Theoretical Study of Heavier Group 14 Analogues of Allene

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We report the first systematic computational study, using both ab initio and DFT methods, of the heavier group 14 analogues of allene: $R_2M{=}C{=}CH_2$ and $H_2C{=}M{=}CH_2$, M = Si, Ge, Sn and Pb, where the substituents R are H, Me, SiH_3, and F. The following trends were observed (mostly at B3LYP/SDD): (a) 1-metalaallenes are more stable than 2-metalaallenes for all M elements; (b) in both 1- and 2-metalaallenes the deviation of the skeleton from linearity, the degree of pyramidalization at M, and the planarization energies at M decrease along the series Pb > Sn > Ge > Si; the silaallenes, except for $F_2Si{=}C{=}CH_2$, are linear and planar at silicon; (c) the SiH_3 substituent favors planarization at M, while F substitution causes strong pyramidalization.

Introduction

The chemistry of low-coordinated compounds containing the heavier group 14 elements, Si, Ge, Sn, and Pb, has attracted much attention in the last two decades because of their unique structures and reactivity and the vast differences in their properties compared to the corresponding carbon compounds.[1−9] A significant number of stable compounds with M=C and M=M (M = Si, Ge, Sn, Pb) double bonds have been prepared and identified, i.e., silenes (Si=C),[2−4] disilenes (Si=Si),[2b,d,4−7] germenes (Ge=C),[3,4,8,9] digermenes (Ge=Ge),[4,6−9] stannenes (Sn=C),[3,4,9] distannenes (Sn=Sn),[4,6,7,9] and diplumbenes (Pb=Pb).[7] A variety of computational studies using different levels of theory have been reported for all the parent heavier group 14 analogues of ethylene, $H_2C{=}MH_2$ and $H_2M{=}MH_2$.[6,10,11]

Much less is known on heavier group 14 compounds containing cummulative double bonds, e.g., of the types $R_2M{=}C{=}CR_2$ and $R_2C{=}M{=}CR_2$.[12] Only recently the first stable 1-sila-[13a,b] and 1-germaallenes[13c,d,14] were synthesized and characterized. The X-ray geometries of the isostructural $(Tip)_2Si{=}C{=}C(Ph)$*t*-Bu[13b] and $(Tip)_2Ge{=}C{=}C(Ph)$*t*-Bu[13c] (Tip = 2,4,6-tri-isopropylphenyl) reported recently by West et al. show that, in contrast to allene, in both compounds the M=C=C skeleton is not linear. Interestingly, the degree of bending at the central C atom is significantly larger in the germaallene (159.2°) than in the silaallene (172.0°), and the Ge atom is more strongly pyramidalized than the Si atom (the sum of the bond angles around Ge is 348.4° compared to 357.2° around silicon). In $(t\text{-}Bu_3Si)_2Sn{=}Sn{=}Sn(SiBu\text{-}t_3)_2$, which was recently synthesized by Wiberg et al.,[15] the Sn−Sn−Sn angle is 155.9° and the sum of the bond angles at the outer Sn atom is 345.6°. Nothing is yet known on 2-metalaallenes, $R_2C{=}M{=}CR_2$.

Also theoretically not much is known on metalaallenes. The parent 1- and 2-silaallenes were studied

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theoretically,[10a,12,16] but most of these studies are now outdated. The heavier analogues of 1- and 2-silaaallene have not been yet studied computationally. Furthermore, almost nothing is known about the effect of substituents on the properties of metalaallenes. However, Trinquier and Malrieu suggested on the basis of qualitative theoretical analysis that distortions from planarity are expected to increase on substituting Si by Ge or Sn and SiH_2 by SiF_2.[16f]

To better understand the properties of the heavier analogues of allene, we have undertaken the first systematic computational study of these compounds, using both ab initio and DFT methods. The results are reported below. The compounds that were calculated are the parent 1-metalaallenes $R_2M{=}C{=}CH_2$, M = Si, Ge, Sn, Pb, R = H (**1**), the dimethyl-substituted (**2**), the disilyl-substituted (**3**), and the difluoro-substituted (**4**) derivatives, and the parent 2-sila-, 2-germa-, 2-stanna-, and 2-plumbaallenes (**5**).

$H_2M{=}C{=}CH_2$	$Me_2M{=}C{=}CH_2$	$(H_3Si)M{=}C{=}CH_2$
1Si, M = Si	**2Si**, M = Si	**3Si**, M = Si
1Ge, M = Ge	**2Ge**, M = Ge	**3Ge**, M = Ge
1Sn, M = Sn	**2Sn**, M = Sn	**3Sn**, M = Sn
1Pb, M = Pb	**2Pb**, M = Pb	**3Pb**, M = Pb

$F_2M{=}C{=}CH_2$	$H_2C{=}M{=}CH_2$
4Si, M = Si	**5Si**, M = Si
4Ge, M = Ge	**5Ge**, M = Ge
4Sn, M = Sn	**5Sn**, M = Sn
4Pb, M = Pb	**5Pb**, M = Pb

Typical questions that we wish to answer are the following: (a) Is the $R_2M{=}C{=}CH_2$ skeleton for M = Si, Ge *inherently* nonlinear, or does the experimentally observed nonlinearity and pyramidality at M[13b,c] reflect other factors, such as substituent effects, crystal packing forces, etc.? (b) How do the bending angle at the central carbon and the pyramidality around M change as a function of M and the nature of the substituents R at M?

We believe that this study provides useful information that will help in the experimental exploration of heavier group 14 analogues of allene.

Computational Methods

All calculations were performed using standard ab initio[17] and density functional theory[18] (DFT) techniques as implemented in the Gaussian 98[19] series of programs. The structures of all molecules were fully optimized at a particular level of theory, and vibrational frequencies were computed at the same level (except for the QCISD and CCD levels), to characterize them as minima (no imaginary frequencies), transition state (one imaginary frequency), or saddle point of second order (two imaginary frequencies). In addition to all-electron basis sets (6-31G(d), 6-311G(d,p), 6-311+G(d), and 6-311++G(2d,p)), which could be used only for M = Si and Ge, we also used two different effective core potentials (ECPs) to describe the inner (nonvalence) electrons: (1) SDD, which includes a Dunning/Huzinaga valence double-ζ basis set on the first-row elements (e.g., C) and on H,[20a] and the Stuttgart/Dresden ECPs for the other elements,[20b] and (2) CEP-31G(d), which uses the Stevens/Basch/Krauss ECP split-valance basis set and includes also a set of polarization functions.[21] Both ECPs include corrections for relativistic effects. For all the DFT calculations we have used the hybrid-density functional B3LYP[22a,b] and B3P86[22a,c] methods. The geometries of the parent 1- and 2-sila- and germaallenes were also optimized using the correlated MP2,[23] QCISD,[24] and CCD[25] methods with a variety of basis sets, which explicity include all electrons, i.e., 6-31G(d), 6-311G(d,p), 6-311+G(d), and 6-311++G(2d,p). For most of the energy comparisons zero-point corrections resulting from differences in zero-point energies (ZPEs) are small (less than 1 kcal mol^{-1}), and therefore they are not included in the discussion below, unless mentioned otherwise. The calculated ZPEs are given in the Supporting Information. Hybridization analysis was performed using the natural bond order (NBO) method as implemented in the NBO 4.0 program.[26]

