**Digermenes >Ge=Ge<, Distannenes >Sn=Sn< and Diplumbenes >Pb=Pb<**

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doi:10.5618/chem.2012.v2.n1.5 || Received: 06-09-2012, Accepted: 25-09-2012, Available online: 26-09-2012

Abstract: This review provides a highlight of the current state of affairs in one of the most challenging fields of contemporary main group organometallic chemistry; namely, doubly-bonded derivatives of heavy group 14 elements >E=E< (E = Ge, Sn, Pb). The chemistry of representative examples is discussed from both synthetic and structural points of view. The similarities and differences of the above-mentioned class of unsaturated organometallic compounds >E=E<, as compared to their organic counterparts >C=C<, will also be discussed throughout this article.

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List of abbreviations:
1. Ad 1-adamantyl
2. Bbt 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl, 2,6-[(Me3Si)_2CH]2-4-[(Me3Si)2C]-C6H2
3. CPMAS cross polarization magic angle spinning
4. Dsi bis(trimethylsilyl)methyl, (Me3Si)2CH
5. Mes 2,4,6-trimethylphenyl, 2,4,6-Me3-C6H2
6. MO molecular orbital
7. NMR nuclear magnetic resonance
8. Tbt 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, 2,4,6-[(Me3Si)2CH]-C6H2
9. Tip 2,4,6-triisopropylphenyl, 2,4,6-3Pr3-C6H2

1. Introduction

Alkenes are of paramount importance for the chemical industry, accordingly making carbon-carbon double bonds is one of the ultimate goals of organic chemistry processes. It is therefore of no surprise that multiple bonding between carbon atoms (or between carbon atom and heteroatom) is a central theme of organic chemistry, greatly contributing to its variety and richness.

Likewise, the analogues of alkenes of the heavy group 14 elements (Si, Ge, Sn and Pb) are of equal importance in the chemistry of the low-coordinate organometallics, however unlike organic alkenes the heavy analogue derivatives are much less abundant (at least, as stable entities). Initially believed to be synthetically inaccessible (a prejudice known as the “double bond rule”: elements with a principal quantum number equal to or greater than three cannot form multiple bonds because of the significant Pauli repulsion of the electrons in the inner shells), these species were later proved to be ubiquitous, participating in a vast number of organometallic transformations. At first, generated and observed as the fleeting reactive intermediates, detectable only under very special conditions (low-temperature inert matrices, for example), “heavy” alkenes R2E=ER2 (E = Si–Pb) were finally isolated as room temperature stable compounds thanks to the right combination of electronic and steric effects of...
substituents R. As milestones of this field, the first stable distannene Dsi₂Sn=SnDsi₂ (Lappert, 1976),¹ the first stable disilene Mes₂Si=SiMes₂ (West, 1981)² and the first stable silene (Me₂Si)₂Si=C(OSiMe₂)Ad (Brook, 1981)³ should be mentioned. To date, many representatives of isolable “heavy” alkenes have been synthesized, and it has now become clear that despite their isoelectronic structure to alkenes, these heavy analogues are distinctly different in synthetic approach, nature of the E=E bond and reactivity.⁴

In this review, we describe the peculiar synthetic methods that lead to stable “heavy” alkenes R₂E=ER₂ (E = Ge–Pb), along with a discussion on their unique structural and bonding situations, from both experimental (X-ray crystallography and NMR spectroscopy) and theoretical viewpoints.⁵ The chemistry of disilenes >Si=Si<, which is most comprehensively covered in preceding excellent reviews,⁶ will not be discussed in this contribution. Given the limited space for this review, the heteronuclear derivatives featuring a double bond between two different group 14 elements or between heavy group 14 element and other main group elements E=E' (E = Si–Pb, E' = group 13, 14, 15 or 16 element) will also not be considered.⁷ Likewise, radical, ionic and aromatic compounds, featuring double bonds to heavy group 14 elements, are also outside the framework of this article.⁸

2. Stable alkene analogues of heavy group 14 elements.

2.1. Synthesis

2.1.1. First Examples. The very first stable digermene and distannene derivatives were prepared by Lappert and co-workers in 1976: digermene Dsi₂Ge=GeDsi₂ ¹⁷ by the reaction of bis(amino)germylene [(Me₂Si)₂N]₂Ge: with DsiLi and the isostructural distannene Dsi₂Sn=SnDsi₂ ¹⁷ by the reaction of bis(amino)stannylene [(Me₂Si)₂N]₂Sn: with DsiLi (Scheme 1). In fact, distannene 2 was the first isolable compound that featured a double bond between heavy group 14 elements. Unlike organic alkenes, which possess quite robust C=C double bonds, both digermene ¹ and distannene 2 were not stable in solution at room temperature, dissociating into the corresponding germylene and stannylene (Scheme 1), as confirmed by UV–Vis studies and trapping reactions.

![Scheme 1](http://ccaasmag.org/CHEM)

![Scheme 2](http://ccaasmag.org/CHEM)

Although Ge=Ge and Sn=Sn bonds in ¹ and 2 were not twisted (as the C=C bonds in alkenes, which are also not twisted), the geometry around the Ge and Sn centers was notably pyramidal with the Dsi-substituents arranged in a trans-bent fashion (unlike the planar geometry of C=C bonds in alkenes) with the sum of the bond angles around Ge in ¹ and around Sn in 2 amounting to 349° and 342°, respectively. The Ge=Ge bond length of 2.347(2) Å, determined for the first time, was notably shorter than standard Ge–Ge single bonds, whereas the Sn=Sn bond length of 2.764(2) Å was remarkably long, being quite comparable with those of typical Sn–Sn single bonds.

