X                   | X-X |
| C  | 1.356       | 1.545 | 152.0                 | 88  |
| Si | 2.140–2.160 | 2.352 | 63.4                  | 74  |
| Ge | 2.213–2.347 | 2.445 |                       |     |
| Sn | 2.768       | 2.810 | 12.9                  |     |
| Pb |             | 2.851 |                       |     |

<sup>a</sup> Taken from refs 1, 3, 4, and 29.

2XH<sub>2</sub>: 32.7 kcal/mol for Ge and 22.5 kcal/mol for Sn), substituted germanium and tin compounds have been observed only in the solid state.<sup>4,29</sup> In solution, they dissociate completely into the corresponding XR<sub>2</sub> fragments.

The H<sub>2</sub>H=XH<sub>2</sub> dissociation products, divalent XH<sub>2</sub> carbene-like structures, are well-known to have singlet ground states (except methylene).<sup>30</sup> According to Jacobsen and Ziegler, the increasing singlet-triplet energy separation in the series from H<sub>2</sub>Si to H<sub>2</sub>Pb is primarily responsible for the decreasing double bond dissociation energy down group 14.<sup>2d</sup> The XH<sub>2</sub> groups formally adopt triplet states to form a double bond (no matter if it is planar or trans-bent), but the energy gain from bond formation must compensate for the excitation energy.

An alternative description of the heavy element X=X double bonds takes the increasing singlet-triplet excitation energy into account.<sup>2a</sup> The trans-bent H<sub>2</sub>X=XH<sub>2</sub> systems can be regarded as complexes: Each XH<sub>2</sub> group donates electron density from its lone pair into the empty p orbital at the other XH<sub>2</sub> fragment (Figure 1b).

In contrast to Trinquier's calculations,<sup>31</sup> we found trans-bent H<sub>2</sub>Pb=PbH<sub>2</sub> (**4b**, X = Pb) to be a true minimum; the lowest IR frequency (60 cm<sup>-1</sup>) corresponds to the Pb-Pb bond breaking. Therefore, we checked this discrepancy at various levels of theory (HF, MP2, MP4SDQ, Becke3LYP),<sup>24</sup> using both our “standard” 4-valence electron pseudopotential<sup>27</sup> and a 14-

valence electron pseudopotential (to provide better polarization and correlation of the 5d subshell).<sup>32</sup> From these calculations we conclude that H<sub>2</sub>Pb=PbH<sub>2</sub> is a real minimum in C<sub>2h</sub> symmetry (**4b**, X = Pb) when electron correlation is included (i.e., only the HF calculations gave an imaginary frequency), although the stability of dihydropbumbene is very low toward dissociation into the divalent H<sub>2</sub>Pb species (10.5 kcal/mol, Table 3).<sup>31,33</sup> The bridged minima Trinquier described for Pb<sub>2</sub>H<sub>4</sub> (and for Pb<sub>2</sub>F<sub>4</sub><sup>34</sup>) might be important as well. In contrast, organic substituents (e.g., alkyl and aryl groups) are less prone to bridge, and most probably a trans-bent R<sub>2</sub>Pb=PbR<sub>2</sub> structure will be preferred. Since we were interested in the chemistry of the Pb=Pb “double bond” (i.e., **4a,b**), we have not considered Trinquier's alternative Pb<sub>2</sub>H<sub>4</sub> isomers.

**Structure and Reactivity.** According to the computed energies (Table 3), the reaction of dioxygen with the Si=Si double bond [H<sub>2</sub>X=XH<sub>2</sub> + O<sub>2</sub> → (H<sub>2</sub>XO)<sub>2</sub> (**1**)] is most exothermic, but this decreases rapidly down group 14. The reaction of diplumbene with oxygen [to give (H<sub>2</sub>PbO)<sub>2</sub>, **1**, X = Pb] is even less favorable than that of ethylene (-38.8 kcal/mol, X = Pb, vs -50.6 kcal/mol, X = C)! However, this is no evidence for a stable Pb=Pb  $\pi$  bond (last paragraph).<sup>33</sup> Rather, the small H<sub>2</sub>Pb=PbH<sub>2</sub> + O<sub>2</sub> reaction energy is due to the preference of Pb<sup>II</sup> over Pb<sup>IV</sup> when electronegative ligands are bound at Pb.<sup>35</sup> The dioxygen reaction with two divalent plumbylene subunits (eq 2) to plumbanone is *endothermic* (+25.2 kcal/mol). Hence, a major problem in the preparation of a diplumbene species besides the low thermodynamic stability of a “Pb=Pb  $\pi$  bond” is to achieve dimerization of two PbR<sub>2</sub> fragments when R groups are electronegative (or, even worse,  $\pi$  donors in addition).