Results and Discussion

1. Parent Metalaallenes. a. 1-Metalaallenes, $H_2M{=}C{=}CH_2$. We have first carried out an extensive set of calculations for $H_2Si{=}C{=}CH_2$ and $H_2Ge{=}C{=}CH_2$ (Table 1) in order to choose a method for calculating the larger substituted systems (for which the most elaborate calculations are not practical), a method combining accuracy and reliability on one hand and efficiency on the other. For discussing the geometry of 1-metalaallenes we define two geometrical parameters (Figure 1a): (a) the bending angle at the central allenic carbon α, which measures the deviation from linearity of the MCC skeleton, and (b) the sum of the bond angles around M, $\sum\theta = \theta_1 + \theta_2 + \theta_3$, which measures the degree

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Table 1. Selected Optimized Geometric Parameters for $H_2M{=}C{=}CH_2$, M = C, Si, Ge, Sn, and Pb[a]

	$H_2C{=}C{=}CH_2$[b,c]	$H_2Si{=}C{=}CH_2$				$H_2Ge{=}C{=}CH_2$			
method/parameter	C=C	Si=C	C=C	α	Σθ	Ge=C	C=C	α	Σθ
HF/6-311G(d,p)	1.294	1.674	1.300	180	360	1.746	1.298	180	360
MP2/6-31G(d)	1.313	1.696	1.321	180	360	1.775	1.318	172.1	357.2
MP2(full)/6-31G(d)	1.311	1.694	1.319	180	360	1.762	1.315	175.5	359.0
MP2/6-311+G(d,p)	1.314	1.694	1.323	180	360	1.784	1.323	166.1	354.4
QCISD/6-31G(d)	1.315	1.699	1.322	180	360	1.793	1.318	166.2	350.4
QCISD/6-311G(d,p)	1.315	1.696	1.323	180	360	1.800	1.322	162.7	349.2
CCD/6-311G(d,p)	1.312	1.693	1.320	180	360	1.784	1.319	166.2	353.5
CCD/6-311++G(2d,p)	1.309	1.694	1.314	180	360	1.786	1.313	166.8	354.1
B3P86/6-31G(d)	1.305	1.688	1.311	180	360	1.767	1.306	167.3	350.6
B3P86/6-311+G(d)	1.302	1.686	1.308	180	360	1.775	1.306	164.0	348.5
B3P86/SDD	1.320	1.708	1.323	180	360	1.809	1.324	163.3	344.9
B3LYP/6-31G(d)	1.307	1.691	1.312	180	360	1.782	1.307	165.4	347.0
B3LYP/6-311G(d,p)	1.302	1.670	1.308	180	360	1.789	1.306	163.1	346.6
B3LYP/6-311+G(d)	1.304	1.670	1.310	180	360	1.792	1.307	162.8	346.5
B3LYP/6-311++(2d,p)	1.301	1.688	1.305	180	360	1.786	1.302	163.3	347.5
B3LYP/SDD	1.323	1.712	1.326	180	360	1.817	1.328	162.3	342.7

	$H_2Sn{=}C{=}CH_2$				$H_2Pb{=}C{=}CH_2$			
method/parameter	Sn=C	C=C	α	Σθ	Pb=C	C=C	α	Σθ
B3P86/SDD	2.028	1.325	157.3	329.1	2.131	1.323	153.2	317.5
B3LYP/SDD	2.038	1.327	157.2	327.2	2.142	1.326	153.4	316.1
B3LYP/CEP-31G(d)	2.024	1.346	154.7	328.1				

[a] Bond lengths in Å, bond angles in deg. For the definitions of α and $\sum\theta$, see Figure 1a. [b] $\alpha = 180°$; $\sum\theta = 360°$ at all levels of theory used. [c] Experiment: 1.308 Å.[27]

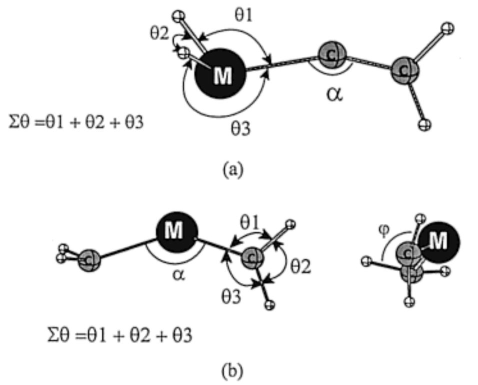

Figure 1. Definition of geometric parameters in (a) 1-metalaallenes and (b) 2-metalaallenes. φ is the shown HCCH dihedral angle.

of pyramidalization at the metal center. The calculated geometries of 1-metalaallenes using a variety of theoretical methods are given in Table 1.

1-Silaallene (**1Si**), at all levels of theory applied, has a classical allenic-type C_{2v} structure, i.e., $\alpha = 180°$ and $\sum\theta = 360°$. In contrast, the 1-germaallene (**1Ge**) is predicted by all levels of theory (except HF) to be strongly bent and pyramidal at germanium, with α and $\sum\theta$ depending strongly on the level of theory used (Table 1). At the most elaborate levels of theory used, QCISD/6-311G(d,p), CCD/6-311G(d,p), and CCD/6-311++G-(2d,p), 1-germaallene is predicted to be significantly bent, with α of 162.7°, 166.2°, and 166.8°, respectively. Similar results, with α in the range 163−167°, are obtained using the two DFT methods (with different basis sets). MP2 calculations find **1Ge** to be slightly bent when using a relatively small basis set ($\alpha = 175°$), but the bending increases to $\alpha = 166°$ with a larger basis set. All the correlated methods predict a pyramidal Ge, with $\sum\theta$ of 347−354°. Only Hartree−Fock (HF) calculations find **1Ge** to be linear and planar ($\sum\theta = 360°$). The differences found in the predicted geometry of **1Ge** between the various methods are not surprising, as the calculated energy difference between the bent and the linear structures is small, only 0.9 kcal mol^{-1} at B3LYP/SDD//B3LYP/SDD. We conclude that 1-germaallene is bent and that electron correlation must be included in the calculations in order to describe correctly the structure of substituted 1-germaallenes. Fortunately, the results in Table 1 show that the efficient hybrid-DFT-B3LYP method gives results similar to the best correlated ab initio methods, and we therefore have used B3LYP for calculating the larger substituted systems. It is particularly encouraging that B3LYP calculations, even with the relatively small SDD-ECP basis set, give for **1Ge** results similar to those obtained with much larger basis sets which treat explicity all the electrons, such as 6-311G(d,p), 6-311+G(d), and 6-311++G(2d,p). This suggests that DFT methods with effective core potential basis sets can be used reliably for calculating 1-stannaallenes and 1-plumbaallenes, for which the use of all-electron basis sets is not practical.