Given the increasing weakness of the E=E bond on going from silicon to lead, it comes as no surprise that the stabilization of the first diplumbene Tip₂Pb=PbTip₂ ³ on with a double bond between two tricoordinate lead atoms was achieved only in 1999: ³ was conveniently prepared by the simple reaction of TipMgBr and PbCl₂ (Scheme 2).¹⁰

Diplumbene ³ revealed a lead–lead separation of 3.0515(3) Å that is slightly longer than that calculated for the parent H₂Pb=PbH₂ and quite comparable with standard Pb–Pb single bonds. Other manifestations of the reduced lead–lead double bond character, significant pyramidalization at both leads (sum of the bond angles around them totaling to 325° and 330°) and twisting of
the Pb=Pb bond by 22°, should also be mentioned.

2.1.2. Digermenes. After the breakthrough preparation of the first stable examples of “heavy” alkenes 1–3 (see above), about 30 isolable digermenes have been isolated and, in most cases, structurally characterized (not counting ionic, radical and aromatic compounds containing Ge=Ge bonds, as well as compounds with conjugated or cumulated Ge=Ge bonds) (Table 1).

Table 1. Crystallographic parameters of the structurally characterized digermenes.a

<table>
<thead>
<tr>
<th>Digermine (synthetic method)</th>
<th>&gt;Ge=Ge&lt; [Å]</th>
<th>Σ(Ge) [°]</th>
<th>&gt;Ge=Ge twist [°]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.r.Geo.GeoAr₂</td>
<td>2.123(2)</td>
<td>358.4</td>
<td>10.0</td>
<td>[11]</td>
</tr>
<tr>
<td>A[r = 2,6-t-C₆H₄]C₆H₆</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₂r.Geo.GeoAr₂</td>
<td>2.347(2)</td>
<td>348.5</td>
<td>0.0</td>
<td>[9]</td>
</tr>
<tr>
<td>A[r = 2,6-t-Me₂C₆H₄]C₆H₆</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-Ar(C)Ge=Ge=Ar(C)Cl</td>
<td>2.445(2)</td>
<td>333.8</td>
<td>NA</td>
<td>[12]</td>
</tr>
<tr>
<td>B[r = 2,6-t-Me₂C₆H₄]C₆H₆</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Z)-Ar(C)Ge=Ge=Ar(C)Cl</td>
<td>2.462(4)</td>
<td>327.8</td>
<td>NA</td>
<td>[13]</td>
</tr>
<tr>
<td>B[r = 2,6-(2,6-Pr₂C₆H₄)C₆H₆]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-Ar(Me)Ge=Ge=Ar(Me)</td>
<td>2.317(3)</td>
<td>342.9</td>
<td>NA</td>
<td>[14]</td>
</tr>
<tr>
<td>B[r = 2,6-t-Bu²C₆H₄]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-Ar(Et)Ge=Ge=Ar(Et)</td>
<td>2.347(3)</td>
<td>343.0</td>
<td>NA</td>
<td>[14]</td>
</tr>
<tr>
<td>B[r = 2,6-t-Bu²C₆H₄]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-Ar(Ph)Ge=Ge=Ar(Ph)</td>
<td>2.318(3)</td>
<td>348.4</td>
<td>NA</td>
<td>[14]</td>
</tr>
<tr>
<td>B[r = 2,6-t-Bu²C₆H₄]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-Ar(C)Ge=Ge=Ar(C)Cl</td>
<td>2.363(2)</td>
<td>348.6</td>
<td>NA</td>
<td>[14]</td>
</tr>
<tr>
<td>B[r = 2,6-t-Bu²C₆H₄]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A.r.Geo.GeoAr₂</td>
<td>2.252(8)</td>
<td>360.0</td>
<td>20.4</td>
<td>[15]</td>
</tr>
<tr>
<td>B[r = 2,6-t-Bu₂-4,5,6-Me₃C₄H₄]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Z)-isomer</td>
<td>2.454(2)</td>
<td>337.6</td>
<td>22.3</td>
<td>[16]</td>
</tr>
<tr>
<td>B[r = t-Bu]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-isomer</td>
<td>2.460(1)</td>
<td>331.5</td>
<td>63.0</td>
<td>[17]</td>
</tr>
<tr>
<td>B[r = t-Bu, R = Pr]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A.r.Geo.GeoAr₂</td>
<td>2.364(4)</td>
<td>NA</td>
<td>NA</td>
<td>[18]</td>
</tr>
<tr>
<td>B[r = 2,6-t-Bu₂C₆H₄]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-B(br)Ge=Ge=B(b)br</td>
<td>2.508(7)</td>
<td>332.6</td>
<td>NA</td>
<td>[19]</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-R(Ar)Ge=Ge=Ra(r)</td>
<td>2.322(4)</td>
<td>341.9</td>
<td>NA</td>
<td>[20]</td>
</tr>
<tr>
<td>B[r = 2,6-(2,6-t-Pr₂C₆H₄)C₆H₆]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = t-Bu-t-C₉C₆C₆C₆C₆</td>
<td></td>
<td>342.5</td>
<td>NA</td>
<td>[20]</td>
</tr>
<tr>
<td>(Z)-Mes(2)Ar=Ge=Ge=Mes(2)Ar</td>
<td>2.301(1)</td>
<td>345.5</td>
<td>7.0</td>
<td>[21]</td>
</tr>
<tr>
<td>(E)-Pr₂Me₂Si₂Ge=Ge=SiMePr₂(2)</td>
<td>2.267(1)</td>
<td>359.6</td>
<td>0.0</td>
<td>[22]</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-Pr₂Si₂Ge=Ge=SiPr₂(2)C₆</td>
<td>2.298(1)</td>
<td>357.0</td>
<td>0.0</td>
<td>[22]</td>
</tr>
<tr>
<td>(Z)-Tb(Mes)Ge=Ge=Tb(Mes) (C)</td>
<td>2.416(2)</td>
<td>355.3</td>
<td>56.6</td>
<td>[23]</td>
</tr>
<tr>
<td>(t-BuMe₂Si₂Ge=Ge=SiMeBu₂(2) (C)</td>
<td>2.346(2)</td>
<td>358.8</td>
<td>52.8</td>
<td>[24]</td>
</tr>
<tr>
<td>(E)-Ar(Hg)Ge=Ge=Ar(Hg)</td>
<td>2.302(3)</td>
<td>NA</td>
<td>NA</td>
<td>[25a]</td>
</tr>
<tr>
<td>D[r = 2,6-(2,6-t-Pr₂C₆H₄)C₆H₆]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar₂Ge=Ge=CH₂Bu₂ (2)Ar</td>
<td>2.343(20)</td>
<td>360.0</td>
<td>NA</td>
<td>[26]</td>
</tr>
</tbody>
</table>