The energy of reaction 1 also is influenced by the variations in the stability of the products, i.e. the planar four-membered (H<sub>2</sub>XO)<sub>2</sub> rings with D<sub>2h</sub> symmetry (**1**): 1,3-Dioxetane (**1**, X = C) is a strained molecule, and reaction 1 is less favorable for carbon than for the heavier group 14 elements. These four-membered rings of Si-Pb have significantly less strain energy.<sup>36</sup>

Likewise, the head-to-tail dimerization of formaldehyde (reaction 4) is slightly endothermic, indicating the exceptional stability of the C=O  $\pi$  bond<sup>10</sup> (and again of the strain in 1,3-dioxetane), while formation of the trimer trioxane [(H<sub>2</sub>CO)<sub>3</sub>, **2**, X = C] is favorable.<sup>9,37</sup> As in reaction 1, the dimerization of dihydrosilanone has the highest reaction energy of group 14

(29) Masamune, S. In *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood Ltd.: Chichester, U.K., 1988; pp 257–268.

(30) For high-level calculations on XH<sub>2</sub> species see: Balasubramanian, K. *J. Chem. Phys.* **1988**, *89*, 5731.

(31) (a) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130. (b) Trinquier, G. *J. Am. Chem. Soc.* **1991**, *113*, 144.

(32) Ross, R. B.; Powers, J. M.; Atashroo, T.; Ermler, W. C.; LaJohn, L. A.; Christiansen, P. A. *J. Chem. Phys.* **1990**, *93*, 6654.

(33) Reference 4, pp 314–315.

(34) Trinquier, G.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1990**, *112*, 9121.

(35) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 1061.

(36) (a) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60. (b) Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329.

(37) Formation of all other cyclo-(H<sub>2</sub>XO)<sub>3</sub> species is favored over formation of the 1,3-dioxo-2,4-dimetaletanes, as well, energy difference per H<sub>2</sub>XO group: -12.62 (C), -18.48 (Si), -12.89 (Ge), -13.96 (Sn), -14.86 (“nonrelativistic” Pb), -9.65 (Pb), in kcal/mol (at Becke3LYP/DZ+P incl. ZPE, from ref 9).

**Table 5.** NLMO Hybridizations, Natural Atomic Charges, and Wiberg Bond Indices (WBI) from the Becke3LYP NBO Analysis<sup>a,b</sup>

| C <sub>2h</sub> -H <sub>2</sub> X=XH <sub>2</sub> ( <b>4b</b> ) | NBO <sup>c</sup>   |                     | PT <sup>d</sup> |        | NLMO <sup>b</sup>            |                    |                     | charges<br>X | WBI  |      |
|---|--------------------|---------------------|-----------------|--------|------------------------------|--------------------|---------------------|--------------|------|------|
|   | σ <sub>XX</sub>    | "π <sub>X-X</sub> " | π → σ*          | σ → π* | σ <sub>HX</sub> <sup>e</sup> | σ <sub>XX</sub>    | "π <sub>X-X</sub> " |              | HX   | X=X  |
| Si  | sp <sup>1.79</sup> | sp <sup>18.00</sup> | 6.3             | 5.2    | sp <sup>1.71</sup>           | sp <sup>1.13</sup> | sp <sup>8.29</sup>  | 0.33         | 0.94 | 1.88 |
| Ge  | sp <sup>2.07</sup> | sp <sup>7.40</sup>  | 43.4            | 13.6   | sp <sup>1.79</sup>           | sp <sup>0.98</sup> | sp <sup>2.71</sup>  | 0.32         | 0.92 | 1.65 |
| Sn  | sp <sup>2.22</sup> | sp <sup>5.78</sup>  | 45.7            | 16.2   | sp <sup>1.80</sup>           | sp <sup>0.86</sup> | sp <sup>1.82</sup>  | 0.49         | 0.88 | 1.49 |
| n-Pb  | sp <sup>2.22</sup> | sp <sup>6.70</sup>  | 36.1            | 10.8   | sp <sup>1.72</sup>           | sp <sup>0.93</sup> | sp <sup>2.26</sup>  | 0.57         | 0.87 | 1.57 |
| Pb  | sp <sup>2.52</sup> | sp <sup>3.82</sup>  | 53.5            | 40.8   | sp <sup>2.07</sup>           | sp <sup>0.69</sup> | sp <sup>0.85</sup>  | 0.50         | 0.87 | 1.09 |