1-Stannaallene is much more strongly bent and pyramidalized at tin than is 1-germaallene: that is, $\alpha = 157.2°$ (154.7°), $\sum\theta = 327.2°$ (328.1°) at B3LYP/SDD (B3LYP/CEP-31G(d)). 1-Plumbaallene is even more strongly distorted from the classical allenic structure with $\alpha = 153.4°$, $\sum\theta = 316.1°$ (at B3LYP/SDD) (Table 1).

The M=C bond lengths in all 1-metalaallenes are similar to those in the corresponding $H_2M{=}CH_2$, i.e., 1.70 Å for M = Si, 1.79 Å for M = Ge, 2.04 Å for M = Sn, and 2.14 Å for M = Pb.[28]

b. 2-Metalaallenes, $H_2C{=}M{=}CH_2$. The optimized geometries at different levels of theory of the parent 2-metalaallenes $H_2C{=}M{=}CH_2$ (M = Si, Ge, Sn, Pb) are

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Table 2. Selected Geometric Parameters for $H_2C{=}M{=}CH_2$ (5Si-5Pb)[a]

	$H_2C{=}Si{=}CH_2$ (**5Si**)				$H_2C{=}Ge{=}CH_2$ (**5Ge**)			
method/parameter	Si=C	α	$\Sigma\theta$	φ	Ge=C	α	$\Sigma\theta$	φ
HF/6-311G(d,p)	1.676	180	360	90	1.745	180	360	90.9
MP2/6-31G(d)	1.702	180	360	90	1.781	163.2	357.6	91.0
MP2/6-311+G(d,p)	1.699	180	360	90	1.780	165.8	357.9	90.7
QCISD/6-31G(d)	1.705	180	360	90	1.795	153.4	357.5	92.8
QCISD/6-311G(d,p)	1.699	180	360	90	1.790	155.5	355.4	91.9
CCD/6-311G(d,p)	1.699	180	360	90	1.778	161.8	357.1	91.4
CCD/6-311++G(2d,p)	1.696	180	360	90	1.771	172.8	359.2	91.3
B3P86/6-31G(d)	1.694	180	360	90	1.760	164.5	357.9	90.8
B3P86/6-311+G(d)	1.689	180	360	90	1.753	173.7	359.3	91.6
B3P86/SDD	1.713	180	360	90	1.781	174.5	359.9	91.1
B3LYP/6-31G(d)	1.698	180	360	90	1.778	154.8	356.3	91.8
B3LYP/6-311G(d,p)	1.693	180	360	90	1.762	172.5	359.5	90.1
B3LYP/6-311+G(d)	1.694	180	360	90	1.767	166.7	358.3	90.6
B3LYP/SDD	1.718	180	360	90	1.783	179.92	360	90.0

	$H_2C{=}Sn{=}CH_2$ (**5Sn**)				$H_2C{=}Pb{=}CH_2$ (**5Pb**)			
method/parameter	Sn=C	α	$\Sigma\theta$	φ	Pb=C	α	$\Sigma\theta$	φ
B3P86/SDD	1.999	142.0	353.1	93.6	2.099	128.6	348.8	97.6
B3LYP/SDD	2.016	135.3	352.0	95.4	2.122	122.0	349.4	101.1
B3LYP/CEP-31G(d)	2.005	134.3	348.5	97.1				

[a] Bond lengths in Å, bond angles in deg. For the definitions of α, $\Sigma\theta$, and φ, see Figure 1b.

summarized in Table 2, and the definitions of the geometrical parameters are given in Figure 1b. 2-Silaallene (**5Si**) has at all levels of theory a linear C−Si−C skeleton (α = 180°), and the carbon centers are planar. In contrast, 2-germaallene (**5Ge**) has C_1-symmetry with strong bending at the Ge atom (α = 153−173°), but the degree of pyramidalization at the carbon atoms is small (Table 2). The bending angle at M is larger in $H_2C{=}Sn{=}CH_2$ (α = 134−135°), and it increases further in $H_2C{=}Pb{=}CH_2$ to α = 122°. The degree of pyramidalization at the carbon atoms, however, is not large even for M = Pb, i.e., $\Sigma\theta$ = 348−352°. The linearization−planarization ($C_1 \rightarrow D_{2d}$) energy increases moderately along the series from 0.01 kcal mol^{-1} for M = Ge to 2.4 kcal mol^{-1} for $H_2C{=}Sn{=}CH_2$ and to 4.7 kcal mol^{-1} for $H_2C{=}Pb{=}CH_2$ (all values at B3LYP/SDD//B3LYP/SDD).[29]

For both 1-metalaallenes and 2-metalaallenes the degree of nonlinearity of the skeleton and the pyramidalization at the external centers (M or C) increase along the series Si < Ge < Sn < Pb (most distorted). The increasing deviation from planarity along the series Si → Pb can be rationalized in the terms of the effect of the metal on the sum of the singlet−triplet energy differences in the carbenoid divalent fragments of the double bond (ΔE_{ST}), as was shown for the corresponding ethylene analogues.[16f,30] As one moves down the periodic table from Si to Pb, ΔE_{ST} of the H_2M fragment increases and larger deviations from planarity and linearity are expected[16f,30] and indeed calculated.