a NA = not available

http://ccaasmag.org/CHEM
There are four major synthetic routes to stable digermenes: 1) photolysis of cyclotrigermanes (A); 2) dimerization of germynes (B); 3) reductive dehalogenation of 1,1-dichlorogermanes (D); and 4) 1,2-addition or cycloaddition of isolable digermynes (E) (Scheme 3, E = Ge). Photolysis of hexaarylcyclotrigermanes (method A) is one of the first methods developed for the preparation of stable tetraarylgermylenes Ar₂Ge=GeAr₂. Method B was used for the synthesis of the first isolable digermene 1 and is most commonly employed for accessing stable digermynes by the reaction of RLi/RMgX with :GeX₂·diox. The second most popular method, reductive dehalogenation of 1,1-dichlorogermanes (method D), allowed isolation of several digermynes with either aryl or silyl substituents. Method E is the most recently developed approach to stable digermynes: 1,2-addition or cycloaddition to digermynes (or their valence isomers), which became available after the recent preparation of digermynes.

2.1.3. Distannenes. Eight stable distannenes have been isolated and structurally characterized to date (Table 2). They can be prepared by one of three general methods: 1) photolysis of cyclotristannanes (A); 2) dimerization of stannylenes (B); and 3) ligand redistribution between the homoaleptic stannylenes R₂Sn: and R’₂Sn: to form heteroleptic stannylenes RR’Sn:, followed by dimerization (C) (Scheme 3, E = Sn).

Similar to the case of digermenes, method A was developed primarily for the synthesis of tetraaryldistannenes Ar₂Sn=SnAr₂. Dimerization of transient stannylenes (method B) represents the most popular route to access a variety of tetraaryl-, tetrasilyl- and mixed dialkyldiaryl- and diaryldisilyldistannenes. All of them, apart from the tetrasilyldistannene (‘Bu₂MeSi)₂Sn=Sn(SiMe³Bu)₂, dissociate in solution into monomeric stannylenes >Sn:. Ligand redistribution to form heteroleptic stannylenes RR’Sn:, followed by dimerization (method C), is employed for the preparation of distannenes with a mixed arylsilyl-substitution pattern at each sp²-Sn center. All distannenes available by this method are also unstable in solution, dissociating into monomeric stannylenes.

2.1.4. Diplumbenes. Unlike disilenes, digermenes and even distannenes, diplumbenes are still scarcely represented as isolable compounds, which, as mentioned above, is caused by the inherent weakness of the Pb=Pb bond. Even the definition of the lead–lead double bond simply based on its length, is problematic, given the fact that double bonds between heavy group 14 elements become progressively longer descending the group, which makes the story even more complicated. Thus, for example, lead–lead separations between tricoordinate Pb centers of 2.903–3.947 Å that can be formally viewed as doubly bonded, are notably longer than standard lead–lead single bonds.

Such compounds (depending on the degree of lead–lead separation) are sometimes classified as diplumbenes with a >Pb=Pb< double bond and sometimes as plumbylene dimers with only a weak association between the two plumbylene monomers. Needless to say the distinction between these two classes is very subtle, and the border separating them is rather formal. In accord with the very long and weak, more dative than covalent, bonds between the plumbylene fragments in either diplumbenes or plumbylene dimers, all these compounds readily dissociate in solution forming corresponding plumbylenes. In terms of bonding, the intrinsic weakness of the donor–acceptor interaction between plumbylenes to form their dimers (in either diplumbene or plumbylene dimer forms) is due to the relativistic contraction of the lead valence s-orbitals, leading to an increase in the s- and p-orbitals energy gap and accordingly to a partial exclusion of s-electrons from the lead–lead bonding.