| cyclo-(H <sub>2</sub> XO) <sub>2</sub> ( <b>1</b> ) | NLMO <sup>b</sup>            |  |                              | charges |      |       | WBI  |      |       |
|---|------------------------------|--|------------------------------|---------|------|-------|------|------|-------|
|   | σ <sub>HX</sub> <sup>e</sup> | σ <sub>X-O</sub>                       | lp <sub>O</sub> <sup>f</sup> | H       | X    | O     | H-X  | X-O  | X...X |
| C   | sp <sup>2.24</sup>           | sp <sup>3.37</sup> –sp <sup>3.01</sup> | sp <sup>0.99</sup>           | 0.17    | 0.30 | –0.64 | 0.92 | 0.90 | 0.03  |
| Si  | sp <sup>1.32</sup>           | sp <sup>1.78</sup> –sp <sup>2.29</sup> | sp <sup>1.57</sup>           | –0.26   | 1.77 | –1.25 | 0.75 | 0.62 | 0.03  |
| Ge  | sp <sup>1.15</sup>           | sp <sup>1.71</sup> –sp <sup>3.54</sup> | sp <sup>0.78</sup>           | –0.22   | 1.62 | –1.19 | 0.87 | 0.61 | 0.02  |
| Sn  | sp <sup>1.03</sup>           | sp <sup>1.51</sup> –sp <sup>4.15</sup> | sp <sup>0.63</sup>           | –0.30   | 1.89 | –1.30 | 0.83 | 0.54 | 0.02  |
| n-Pb  | sp <sup>1.06</sup>           | sp <sup>1.55</sup> –sp <sup>3.81</sup> | sp <sup>0.71</sup>           | –0.35   | 2.09 | –1.38 | 0.81 | 0.49 | 0.02  |
| Pb  | sp <sup>0.91</sup>           | sp <sup>1.42</sup> –sp <sup>5.91</sup> | sp <sup>0.40</sup>           | –0.24   | 1.69 | –1.22 | 0.83 | 0.57 | 0.02  |

<sup>a</sup> See Computational Details and ref 28. n-Pb: lead computed with a nonrelativistic pseudopotential. <sup>b</sup> The NLMO hybridization represents the MO structure in terms of a localized Lewis structure with "hyperconjugation tails" (i.e., deviations from the Lewis structure are considered). <sup>c</sup> Strictly localized orbitals (incomplete description of the wave function). <sup>d</sup> PT: perturbation theory (orbital mixing); energies in kcal/mol (i.e., hyperconjugation from the occupied σ and π orbitals into the empty antibonding MO's). *Attention:* The energy values have only qualitative significance! <sup>e</sup> Hydrogen: only s orbital contributions. <sup>f</sup> Oxygen in-plane lone pair; the out-of-plane lone pair has p character.

H<sub>2</sub>X=O compounds, due to the strong Si–O σ bond (intramolecular electrostatic interactions between the oxygen and the silicon atoms).<sup>10</sup> There is less difference in the X=O dimerization than in the X=X oxygenation energies. The latter correlate qualitatively with the Allred–Rochow electronegativity scale (Si, –96.9 kcal/mol, χ = 1.74; Ge, –81.7 kcal/mol, χ = 2.02; Sn, –95.5 kcal/mol, χ = 1.72; "nonrelativistic" Pb, –104.1 kcal/mol, χ = 1.55). Lead is again somewhat exceptional: Due to relativistic effects, Pb<sup>IV</sup> compounds with two electronegative ligands (i.e., O–Pb–O groups in the four-membered rings) are unfavorable<sup>35</sup> and the energy of reaction 4 is smaller (–74.5 kcal/mol) than that expected from the Pb electronegativity (consider also the small reaction energy of dioxygen with diplumbylene discussed above, –38.8 kcal/mol).<sup>38,39</sup>