The trend of increasing deviation from the classical allenic structure along the series Si → Pb can be also rationalized in terms of increasing p character in the M−C or M−H σ-bonds as one moves down the periodic table from Si to Pb. Consequently, the π-orbital mixes more s-character when moving down the column, similarly to the well-known behavior of NH_3 versus PH_3.[31] In agreement with this interpretation, the calculated hybridizations of the M−C and/or M−H σ-bonds (using NBO analysis) are sp^2 in **1Si**, sp$^{2.29}$ in **1Ge**, sp$^{2.57}$ in **1Sn**, sp$^{2.79}$ in **1Pb**, sp in **5Si** and **5Ge**, sp$^{1.2}$ in **5Sn**, and sp$^{1.44}$ in **5Pb**. The M=C (M = Ge, Sn, Pb) bond is somewhat shorter (by ca. 0.02 Å) in 2-metalaallenes than in 1-metalaallenes, reflecting the change in C-hybridization from sp to sp^2, respectively, except for r(Si=C), which is the same in **1Si** and **5Si**.

c. Relative Stability of 1-Metalaallenes and 2-Metalaallenes. Two major factors contribute to the differences in the relative stability of 1- and 2-metalaallenes as M changes: (1) In 1-metalaallenes one C=C and one M=C bond are present, while in 2-metalaallenes there are two M=C bonds and no C=C bonds. M=C double bonds become weaker, as M is changed along the series from Si to Pb.[10a] This effect makes the 2-metalaallene less stable compared to the corresponding 1-metalaallene along the Si → Pb series. (2) Two M−H bonds in 1-metalaallenes are substituted by two C−H bonds in 2-metalaallenes. As M−H bonds become weaker on moving down group 14 of the periodic table,[10a,32] this contribution favors the 2-metalaallene compared to the corresponding 1-metalaallene along the Si → Pb series. The opposing influence of these two effects makes the qualitative prediction of the relative stability of analogous 1- and 2-metalaallenes difficult.

On the basis of the calculations for all metals the 1-metalaallenes are more stable than the corresponding 2-metalaallenes (Table 3). The energy difference between the 1- and 2-isomers depends on M, but the range of values is not large, estimated to be around 12−17 kcal mol^{-1}. For M = Si and Ge, for which the most elaborate calculations could be carried out, we find that the QCISD/6-311G(d,p) and B3LYP/6-311G(d,p) calculations give similar results, but that B3LYP/SDD gives ΔE values which for M = Si and Ge are 5.9 and 5.4 kcal mol^{-1}, respectively, too small. From this comparison we conclude that also for M = Sn and Pb the ΔE values

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(29) For M = Ge: 0.05 kcal mol^{-1} at MP2/6-31G(d), 0.41 kcal mol^{-1} at B3LYP/6-31G(d), 0.02 kcal mol^{-1} at B3LYP/6-311G(d,p), 0.41 kcal mol^{-1} at QCISD/6-311G(d,p). For M = Sn: 3.7 kcal mol^{-1} at B3LYP/CEP-31G(d).

(30) (a) Malrieu, J. P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916. (b) Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8589.

(31) Kutzelnigg, W. *Angew. Chem.* **1984**, *23*, 272.

(32) Basch, H.; Hoz, T. In *Organic Germanium, Tin and Lead Compounds*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1995; Chapter 1.

Table 3. Relative Energies[a] (kcal mol^{-1}) of 1-Metalaallenes and 2-Metalaallenes

method	Si	Ge	Sn	Pb
B3LYP/SDD	10.7	9.2	14.2	14.2
MP2/6-31G(d)	17.2	9.0		
QCISD/6-311G(d,p)	16.6	13.3		
B3LYP/6-311G(d,p)	16.1	12.6		
B3LYP/CEP-31G(d)	11.8		10.0	

[a] All energies include zero-point energy corrections. A positive number indicates that the 1-metalaallene is more stable than the corresponding 2-metalaallene.

Table 4. Calculated Reaction Energies[a] (kcal mol^{-1}) for Eqs 1 and 2

	ΔE(eq 1)	ΔE(eq 2)
Si	-1.1 $(-0.9)^b$	-9.2 $(-15.3)^b$
Ge	-1.4 $(-2.0)^b$	-7.7 $(-12.4)^b$
Sn	3.0 $(4.2)^c$	-7.6 $(-2.2)^c$
Pb	8.7	-1.6

[a] At B3LYP/SDD//B3LYP/SDD. [b] At B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p). [c] At B3LYP/CEP-31G(d)//B3LYP/CEP-31G(d).

calculated at B3LYP/SDD are ca. 5−6 kcal mol^{-1} too small. ΔE for M = Si is ca. 16 kcal mol^{-1} (in good agrement with previous MP3/6-31G(d)//3-21G calculations[16b] giving 15.5 kcal mol^{-1}), and it is smaller, around 12−13 kcal mol^{-1}, for M = Ge. ΔE for both M = Sn and Pb is ca. 14 kcal mol^{-1} at B3LYP/SDD, but estimated to be in reality ca. 19−20 kcal mol^{-1}, 3.5 and 5.0 kcal mol^{-1} higher than for M = Si and Ge, respectively. The relatively small change in ΔE as a function of M can be understood by the two opposite effects mentioned in the previous paragraph. This information may have interesting implications for future attempts to synthesize the yet unknown 2-metalaallenes.

To compare the stability of the M=C double bond in 1-metalaallenes and 2-metalaallenes with that in the corresponding $H_2C{=}MH_2$, we have calculated the isodesmic eqs 1 and 2. The results are summarized in Table 4.

$$H_2M{=}C{=}CH_2 + H_2C{=}CH_2 \rightarrow H_2C{=}C{=}CH_2 + H_2M{=}CH_2 \quad (1)$$

$$H_2C{=}M{=}CH_2 + H_2C{=}CH_2 \rightarrow H_2C{=}C{=}CH_2 + H_2M{=}CH_2 \quad (2)$$

1-Sila and 1-germaallene (eq 1) are slightly (by 1−2 kcal mol^{-1}) less stable than the corresponding metalaethylenes, while 1-stanna- and particularly 1-plumbaallenes are significantly *stabilized* relative to corresponding $H_2M{=}CH_2$ (by 3.0 and 8.7 kcal mol^{-1}, respectively). This behavior can be rationalized on the basis of eq 3, which shows that vinylcarbene is strongy *stabilized* compared to methylene (ΔE(eq 3) = 37.0 kcal mol^{-1} at B3LYP/6-311G(d,p)+ZPE). Thus, the increasing carbene-like character of 1-metalaallenes on going down the Si → Pb series leads to stabilization of 1-metalaallenes relative to $H_2M{=}CH_2$. The same trend of increasing stabilization on going from Si to Pb relative to the corresponding $H_2M{=}CH_2$ is found also for the 2-metalaallenes; that is, ΔE(eq 2) = −9.2, −7.7, −7.6, and −1.6 kcal mol^{-1} for Si, Ge, Sn, and Pb, respectively (Table 4).