In view of all mentioned above, one should not expect
an abundance of stable diplumbenes, and this is indeed the case with only eight examples reported to date: four as diplumbenes and four as plumbylene dimers. These compounds, only marginally distinctive by the degree of their lead-lead separations, are all prepared by the dimerization of plumbylenes: either homoleptic (method B: Scheme 3, E = Pb) or heteroleptic (method C: Scheme 3, E = Pb) (Table 3).

Table 2. Crystallographic and spectral parameters of the structurally characterized distannenes.$^a$

<table>
<thead>
<tr>
<th>Distannene (Synthetic Method)</th>
<th>$&gt;$Sn=Sn&lt; [Å]</th>
<th>(\chi) (Sn) [°]</th>
<th>$&gt;$Sn=Sn twist [°]</th>
<th>$^2$Sn NMR (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dis$_2$Sn=SnDis$_2$ (B)</td>
<td>2.764(2)</td>
<td>342.0</td>
<td>0.0</td>
<td>NA</td>
<td>[1,9d]</td>
</tr>
<tr>
<td>(E)-Ar-R(Sn=Sn)(Ar)-R (B)</td>
<td>2.7705(8)</td>
<td>329.7</td>
<td>NA</td>
<td>1205.7</td>
<td>[27]</td>
</tr>
<tr>
<td>Ar$_2$Sn=SnAr$_2$ (B)</td>
<td>2.910(1)</td>
<td>320.9</td>
<td>44.0</td>
<td>1401.0 (sol.)</td>
<td>[28]</td>
</tr>
<tr>
<td>[(Me$_2$Si)$_2$Sn]$_2$Sn=Sn[(SiMe$_2$)$_2$Sn]$_2$ (B)</td>
<td>2.8247(6)</td>
<td>352.0</td>
<td>63.2</td>
<td>NA</td>
<td>[29, 30b]</td>
</tr>
<tr>
<td>(E)-Mes$_2$[Me$_2$Si$_2$]Sn=Sn[Me$_2$Si$_2$]Mes$_2$ (B)</td>
<td>2.7023(6)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>[30]</td>
</tr>
<tr>
<td>(Bu$_2$Me$_2$Si)$_2$Sn=Sn[(SiMe$_2$)$_2$Bu]$_2$ (B)</td>
<td>2.6663(10)</td>
<td>360.0</td>
<td>44.6</td>
<td>630.7</td>
<td>[31]</td>
</tr>
<tr>
<td>(E)-R(Ar)-Sn=Sn(R)Ar (B)</td>
<td>2.8516(19)</td>
<td>325.4</td>
<td>NA</td>
<td>381.0</td>
<td>[20]</td>
</tr>
<tr>
<td>(E)-Ar[[Mes$_2$Si$_2$]Sn=Sn[Ar][Si(SiMe$_3$)$_2$] [Ar = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$] (C)</td>
<td>2.833(1)</td>
<td>337.9</td>
<td>NA</td>
<td>NA</td>
<td>[32]</td>
</tr>
<tr>
<td>(E)-Ar[[Mes$_2$Si$_2$]Sn=Sn[Ar][Si(SiMe$_3$)$_2$] [Ar = 2-Bu-4,5,6-Me$_2$C$_6$H$_3$] (C)</td>
<td>2.7914(14)</td>
<td>337.4</td>
<td>NA</td>
<td>1506</td>
<td>[33]</td>
</tr>
</tbody>
</table>

$^a$ NA = not available

Table 3. Crystallographic and spectral parameters of the structurally characterized diplumbenes.$^a$

<table>
<thead>
<tr>
<th>Diplumbene or plumbylene dimer</th>
<th>$&gt;$Pb=Pb&lt; [Å]</th>
<th>(\chi) (Pb) [°]</th>
<th>$&gt;$Pb=Pb twist [°]</th>
<th>$^2$Pb NMR (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl$_2$Pb=Pb=Tl$_2$</td>
<td>3.0515(3)</td>
<td>325.4</td>
<td>21.7</td>
<td>NA</td>
<td>[10]</td>
</tr>
<tr>
<td>(E)-Tl[Me$_2$Si$_2$]Pb= Pb=Tl[Si(SiMe$_3$)$_2$]</td>
<td>2.9899(5)</td>
<td>339.0</td>
<td>NA</td>
<td>NA</td>
<td>[34]</td>
</tr>
<tr>
<td>(E)-Mes$_2$[Me$_2$Si$_2$]Pb= Pb=Mes$_2$[Si(SiMe$_3$)$_2$]</td>
<td>2.9003(11)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>[30]</td>
</tr>
<tr>
<td>(E)-Ar/Mes$_2$Pb=Pb/Ar (Av = 2,6-(2,6-Pt$_2$C$_6$H$_3$)$_2$C$_6$H$_2$)</td>
<td>3.1601(6)</td>
<td>322.7</td>
<td>0.0</td>
<td>8738.0</td>
<td>[35]</td>
</tr>
<tr>
<td>(E)-Ar[[Mes$_2$Si$_2$]Pb]$_2$ [Av = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$] [plumbylene dimer]</td>
<td>3.537(1)</td>
<td>336.8</td>
<td>NA</td>
<td>NA</td>
<td>[32]</td>
</tr>
<tr>
<td>(E)-Ar[[Mes$_2$Si$_2$]Pb]$_2$ [Av = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$] [plumbylene dimer]</td>
<td>3.3665(11)</td>
<td>NA</td>
<td>NA</td>
<td>7545.0</td>
<td>[36]</td>
</tr>
<tr>
<td>Mes$_2$Pb[MgthV(Br)Br]$_2$ [plumbylene dimer]</td>
<td>3.3549(6)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>[34]</td>
</tr>
<tr>
<td>[Ar(Ar)Pb]$_2$ [Av = 2,6-(2,6-Pt$_2$C$_6$H$_3$)$_2$C$_6$H$_2$; Ar = 4-(2,6-C$_6$H$_3$)C$_6$H$_3$] [plumbylene dimer]</td>
<td>3.947(1)</td>
<td>NA</td>
<td>74.2</td>
<td>7275.0</td>
<td>[35]</td>
</tr>
</tbody>
</table>