The different reaction energies computed for reactions 1 and 4 for the same element X can be explained by the different properties of H<sub>2</sub>X=XH<sub>2</sub> and H<sub>2</sub>X=O "double bonds". The H<sub>2</sub>X=XH<sub>2</sub> ethene congeners (X = Si–Pb) can adopt more stable bent structures, but H<sub>2</sub>X=O compounds do not do this. They have very polar σ bonds and unfavorable π bonds.<sup>9</sup>

The X–O–X angles of (H<sub>2</sub>XO)<sub>2</sub> (**1**) are in the expected range for four-membered rings, 87–97°, but the X...X through-ring distances (X = Si, Ge, Sn, Pb) are very short (Table 2).<sup>16,18</sup> Nevertheless, the X–O distances are not unusual: All bond lengths are about 3–4 pm longer than in the corresponding six-membered rings cyclo-(H<sub>2</sub>XO)<sub>3</sub> (**2**), which we have reported recently.<sup>9</sup> Since both species, (H<sub>2</sub>XO)<sub>2</sub> and (H<sub>2</sub>XO)<sub>3</sub>, are based on the (O–XH<sub>2</sub>–O) group, the X–O bonds should utilize the same types of bonding (semipolar) and are therefore comparable.

**Electronic Structure.** The planar H<sub>2</sub>X=XH<sub>2</sub> species (**4a**) have typical, nonpolar π bonds. The trans-bent minimum

structures (**4b**) are more interesting: Si<sub>2</sub>H<sub>4</sub> is only weakly bent (planarization barrier: 1.2 kcal/mol) and possesses an almost "normal" double bond (i.e., with a σ/π separation like that of ethene, Table 5). The germanium, tin, and "nonrelativistic" lead X<sub>2</sub>H<sub>4</sub> compounds are best described by the π–σ\* interaction model (Figure 1a).<sup>2b–d</sup> The formal steps of the π–σ\* mixing are shown in the NBO analysis (Table 5).<sup>28</sup> The strictly localized natural bond orbitals (NBO) of the "π" MOs have significant p character, in contrast to the σ NBOs, which reveal increasing s contributions down group 14. The dominant hyperconjugative interaction arises from mixing of the π<sub>X-X</sub> NBO with the σ\*<sub>X-X</sub> NBO. In the natural localized molecular orbitals (NLMO) these orbital interactions are included; as a result, the X valence s contributions to the "π" bonds increase significantly.

Both C<sub>2h</sub> "H<sub>2</sub>Pb=PbH<sub>2</sub>" NLMOs reveal almost the same hybridization with major contributions from the relativistically stabilized 6s orbital (sp<sup>0.7</sup> and sp<sup>0.85</sup>). Likewise, the σ–π\* interaction is almost as large as the π–σ\* interaction. However, this mixing cannot be understood in terms of the H<sub>2</sub>PbPbH<sub>2</sub> complex model<sup>2a</sup> (i.e., no lone pair donation from one PbH<sub>2</sub> unit into the empty p orbital of the other PbH<sub>2</sub>, Figure 1b). Rather, there is a normal σ bond, while almost no π interactions occur (PbPb WBI: 1.09, Table 5). Instead of a π bond, trans-bent "H<sub>2</sub>Pb=PbH<sub>2</sub>" could be regarded as a H<sub>2</sub>Pb•–PbH<sub>2</sub> singlet biradical (with modest interactions between the semi-occupied orbitals), which have considerable contributions from the relativistically stabilized 6s orbital.<sup>40,41</sup>

According to the procedure suggested by Windus and Gordon,<sup>42</sup> the "π" bond energy can be evaluated from the energy difference between the trans-bent X<sub>2</sub>H<sub>4</sub> structures (**4b**) and C<sub>2</sub> symmetric rotated H<sub>2</sub>X\*–XH<sub>2</sub> isomers. This rotation barrier should be larger than the rotation barrier of the planar D<sub>2h</sub> species (**4a**),<sup>2d</sup> because there the π bond, formed by p orbitals,

(38) Two separated *cis*-HPbOH molecules are favored over 1,3-dioxo-2,4-diplumbaetane by 66.80 kcal/mol (Becke3LYP incl. ZPE, from ref 9)! Relative energies of 2 HXOH molecules vs the (H<sub>2</sub>XO)<sub>2</sub> rings of the other group 14 elements (kcal/mol): 86.54 (C), 90.41 (Si), 19.32 (Ge), –2.20 (Sn), 4.38 ("nonrelativistic" Pb).