$$H_2C{=}C{:} + H_2C{=}CH_2 \rightarrow H_2C{:} + H_2C{=}C{=}CH_2 \quad (3)$$

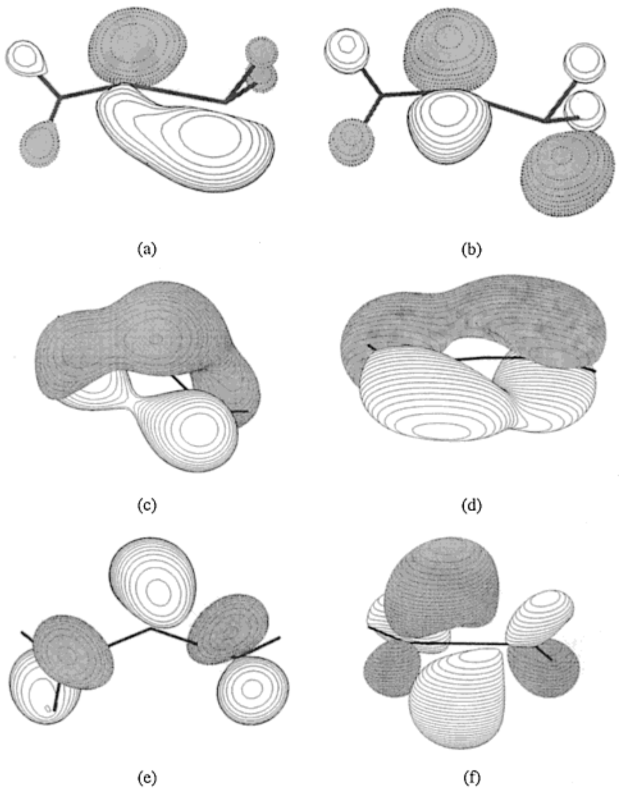

Figure 2. Molecular orbitals of (a) HOMO of 1-metalaallene, (b) LUMO of 1-metalaallene, (c) HOMO-1 of 2-metalaallenes, (d) HOMO of 2-metalaallenes, (e) LUMO of 2-metalaallenes, and (f) LUMO+1 of 2-metalaallenes. The orbitals shown are for M = Sn at B3LYP/SDD//B3LYP/SDD.

d. Molecular Orbitals of 1- and 2-Metalaallenes. All 1-metalaallenes possess the classic allenic molecular orbitals, but due to the presence of M, the HOMO and HOMO-1 are not degenerate. The lower energy orbital (HOMO-1) is mostly the C=C π-orbital and the HOMO is mostly the M=C π-orbital. The LUMO+1 and LUMO are the corresponding π*-orbitals, π*(C=C) and π*(C=M), respectively. Due to the deviation from linearity and pyramidalization, the HOMO changes its shape as a function of M, reflecting an increasing localization of the orbital on M and a higher mixing of s-character into the π-orbital at M when moving down the column (Figure 2a,b). The energies of the HOMO-1 and LUMO+1, which are associated mainly with the C=C bond, remain as expected almost unchanged along the Si → Pb series. On the other hand, the energies of the HOMO and the LUMO, which are associated mainly with the M=C bond, significantly increase and decrease, respectively, along the Si → Pb series (Figure 3). The energy changes in the frontier orbitals as a function of M are very similar to those found in the corresponding metalaethylenes (calculated by us at the same level). The HOMO−LUMO gap decreases steadily from 14.4 eV in $H_2C{=}C{=}CH_2$ to 8.2 eV in $H_2Pb{=}C{=}CH_2$. A smaller HOMO−LUMO gap is usually equated with a higher reactivity,[33] and thus we predict that **1** will be less stable kinetically as one moves down group 14 from C to Pb.

In 2-metalaallenes the HOMO and HOMO-1 (Figure 2c−f) both have the expected π-nature, but due to the

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[33] Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: New York, 1976.

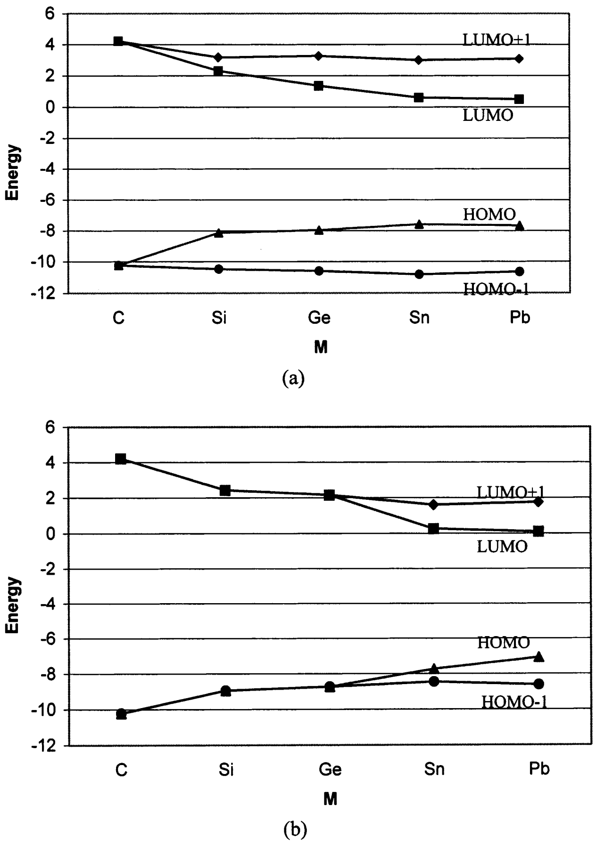

Figure 3. (a) Frontier orbital energies (eV) as a function of M (M = C, Si, Ge, Sn, Pb) of (a) 1-metalaallenes and (b) 2-metalaallenes (at HF/SDD//B3LYP/SDD). (●) HOMO-1, (▲) HOMO, (■) LUMO, (◆) LUMO+1.

twisted geometry both orbitals are delocalized over the entire C−M−C skeleton. The HOMO and HOMO-1 lie roughly in perpendicular planes. In the HOMO-1 one of the phases of the wavefunction occupies the outer sphere of the skeleton (i.e., where the sphere $\angle$CMC > 180°) and the opposite phase in the inner sphere (i.e., where $\angle$CMC < 180°). This orbital is more localized at the central metal atom and is more directed outward than the HOMO. The LUMO is also concentrated on the central metal, it has a π^*-nature, and it is antibonding between each of the three C−M−C atoms. The LUMO+1 is very similar to the LUMO, except that it lies roughly in a perpendicular plane (Figure 2c−f).

According to FMO theory,[33] the shapes of these frontier orbitals will dictate the regioselectivity of attack of nucleophiles (LUMO, LUMO+1) and electrophiles (HOMO, HOMO+1) on these molecules.