$^a$ NA = not available
Only the first diplumbene $\text{Tip}_2\text{Pb}=\text{PbTip}_2$ and $\text{MgBr}_2$-stabilized plumbylene dimer $\{\text{Mes}_2\text{Pb} \cdots \{\text{Br} \cdots \text{Mg}(\text{thf})_4\cdots \text{Br}\}\}_2$ (synthesis: $\text{MesMgBr} + \text{PbCl}_2$) were prepared by method B (Scheme 3; $E = \text{Pb}$). Interestingly, a similar reaction of the bulkier $\text{ArMgCl}$ ($\text{Ar} = 2,4,6-$Et$_3$-C$_6$H$_2$) with PbCl$_2$ resulted in the formation of an unusual dimeric form $\text{Ar}_2\text{Pb} \cdots \{\text{Br} \cdots \text{Mg}(\text{thf})_4\cdots \text{Br}\} \cdots \text{PbAr}_2$, in which two plumbylene monomers are linked by the bromine atoms of the linear Br–Mg(thf)$_4$–Br fragment with no direct Pb–Pb bonding. All other stable compounds, either diplumbenes or plumbylene dimers, were synthesized by the dimerization of heteroleptic plumbylenes, that is, by method C (Scheme 3, $E = \text{Pb}$) (Table 3).

2.2. Structure (NMR spectroscopy, X-ray crystallography)

2.2.1. Digermerenes: X-ray crystallography. In the absence of a magnetically useful nucleus (the $^7\text{Ge}$ nucleus has a large quadrupole moment and low sensitivity, leading to a remarkable broadening of its resonance signals, which greatly limits the analytical applicability of $^7\text{Ge}$ NMR spectroscopy), the most important structural information on digermenes can be obtained from X-ray crystallographic studies (Table 1). The overall geometry of the Ge=Ge bond is totally governed by the substituents’ electronic influence: electronegative substituents cause remarkable trans-bending at the sp$^2$-Ge, stretching and weakening the Ge=Ge bond, whereas electropositive groups have the opposite effect, namely: planarization at the germaniums, shortening and strengthening of the Ge=Ge bond. Steric bulk of the substituents at the germanium centers may also contribute to the structural distortions of the Ge=Ge bond, causing its substantial stretching and twisting in the case of very large substituents.

The most important structural parameter, namely, the length of the Ge=Ge bond, was found to span over the wide range of 2.21–2.51 Å (shorter than standard Ge–Ge single bonds), although the majority of them (59%) were found to fit within the more narrow range of 2.30–2.39 Å (Figure 1). These last values, although slightly longer than the 2.22 Å estimate, based on the double bond covalent radius of Ge (1.11 Å), are nevertheless shorter than the sum of the single bond covalent radii for two Ge atoms (2.42 Å)\(^{38}\).

Among the isolable digermenes, only one peralkyl-substituted derivative, $\text{Dsi}_2\text{Ge} = \text{GeDsi}_2$ 1, has been structurally characterized: it has a typical length for its Ge=Ge bond, which is trans-bent and not twisted: 2.347(2) Å (Ge=Ge bond length); 348.5° (sum of the bond angles around the Ge atoms, indicating the degree of pyramidality); 0.0° (twisting about Ge=Ge bond) (Table 1).\(^9\)

![Digermerenes: Bond Lengths](http://ccaasmag.org/CHEM)

*Figure 1. Statistical distribution (in %) of the Ge=Ge double bond lengths for the isolable digermenes (see also Table 1).*

When compared with the above-described tetraalkydigermene, tetraaryldigermenes typically possess shorter and less trans-bent Ge=Ge bonds, which may be twisted when substituted by very bulky groups: 2.213(2)–2.416(2) Å (bond length); 345.5–360.0° (sum of the bond angles); 7.0–20.4° (twisting) (Table 1).