(39) Alternative isomers on the X<sub>2</sub>O<sub>2</sub>H<sub>4</sub> potential energy surface are complexes from two *cis*-HXOH molecules (C<sub>2v</sub> symmetry) with divalent X atoms. For tin and lead, these complexes are surprisingly stable compared with the 1,3-dioxo-2,4-dimetaletanes (Becke3LYP/DZ+P incl. ZPE, rel. energy in kcal/mol): –98.69 (Pb), –37.04 ("nonrelativistic" Pb), –38.27 (Sn), –6.22 (Ge), 73.41 (Si), 127.61 (C). Total and zero-point vibrational energy of the (HXOH)<sub>2</sub> complexes in au and kcal/mol: –45.59840, 37.37 (C), –42.30626, 29.43 (Si), –42.18405, 27.06 (Ge), –41.35243, 25.16 (Sn), –40.86048, 24.39 ("nonrelativistic" Pb), –41.43891, 24.11 (Pb).

(40) (a) Teramae, H. *J. Am. Chem. Soc.* **1987**, *109*, 4140. (b) Such a "radical" model with some π contributions was also proposed for the heavier congeners of benzene, X<sub>6</sub>H<sub>6</sub> (X = Si–Pb), which adopt puckered D<sub>3d</sub> symmetric structures: Nagase, S.; Kobayashi, K.; Kudo, T. *Main Group Met. Chem.* **1994**, *17*, 171. See also ref 20.

(41) Following Teramae's suggestion,<sup>40a</sup> we calculated *cis*-bent H<sub>2</sub>Pb=PbH<sub>2</sub> (C<sub>2h</sub>) at CASSCF(4,4)/DZ+P to evaluate the amount of singlet biradical character. The calculation gave 88.1%, supporting our description of the diplumbene molecule. See also: (a) Fukutome, H. *Int. J. Quantum Chem.* **1981**, *20*, 955. (b) Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1977**, *66*, 3045. (c) Yamaguchi, K. *Theochem* **1983**, *103*, 101.

is unfavorable energetically. Indeed, when relativistic effects are ignored (“n-Pb”) the rotation of the trans-bent  $C_{2h}$   $H_2Pb=PbH_2$  structure (**4b**) requires 26.2 kcal/mol (the according transition state optimized to  $C_{2v}$  symmetry, cis-bent  $H_2Pb=PbH_2$ ), while the  $90^\circ$  rotation of planar  $D_{2h}$  diplumbene (**4a**) to  $D_{2d}$  costs only 15.5 kcal/mol.<sup>43</sup> When relativistic effects are included, our calculated  $D_{2h} \rightarrow D_{2d}$  rotation barrier (20.3 kcal/mol) is very close to the “intrinsic bond energy” (which is the energy gain due to orbital overlap) of the  $Pb=Pb$   $\pi$  bond obtained by Jacobsen and Ziegler (20.6 kcal/mol).<sup>2d</sup> This agreement indicates that almost no double hyperconjugation occurs in the rotated  $H_2Pb^* \cdot PbH_2$  isomers (i.e., our results should be reliable). However, the rotation barrier of trans-bent  $H_2Pb=PbH_2$  (**4b**,  $C_{2h}$ ) is *smaller* (13.1 kcal/mol; symmetry of the transition state,  $C_2$ ),<sup>43</sup> in contrast to Jacobsen and Ziegler’s “intrinsic bond energy” of 42 kcal/mol. Therefore, we conclude that the “ $\pi$ ” orbital overlap is not very large in trans-bent  $H_2Pb=PbH_2$ .<sup>41</sup> The driving force for trans-bending are the significant 6s contributions to the Pb orbitals, which form the “ $\pi$ ” bond.