2. Substituted 1-Metalaallenes. a. Geometries. The 1,1-dimethyl-, 1,1-disilyl-, and 1,1-difluoro-1-metalaallenes, $R_2M{=}C{=}CH_2$, R = Me (**2**), SiH_3 (**3**), F (**4**), respectively, were studied. 1,1-Dimethyl-1-germaallene (**2Ge**) was calculated at several levels of theory, and the results are given in Table 5. The most reliable method (QCISD/6-31G(d)) predicts a slightly bent structure at C and nearly planar geometry at Ge. The predictions of other methods vary from $\alpha = 160{-}180°$ and $\Sigma\theta = 346{-}360°$. This again exemplifies the very shallow minimum in which 1-germaallene resides. In general B3LYP seems to perform better than B3P86.

The results in Tables 1 and 5 support the reliability of the relatively inexpensive B3LYP/SDD level, making it the method of choice for comparing the substituted germa-, stanna-, and plumbaallenes. The calculated geometries for all substituted metalaallenes **1**−**4** are summarized in Table 6.

Table 5. Selected Geometric Parameters for $Me_2Ge{=}C{=}CH_2$[a]

method	Ge═C	C═C	α	$\Sigma\theta$
HF/6-311G(d,p)	1.746	1.302	180	360
MP2/6-31G(d)	1.770	1.320	180	360
QCISD/6-31G(d)	1.774	1.321	173.8	359.0
B3P86/6-31G(d)	1.752	1.309	180.0	360
B3P86/6-311+G(d)	1.754	1.309	180.0	360.0
B3P86/SDD	1.808	1.329	160.9	148.6
B3LYP/6-31G(d)	1.762	1.311	172.9	358.5
B3LYP/6-311G(d,p)	1.784	1.310	162.8	352.1
B3LYP/6-311+G(d)	1.784	1.311	162.7	352.3
B3LYP/SDD	1.817	1.331	159.6	346.7

[a] Bond lengths in Å, bond angles in deg. For the definitions of α and $\Sigma\theta$, see Figure 1a.

Three major conclusions can be derived from the data in Table 6.

(1) The degree of pyramidalization at M and the bending angle at the central allenic carbon atom increase when moving down the periodic column: Si < Ge < Sn < Pb. All substituted 1-silaallenes, except for R = F (**4Si**), have the classic C_{2v} allenic structure (i.e., $\alpha = 180°$, $\Sigma\theta = 360°$). In contrast, all other metalaallenes are bent and pyramidalized. The average α and $\Sigma\theta$ values of the parent (**1**), 1,1-dimethyl (**2**), and 1,1-disilyl (**3**) substituted 1-metalaallenes are as follows: for Si $\alpha = 180°$, $\Sigma\theta = 360°$, for Ge $\alpha = 162°$, $\Sigma\theta = 345°$, for Sn $\alpha = 157°$, $\Sigma\theta = 328°$, for Pb $\alpha = 154°$, $\Sigma\theta = 316°$. These results support the earlier qualitative predictions by Trinquier and Malrieu.[16f]

(2) Silyl substitution at M reduces the bending at the allenic C (increases α) by 5−7°, but it has a relatively small effect on the pyramidality at M ($\Sigma\theta$). Similar silyl effects on geometry are known: for example, a silyl substituent induces planarization at nitrogen in H_3SiNH_2[10b] and in disilenes.[30b] Dimethyl substitution at M has an opposite effect and to a smaller extent: it decreases α by 3−4°, and it hardly changes the pyramidality at M. On the other hand, 1,1-difluoro substitution has a dramatic effect on the structure of all 1-metalaallenes: 1,1-difluoro-1-silaallene (**4Si**) is strongly bent and pyramidalized with $\alpha = 147.1°$ and $\Sigma\theta = 332.5°$. In 1,1-difluoro-1-germaallene (**4Ge**) and 1,1-difluoro-1-stanaallene (**4Sn**) bending increases up to $\alpha = 140°$. The fluorine effect reaches its maximum in 1,1-difluoro-1-plumbaallene (**4Pb**). **4Pb** spontaneously rearranges to the isomeric plumbylene, $H_2C{=}CFPbF$, and **4Pb** is *not* a stationary point on the PES. The increased deviation from planarity along the Si → Pb series and the effect of the substituents on the structure can be rationalized in terms of the effect of the metal and/or of the substituents on ΔE_{ST} of corresponding R_2M species[16f,30] (see above). ΔE_{ST} of the R_2M fragment increases along the order $(H_3Si)_2M < H_2M < Me_2M \ll F_2M$, which is consistent with the observed deviation from planarity, i.e., $\mathbf{3} < \mathbf{1} < \mathbf{2} \ll \mathbf{4}$.

(3) The effect of methyl, silyl, and flouro substitution on the M═C bond length is very small, ca. 0.01−0.02 Å.

b. Structures of West's 1-Sila- and 1-Germaallenes. Our computational study provides insights into

Table 6. Selected Geometric Parameters for $R_2M=C=CH_2$ (1−4)[a]

molecule	M=C	C=C	α	Σθ
$H_2Si=C=CH_2$ (**1Si**)	1.712(1.670)[1.705]	1.326(1.308)[1.348]	180	360
$Me_2Si=C=CH_2$ (**2Si**)	1.712(1.688)[1.705]	1.330(1.312)[1.349]	180	360
$(H_3Si)_2Si=C=CH_2$ (**3Si**)	1.724(1.705)[1.723]	1.327(1.306)[1.347]	180	360
$F_2Si=C=CH_2$ (**4Si**)	1.788(1.718)[1.765]	1.328(1.314)[1.353]	147.1(148.7)[142.4]	332.5(345.7)[341.5]
$H_2Ge=C=CH_2$ (**1Ge**)	1.817(1.789)	1.328(1.306)	162.3(163.1)	342.7(346.6)
$Me_2Ge=C=CH_2$ (**2Ge**)	1.817(1.784)	1.331(1.310)	159.6(162.8)	346.7(352.1)
$(H_3Si)_2Ge=C=CH_2$ (**3Ge**)	1.818(1.791)	1.329(1.306)	165.9(170.2)	346.1(352.4)
$F_2Ge=C=CH_2$ (**4Ge**)	1.972(1.910)	1.324(1.308)	140.0(136.9)	317.0(326.5)
$H_2Sn=C=CH_2$ (**1Sn**)	2.038[2.024]	1.327[1.346]	157.2[154.7]	327.2[328.1]
$Me_2Sn=C=CH_2$ (**2Sn**)	2.037[2.024]	1.332[1.349]	154.5[152.0]	330.0[335.0]
$(H_3Si)_2Sn=C=CH_2$ (**3Sn**)	2.036[2.014]	1.328[1.346]	161.0[160.5]	327.4[335.0]
$F_2Sn=C=CH_2$ (**4Sn**)	2.197[2.173]	1.323[1.343]	141.1[136.4]	308.5[313.9]
$H_2Pb=C=CH_2$ (**1Pb**)	2.142	1.326	153.4	316.1
$Me_2Pb=C=CH_2$ (**2Pb**)	2.148	1.331	150.3	321.9
$(H_3Si)_2Pb=C=CH_2$ (**3Pb**)	2.142	1.325	159.4	311.3