Tetrasilyldigermenes are the least distorted among all stable digermenes, being deformed rather insignificantly and featuring relatively short Ge=Ge bonds: 2.267(1)–2.298(1) Å (bond length); 357.0–359.6° (sum of the bond angles); 0.0° (twisting) (Table 1). Tetrasilyldigermene ($\text{Bu}_2\text{MeSi})_2\text{Ge} = \text{Ge(SiMe}_2\text{Bu}_2)_2$ with the very bulky electropositive silyl substituents is the only remarkable exception from the above tendencies. Albeit still planar at both sp$^2$-germaniums (sum of the bond angles totaling 358.8° and 359.2°), this uncharacteristically colored deep-blue digermene
features an extraordinarily twisted (52.8°) Ge=Ge bond of 2.346(2) Å.\textsuperscript{24}

Extreme values for the twisting and stretching of the Ge=Ge bond were found in the mixed bis(aminobis(silyl)-substituted digermerne (63.0° for the record twisting, Table 1)\textsuperscript{17} and in the (E)-Bbt(Br)Ge=Ge(Bbt)Br digermerne (2.5087(7) Å for the record stretching, Table 1)\textsuperscript{19}.

2.2.2. Distannenes: \textsuperscript{119}Sn NMR spectroscopy. \textsuperscript{119}Sn NMR spectroscopy is the most important tool to elucidate the structure of distannenes in solution. Typically, the solution \textsuperscript{119}Sn NMR resonances of stable acyclic distannenes were found at very low-field, well above +1000 ppm, which is in the region more diagnostic of monomeric stannylenes than dimeric distannenes (Table 2). This points to a dissociation (at least partial) of the >Sn=Sn< bond in solution into a pair of stannylene >Sn:. Accordingly, such formally doubly-bonded distannene derivatives actually had the reactivity of stannylene, not distannenes. Only the tetraaryldistannene Tip2Sn=SnTip2 has been claimed to behave as true distannene that retains the structural integrity of its Sn=Sn bond in solution [(δ\textsuperscript{119}Sn): 427.3 ppm] and reacts as a distannene, however, it has not been isolated as pure compound.\textsuperscript{39}

To date, the only isolable acyclic distannene, which possesses an authentic Sn=Sn double bond both in the solid state and in solution, is tetrasilyldistannene ('Bu\textsubscript{3}MeSi)\textsubscript{2}Sn=Sn(SiMe\textsubscript{3}Bu\textsubscript{2})\textsubscript{2} prepared by the reaction of silyl sodium 'Bu\textsubscript{2}MeSiNa and SnCl\textsubscript{2}•diox complex.\textsuperscript{31} The resonance of the doubly-bonded tin centers was observed at +630.7 ppm, which is in the region typical for >Sn=Sn< bond in distannenes but clearly beyond the range of stannylene >Sn: NMR resonances. This was further corroborated by the reactivity of (Bu\textsubscript{3}MeSi)\textsubscript{2}Sn=Sn(SiMe\textsubscript{3}Bu\textsubscript{2})\textsubscript{2} in solution, which reacted exclusively as a distannene and not as a stannylene.

X-ray crystallography. Although the distances between the doubly bonded tin atoms in distannenes are found between 2.67 and 2.91 Å, the most abundant set (34%) fits within the narrower range of 2.78–2.83 Å, which is nearly equal to (or even longer than) that of standard Sn–Sn single bonds (Figure 2).

![Image](http://ccaasmag.org/CHEM)

**Figure 5.** Statistical distribution (in %) of the Sn=Sn double bond lengths for the isolable distannenes (see also Table 2).

Actually, the experimental values (2.78–2.83 Å) for the Sn=Sn bond are markedly greater than the sum of the Sn atoms double bond covalent radii (2.60 Å)\textsuperscript{37} but quite comparable to the sum of the single bond covalent radii for two Sn atoms (2.80 Å).\textsuperscript{38} The tin-tin bond length extremes in distannenes are represented by the shortest (and strongest) Sn=Sn bond of 2.6683(10) Å in tetrasmelyldistannene (Bu\textsubscript{3}MeSi)\textsubscript{2}Sn=Sn(SiMe\textsubscript{3}Bu\textsubscript{2})\textsubscript{2} and the longest bond of 2.910(1) Å in tetraaryldistannene Ar\textsubscript{2}Sn=SnAr\textsubscript{2} (Ar = 2′Bu\textsubscript{4}C\textsubscript{6}H\textsubscript{10}, Me\textsubscript{3}C\textsubscript{6}H)\textsuperscript{28} (Table 2).

In accord with the general trends observed on going down group 14, distannenes revealed stronger pyramidalization at the tin centers than that of the corresponding disilenes and digermerne. Again, expectedly, tetraaryl- and tetraalkyldistannenes are far more pyramidalized than their tetrasmelyl-substituted counterparts: 320.9° and 342.0° vs. 360.0° (Table 2). When substituted with extraordinarily bulky groups, the Sn=Sn bond reveals not only stretching but extreme twisting as well: from 44.0° to 63.2° (Table 2).