Our NBO analysis<sup>28</sup> of the  $(H_2XO)_2$  rings (**1**) does *not* support the  $X \cdots X$   $\pi$  interaction model of Grev and Schaefer described in the Introduction.<sup>18</sup> The covalent metal–metal interactions are very small (Table 5), and there is no direct X–X bond. The short  $Si \cdots Si$  distance is a result of electrostatic repulsion between the very negatively charged O atoms. From simple electrostatic point charge considerations, the  $O \cdots O$  repulsion in the  $(H_2SiO)_2$  ring is even larger than in the smaller  $(H_2CO)_2$  ring [less negatively charged oxygens:  $-0.64$  ( $X = C$ ),  $-1.25$  ( $X = Si$ )]. Since the X–O bond lengths do not vary much (consider the constant 3.5–4.5 pm decrease vs the  $(H_2XO)_3$  rings (**2**), Table 2),<sup>9</sup> the  $(H_2XO)_2$  geometries are fixed. Any increase of the  $Si \cdots Si$  distance (i.e., increase of  $\angle SiOSi$ ) would decrease the  $O \cdots O$  distance. As X gets heavier (and the rings larger), the  $O \cdots O$  repulsion in **1** becomes smaller and  $\angle XOX$  can increase smoothly to about  $95^\circ$ . Hence, the very short distances in 1,3-dioxa-2,4-disilaetanes (**1**,  $X = Si$ ) result from the quite inflexible Si–O bond length,<sup>21</sup> which cannot change significantly.

(42) Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 9559.

(43) Absolute and relative energies of the rotated  $Pb_2H_4$  structures (au and kcal/mol):  $-9.20073$ ,  $13.09$  ( $C_2$  vs  $C_{2h}$  trans-bent “ $H_2Pb=PbH_2$ ”);  $-9.15116$ ,  $20.34$  ( $90^\circ$  rotation of the  $D_{2h}$  planar  $Pb_2H_4$  geometry). “Nonrelativistic” lead:  $-8.59509$ ,  $26.17$  ( $C_{2v}$  vs  $C_{2h}$  trans-bent “ $H_2Pb=PbH_2$ ”);  $-8.60047$ ,  $15.52$  ( $90^\circ$  rotation of the  $D_{2h}$  planar  $Pb_2H_4$  geometry). However, spin–orbit coupling in open-shell species may affect the relative energies.

As in the  $H_2X=O$  compounds,<sup>9</sup> the heavy elements alter the hybridizations of the neighboring oxygen atoms (Table 5): The X s valence orbital contributions to the  $\sigma_{X-O}$  NLMOs of the 1,3-dioxa-2,4-dimetaletanes (**1**) increase ( $Si \rightarrow Pb$ ), while the oxygen 2p orbital contributions become larger. To compensate, the in-plane oxygen lone pair has considerable 2s character. The most dramatic effects are found in  $(H_2PbO)_2$ ; The oxygen in-plane lone pair adopts  $sp^{0.4}$  hybridization, while the  $\sigma_{O-Pb}$  NLMO is formed from  $sp^{5.9}$ – $sp^{1.4}$  hybrid orbitals (N.B.:  $sp^{5.9}$  at O and  $sp^{1.4}$  at Pb, not the reverse!).

## Conclusions

The thermodynamic stability of  $R_2X=XR_2$  “double bonds” toward reaction with dioxygen increases down group 14, but the tendency to dissociate into divalent  $XR_2$  units increases even more. Moreover, the “double bonds” of the  $C_{2h}$  bent structures (**4b**) are not “normal”  $\pi$  bonds as in ethene (formed by p orbitals only).<sup>2</sup> On the other hand, when a heteroelement like oxygen is bound to a group 14 metal, dissociation (i.e.,  $H_2X=O$  into  $XH_2$  and O) is not possible, and the  $X=O$   $\pi$  bond has only p valence orbital contributions.<sup>9</sup> However, such compounds are extremely polar,  $R_2X^+::O^-$ , and may exist as monomers only in isolation in the gas phase or matrixes.

In order to be observed in condensed phases,  $R_2X=XR_2$  and  $R_2X=O$  derivatives with heavier group 14 element double bonds will normally require kinetic stabilization (i.e., steric protection). 1,3-Dioxa-2,4-dimetaletanes, **1** (and other four-membered rings with two electronegative heteroelements), are preferred energetically, because of the favorable bonding to the X atoms.<sup>8,9</sup> The four  $\sigma_{X-O}$  bonds are stabilized by strong intramolecular electrostatic interactions. The only exception are lead compounds; due to relativistic effects, monomeric divalent *cis/trans*-HPbOH is preferred over the  $(H_2PbO)_3$  trimer (**2**,  $X = Pb$ )<sup>9</sup> and, of course, over the dimer  $(H_2PbO)_2$ .<sup>38,39</sup> Nevertheless, NBO analysis of the electronic structure shows the 1,3-dioxa-2,4-dimetaletanes (**1**) to be normal molecules without significant cross-ring  $X \cdots X$  bonding.

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