[a] At B3LYP/SDD (no parentheses), B3LYP/6-311G(d,p) (in parentheses), and B3LYP/CEP-31G(d) (in brackets). Bond lengths in Å, bond angles in deg. For the definitions of α and Σθ, see Figure 1a.

the recently reported structures of the analogous 1-sila- (**6Si**)[13b] and 1-germaallenes (**6Ge**)[13c] bearing the same aryl and alkyl substituents. Their X-ray analysis reveals α = 172.0°, Σθ = 357.2° for **6Si** and α = 159.2°, Σθ = 348.4° for **6Ge**.

$(Tip)_2M=C=C(t\text{-}Bu)Ph$, (Tip= 2,4,6 tri-isopropylphenyl)
6Si, M=Si;
6Ge, M=Ge

To model these molecules more closely, we have calculated (at B3LYP/SDD) $Ph_2Si=C=CH_2$ (**7Si**) and $Ph_2Ge=C=CH_2$ (**7Ge**). Both compounds have structures similar to those of the corresponding dimethyl derivatives. Thus, **7Si** is linear and planar, while **7Ge** is bent (α = 163.1°) and slightly pyramidal (Σθ = 353.4°). Thus, on the basis of the calculations, we conclude that the pyramidalization at the silicon atom and the bending of the SiCC skeleton observed in **6Si** are *not* inherent properties of this molecule. The observed distortions from the ideal linear structure must be due to effects not included in the calculated model $Ph_2Si=C=CH_2$.[34] These effects might be due either to steric effects of the bulky Tip substituents or to crystal-packing effects in the solid state. The energy required for distortion of linear $Me_2Si=C=CH_2$ to α of 172° is only 0.12 kcal mol^{-1}, and a similar small energy is expected also for the distortion of **6Si**.

In contrast to **6Si**, in **6Ge** the observed significant distortion of the M−C−C skeleton can be attributed to both an inherent property of the 1-germaallenes and the effect of the substituents (note that the pyramidalization parameters for **6Ge** or **7Ge** are almost equal to those of **1Ge**). The fact that the barriers for linearization and planarization of 1-germaallenes are very small, ca. 1 kcal mol^{-1} (see also below), allows considerable flexibility in the possible α and Σθ values which substituted 1-germaallenes may adopt.

c. Linearization and Planarization Energies of Metalaallenes. We have also calculated the linearization and planarization energies (Δ*E*) for all nonplanar 1-metalaallenes (i.e., all structures except **1Si**, **2Si**, and **3Si**), and the results are presented in Table 7. For all these molecules the C_{2v}-structures are the transition structures for the interconversion between two mirror image C_s-structures (the imaginary frequency leads to pyramidalization at M and bending of the M−C−C skeleton). In general, the larger the degree of pyramidalization at M, the larger the required planarization−linearization energy. For all R substituents studied Δ*E* follows the order Pb > Sn > Ge > Si. For the parent and the 1,1-dimethyl- and the 1,1-disilyl-substituted 1-germaallenes the planarization energies are small (ca. 1 kcal mol^{-1}), but they increase for the 1-stannaallenes (ca. 4 kcal mol^{-1}) and become substantial, ca. 11 kcal mol^{-1}, for the 1-plumbaallenes. Difluoro substitution increases substantially the planarization−linearization energies of the 1-metalaallenes, i.e., to ca. 6 kcal mol^{-1} for M = Si, ca. 20 kcal mol^{-1} for M = Ge, and ca. 29 kcal mol^{-1} for M = Sn.

Table 7. Planarization−Linearization Energies (kcal mol^{-1}) of $R_2M=C=CH_2$ (M = Si, Ge, Sn, Pb; R = H, Me, SiH_3, F)[a]

molecule	Δ*E*
$F_2Si=C=CH_2$ (**4Si**)	6.0
$H_2Ge=C=CH_2$ (**1Si**)	0.9[b]
$Me_2Ge=C=CH_2$ (**2Ge**)	1.1
$(H_3Si)_2Ge=C=CH_2$ (**3Ge**)	0.6
$F_2Ge=C=CH_2$ (**4Ge**)	20.6
$H_2Sn=C=CH_2$ (**1Sn**)	4.2
$Me_2Sn=C=CH_2$ (**2Sn**)	4.4
$(H_3Si)_2Sn=C=CH_2$ (**3Sn**)	3.2
$F_2Sn=C=CH_2$ (**4Sn**)	29.4
$H_2Pb=C=CH_2$ (**1Pb**)	11.1
$Me_2Pb=C=CH_2$ (**2Pb**)	12.1
$(H_3Si)_2Pb=C=CH_2$ (**3Pb**)	9.1
$F_2Pb=C=CH_2$ (**4Pb**)	*c*

[a] At B3LYP/SDD//B3LYP/SDD. [b] 0.63 kcal mol^{-1} at B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) and 0.51 kcal mol^{-1} at QCISD/6-311G(d,p)//QCISD/6-311G(d,p). [c] Not a stationary point.

It is interesting to note that the planarization energies in $H_2M=C=CH_2$ are somewhat smaller than in the corresponding $H_2M=MH_2$, i.e., ca. 2 kcal mol^{-1} for M = Si, ca. 5 kcal mol^{-1} for M = Ge, ca. 8 kcal mol^{-1} for M = Sn, and ca. 20 kcal mol^{-1} for M = Pb.[35] For comparison we have also calculated the potential energy profile for pyramidalization at M in $H_2M=CH_2$ (Figure 4). Sila-, germa-, and stannaethylenes are planar, while plum-