The above-mentioned tetrasmelyldistannene (Bu\textsubscript{3}MeSi)\textsubscript{2}Sn=Sn(SiMe\textsubscript{3}Bu\textsubscript{2})\textsubscript{2}, which features a genuine Sn=Sn bond both in the solid state and in solution, showed a rather unusual combination of structural characteristics caused by the presence of the very bulky (on the one hand) and strongly electropositive (on the
other hand) silyl substituents.\(^{31}\) Namely, this distannene was found to have a very short Sn=Sn bond of 2.6683(10) Å, which, although greatly twisted (44.6°), is nonetheless absolutely undistorted at the doubly-bonded tins (sum of the bond angles 360°) (\textbf{Table 2}). In distannenes chemistry, such unprecedented structural motif of (Bu\(_2\)MeSi)\(_2\)Sn-Sn(SiMe\(_3\)Bu\(_2\))\(_2\) (short, nonpyramidal, highly twisted Sn=Sn bond) can be understood in terms of \textit{out-of-plane}, rather than the classical \textit{in-plane}, interaction of the two triplet stannylenes (\textbf{Scheme 4}).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{scheme4.png}
\caption{Out-of-plane interaction of the two triplet stannylenes.}
\end{figure}

\begin{table}
\centering
\begin{tabular}{|c|c|}
\hline
\textbf{Transition} & \textbf{Wavelength (nm)} \\
\hline
\textit{Singlet} & 494 \textit{red} \\
\textit{Triplet} & 207 \textit{green} \\
\textit{Quasibound} & 322 \textit{yellow} \\
\hline
\end{tabular}
\caption{Electronic transitions of the silyl-substituted stannylenes.}
\end{table}

The triplet state of bis(silyl)stannylene (Bu\(_2\)MeSi)\(_2\)Sn might be accessible due to its relatively small singlet–triplet energy separation \(\Delta E_{S-T}\) of 8.5 kcal/mol, thanks to both the electronic effects of the \(\sigma\)-donating silyl groups and their large steric bulk.\(^{31}\)

Accordingly, deep-green colored tetrasilyl-distannene (Bu\(_2\)MeSi)\(_2\)Sn=Sn(SiMe\(_3\)Bu\(_2\))\(_2\) showed a substantial red shift in its electronic spectrum with the longest wavelength absorption at 670 nm (cf.: 494 nm for tetraaryldistannene Tip\(_2\)Sn=SnTip\(_2\)). This was attributed to the extreme twisting of the Sn=Sn bond that destabilizes its HOMO due to the mixing of 5\(p_\pi\)-5\(p_d\)(Sn=Sn) and \(\sigma\)(Sn–Si) orbitals (on the one hand) and reduced 5\(p_\pi\)-5\(p_n\) orbital overlap caused by double bond twisting (on the other hand).

2.2.3. Diplumbenes: \(^{207}\)Pb NMR spectroscopy. As was mentioned in the Section 2.1.4, all diplumbenes or plumbylene dimers dissociate in solution into the monomeric plumbyes, therefore they displayed either no signals or very low-field \(^{207}\)Pb NMR resonances (above +7000 ppm), which points to the presence of monomeric plumbylenes >Pb: rather than dimeric diplumbenes >Pb=Pb (\textbf{Table 3}).

\begin{table}
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Transverse} & \textbf{Longitudinal} & \textbf{A} \\
\hline
\textit{Singlet} & 2.9031(11) Å & 3.947(1) Å \\
\textit{Triplet} & 3.1601(6) Å & 3.947(1) Å \\
\hline
\end{tabular}
\caption{Lead–lead separation in diplumbenes and plumbylene dimers.}
\end{table}

\(X\)-ray crystallography. At present, structural data are available for the tetraaryl-, aryl(alkyl)-, aryl(silyl)diplumbenes and plumbylene dimers (\textbf{Table 3}). The lead–lead separation in these compounds covers a very broad range of more than 1 Å: from 2.9031(11) Å to 3.947(1) Å [from 2.9031(11) Å to 3.1601(6) Å (for diplumbenes) and from 3.3549(6) Å to 3.947(1) Å (for plumbylene dimers)]. Remarkably, all these Pb–Pb distances are substantially longer than usual Pb–Pb single bonds. As the heaviest element of group 14, lead manifested a remarkable \textit{trans}-bending in both diplumbenes and plumbylene dimers: from 322.7° to 339.0°. Depending on the extent of steric interaction between substituents, diplumbenes and plumbylene dimers showed either not twisted (twist angle 0.0°) or extremely twisted (twist angle 72.4°) lead-lead bonds.

The valence isomers of the diplumbenes, such as plumbylplumbylenes with a single bond between divalent and tetravalent lead centers, are not discussed in this article.

2.3. Bonding in the “heavy” alkenes. Alkenes in organic chemistry feature plumbymethylene dimers: from 322.7° to 339.0°. Depending on the extent of steric interaction between substituents, diplumbenes and plumbylene dimers showed either not twisted (twist angle 0.0°) or extremely twisted (twist angle 72.4°) lead-lead bonds.
was proposed for the first time by Lappert and co-workers as early as 1976 to explain the bonding pattern in the \textit{trans}-bent distannene \textit{Dsi}_2\textit{Sn}≡\textit{SnDsi}_2 \textsuperscript{2} \textsuperscript{9}.