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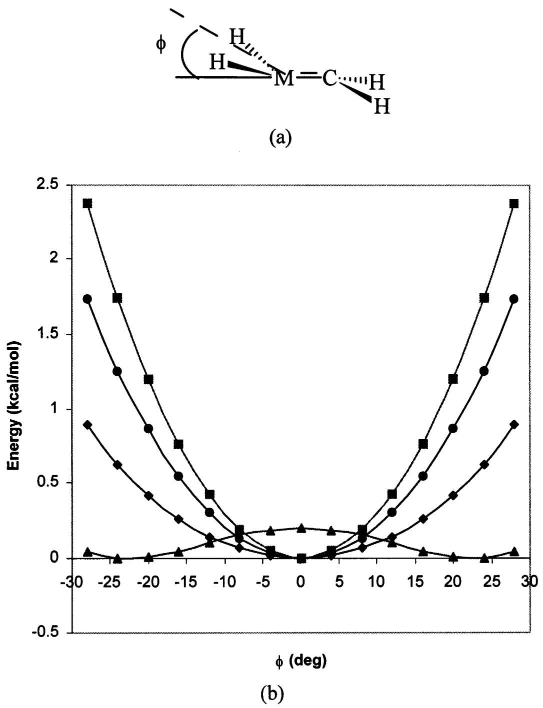
[34] The fact that the substituents on the carbon atom in **6Si** are not identical precludes in principle a strict C_{2v}-symmetry for this molecule, but this effect is expected to be small. Thus, $Me_2Si=C=CHMe$ has only a slightly bent structure with α = 177.7° and Σθ = 359.8°.

[35] The discussed values are the average values derived from the data at several levels of calculations available in the literature.[10,11]



(a)

(b)

Figure 4. Energy (kcal mol^{-1}) as a function of the bending angle at M (ϕ) for $H_2M{=}CH_2$. (■) M = Si, (●) M = Ge, (◆) M = Sn, (▲) M = Pb. Calculations for M = Si, Ge at B3LYP/6-311G(d,p) and for M = Sn, Pb at B3LYP/SDD.

Table 8. Calculated Reaction Energies (kcal mol^{-1}) for Eq 4

molecule/method	B3LYP/SDD	B3LYP/6-311G(d,p)
$H_2Si{=}C{=}CH_2$ (**1Si**)	−1.1	−0.9
$Me_2Si{=}C{=}CH_2$ (**2Si**)	−2.1	−1.7
$(H_3Si)_2Si{=}C{=}CH_2$ (**3Si**)	1.0	1.8
$F_2Si{=}C{=}CH_2$ (**4Si**)	−2.1	−5.6
$H_2Ge{=}C{=}CH_2$ (**1Ge**)	−1.4	−2.0
$Me_2Ge{=}C{=}CH_2$ (**2Ge**)	−1.7	−3.1
$(H_3Si)_2Ge{=}C{=}CH_2$ (**3Ge**)	1.0	0.4
$F_2Ge{=}C{=}CH_2$ (**4Ge**)	7.6	2.3
$H_2Sn{=}C{=}CH_2$ (**1Sn**)	3.0	4.2[a]
$Me_2Sn{=}C{=}CH_2$ (**2Sn**)	2.6	4.1[a]
$(H_3Si)_2Sn{=}C{=}CH_2$ (**3Sn**)	4.1	4.9[a]
$F_2Sn{=}C{=}CH_2$ (**4Sn**)	13.1	12.5[a]
$H_2Pb{=}C{=}CH_2$ (**1Pb**)	8.7	
$Me_2Pb{=}C{=}CH_2$ (**2Pb**)	8.8	
$(H_3Si)_2Pb{=}C{=}CH_2$ (**3Pb**)	9.4	

[a] At B3LYP/CEP-31G(d).

baethylene is trans-bent with $\phi = 20.9$.[28] However, the pyramidalization energy at M is small for all M (e.g., ca. 1 kcal mol^{-1} for a bending angles of 20°), decreasing slightly along the Si > Ge > Sn series. The planarization energy of plumbaethylene is small, only 0.5 kcal mol^{-1}.

d. Effect of Substituents on Thermodynamic Stability. ΔE for isodesmic eq 4 (Table 8) denote the effect of the substituents R on the thermodynamic stability of the 1-metalaallene relative to their effect on the analogous metalaethylene. For the specific metal methyl or silyl substitution do not change significantly the energy of eq 4. In contrast, fluorine substitution has a dramatic effect: $F_2Ge{=}C{=}CH_2$ and $F_2Sn{=}C{=}CH_2$ are stabilized relative to the corresponding metalaethylenes by 7.6 and 13.1 kcal mol^{-1}, respectively. This can be understood by the fact that difluoro substitution stabilizes strongly F_2M, and this increases the carbene-like character[16f,30] of the 1,1-difluoro-1-metalaallenes, stabilizing metalaallenes (see eq 3) relative to the corresponding metalaethylenes. For a specific R substituent (except for R = H), ΔE of eq 4 increases along the Si → Pb series. However the degree of stabilization along the series is not the same for different substituents: it is smaller for R = SiH_3, somewhat larger for R = Me, and the largest for R = F.

$$R_2M{=}C{=}CH_2 + H_2C{=}CH_2 \rightarrow H_2C{=}C{=}CH_2 + R_2M{=}CH_2 \quad (4)$$

Conclusions

Twenty different 1-metalaallenes, $R_2M{=}C{=}CH_2$, and 2-metalaallenes, $H_2C{=}M{=}CH_2$, where M = Si, Ge, Sn, Pb and R = H, Me, SiH_3, and F, have been studied by ab initio and density functional methods. Several interesting trends have been found: (a) Only 1-silaallenes (except for the 1,1-difluoro derivative) maintain the classical C_{2v} linear geometry of allene. All other 1-metalaallenes are bent at the central carbon atom and are pyramidalized at M. The degrees of nonlinearity of the M−C−C or C−M−C skeleton and of the pyramidalization at M increase on moving down the group 14 elements, i.e., Si < Ge < Sn < Pb. (b) 1,1-Disilyl substitution induces both linearity and planarization, while fluorine substitution increases the degree of the nonlinearity of the M−C−C skeleton and the pyramidality at M. (c) The energies required for linearization and planarization increase with increasing pyramidalization, i.e., along the series Si < Ge < Sn < Pb, and they are significantly higher for R = F than for R = H, Me, SiH_3. (d) The observed nonlinearity and pyramidalization at M found experimentally in **6Si** are not an inherent structural property of 1-silaallenes, and we ascribe it to either steric effects of the bulky substituents or crystal-packing forces. In contrast, the observed nonlinearity and pyramidalization of the corresponding 1-germaallene **6Ge** are due to inherent electronic effects.

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Supporting Information Available: Calculated vibration modes for **1**, absolute energies for **1**−**5** in linear and bent conformations, and absolute energies for metalaethylenes and ZPEs for all molecules at B3LYP/SDD//B3LYP/SDD. This material is available free of charge via the Internet at http://pubs.acs.org.

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