As an alternative approach, the \textit{trans}-bending of heavy alkenes has been rationalized in the framework of a stabilizing mixing of the \textit{\pi} and \textit{\sigma}*-orbitals of the \textit{E}=\textit{E} bond, enabled upon \textit{trans}-bending at the \textit{E} centers (Scheme 6).

\begin{center}
\begin{tikzpicture}
\node[anchor=west] (a) at (0,0){Triplet-triplet interaction};
\node[anchor=west] (b) at (0,-2){Singlet-singlet interaction};
\node[anchor=west] (c) at (2,0){\textit{E}=\textit{E}};
\node[anchor=west] (d) at (2,-2){\textit{E}=\textit{E}};
\node[anchor=west] (e) at (0.5,0.5){\textsuperscript{\textit{\pi}}_{\textit{E}=\textit{E}}};
\node[anchor=west] (f) at (0.5,-1){\textsuperscript{\textit{\sigma}^*}_{\textit{E}=\textit{E}}};
\node[anchor=west] (g) at (0,0.5){\textit{\pi} \textsuperscript{-} \textit{\sigma}^* \text{orbital mixing}};
\node[anchor=west] (h) at (0,-1){\text{non-classical trans-bent}};
\node[anchor=west] (i) at (2,0.5){\text{classical planar}};
\node[anchor=west] (j) at (2,-1){\text{donor-acceptor double bond}};
\node[anchor=west] (k) at (0,-0.5){\text{Paul repulsion}};
\node[anchor=west] (l) at (2,-0.5){\text{A}};
\node[anchor=west] (m) at (2,-2.5){\text{B}};
\node[anchor=west] (n) at (0,-2.5){\text{C}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 5}

The extent of such \textit{\pi}–\textit{\sigma}*-orbital mixing, which appeared to be a manifestation of the second-order Jahn–Teller effect, depends on the \textit{\pi}–\textit{\sigma}*-energy separation and results in the overall lowering of the \textit{\pi}-orbital energy level, and consequently, in its stabilization \textsuperscript{40}.

The magnitude of the \textit{\pi}–\textit{\sigma}*-energy gap in the planar \textit{H}_2\textit{E}=\textit{EH}_2 (\textit{E}=\textit{C}–\textit{Pb}) substantially decreases descending group 14, leading to stronger \textit{\pi}–\textit{\sigma}*-mixing and greater bending at the heavier \textit{E}. The electronegativity of the substituents \textit{R} in the heavy alkene analogues \textit{R}_2\textit{E}=\textit{ER}_2 is also of great importance to the degree of \textit{trans}-bending. Thus, for example, electron-withdrawing substituents (\textit{F}, \textit{OH}, \textit{NH}_2) that increase the degree of the \textit{\pi}–\textit{\sigma}*-interaction, cause notable \textit{trans}-bending at \textit{E} and accordingly weaken the \textit{E}=\textit{E} bond. By contrast, electron-releasing groups (\textit{BH}_2, \textit{SiH}_3) cause much smaller bending deformations at \textit{E} (in the limiting case of persilyl-substituted derivatives (\textit{H}_3\textit{Si})_2\textit{E}=\textit{E}(\textit{SiH}_3)_2 a planar geometry can even be achieved) and strengthen the \textit{E}=\textit{E} bond.

The above-discussed structural deformations, such as \textit{trans}-bending at \textit{E} and twisting around the \textit{E}=\textit{E} bond, can be experimentally observed in the X-ray crystal structures of the stable “heavy” alkenes: \textit{trans}-bending is typically defined as the angles \textit{\alpha} and \textit{\alpha}' between the \textit{R}–\textit{E}–\textit{R}'–\textit{E}–\textit{R}’ mean planes and the \textit{E}–\textit{E} bond axis (Scheme 7, A), whereas twisting is determined by the dihedral angle \textit{\beta} between the \textit{R}–\textit{E}–\textit{R} and \textit{R}’–\textit{E}–\textit{R}’ mean planes (Scheme 7, B).

\begin{center}
\begin{tikzpicture}
\node[anchor=west] (a) at (0,0){\textit{\pi} \textit{E}=\textit{E}};
\node[anchor=west] (b) at (2,0){\textit{\sigma}^* \textit{E}=\textit{E}};
\node[anchor=west] (c) at (4,0){trans-bent geometry at \textit{E}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 6}
The field of stable doubly-bonded derivatives of heavy group 14 elements – started in the 1970–80s by the pioneering syntheses of the first distannene, disilene and silene – is emerging and flourishing. Accordingly, to date a number of digeremenes >Ge=Ge, distannenes >Sn=Sn< and diplumbenes >Pb=Pb< have been isolated and, in the majority of cases, structurally characterized. They are no longer phantom species with an exceedingly short lifetime, but readily available preparative-scale reagents that are very useful for the synthesis of new organometallic compounds. The structural distinctions between “heavy” alkenes >E=E< (E = Si–Pb) and their lighter counterparts >C=C< are now firmly established experimentally and the reasons behind these distinctions are well understood theoretically. The fundamental issue of the nature of the >E=E< bond, as compared with that of prototypical alkenes >C=C<, is comprehensively addressed both experimentally and theoretically to disclose the principal differences in the bonding types: classical covalent in the planar alkenes vs. nonclassical donor–acceptor in their trans-bent “heavy” analogues.

As for the future prospects, one could expect further developments of novel general approaches for the synthesis of a variety of disilenes, digeremenes, distannenes and diplumbenes with different substitution pattern (alkyl, aryl, silyl groups, etc.). Use of these “heavy” alkenes as novel ligands for coordination compounds, or even as precursors for silylene, germylene and stannylene transition metal complexes, is another highly attractive direction that has not yet been realized and eagerly anticipated in the near future.

References


[Note]: Some corrections were made to Tables 2 and 3, and References [6d], [8h] and [8i] on October 1st, 2012.