Polyhedral Compounds of the Heavier Group 14 Elements: Silicon, Germanium, Tin, and Lead

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Introduction

Carbon compounds have played a central role in organic chemistry. It is currently of considerable interest to replace skeletal carbons by the heavier homologues (M = Si, Ge, Sn, and Pb) with the expectation of observing novel physical and chemical properties.[1-3] Most unsaturated and strained ring compounds incorporating the heavier group 14 elements in their skeletons were once thought either to be nonexistent or to exist only as reactive intermediates. However, extensive research over the past decade has increased dramatically the list of such heavier compounds in chemistry textbooks. Thus, compounds featuring double bonding between the heavier group 14 elements have been synthesized and isolated.[4] Furthermore, significant progress has been made in synthesizing small rings in which these elements are embedded.[4]

Since polyhedral or polycyclic strained compounds have always been intriguing synthetic targets in carbon chemistry, current interest is naturally directed toward the heavier analogues. In this Account we summarize our recent theoretical studies of compounds whose skeletons are composed of the heavier group 14 elements[5] and recent experimental data on their successful syntheses and isolation.[6] Our primary aim here is to clarify the characteristic features of these heavier skeletons as compared with carbon skeletons and to enrich the chemistry of the heavier polyhedral compounds. It is useful in this context to have a simple conceptual framework, and the concept of "hybridization" is most helpful for an intuitive and unified understanding of the essential differences in chemical bonding between carbon compounds and their heavier analogues.

Strain Energies

Compounds Containing Four-Membered Rings. Polyhedranes ($C_{2n}H_{2n}$) such as tetrahedrane ($n = 2$), prismane ($n = 3$), and cubane ($n = 4$) have long been synthetic targets of interest as models for the study of strain, which have unique properties and aesthetic appeal due to their high symmetry (Chart 1).

It is apparent from the carbon bond angles in the polyhedranes that deviate greatly from the normal tetrahedral value of 109.5° that they are highly

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Table 1. Strain Energies (kcal/mol) Calculated Using Homodesmotic Reactions[a]

	M = C	M = Si[b]	M = Ge	M = Sn
tetrahedrane (M_4H_4; T_d)	141.4	140.9	140.3	128.2
prismane (M_6H_6; D_{3h})	145.3	113.8	109.4	93.8
cubane (M_8H_8; O_h)	158.6	93.5	86.0	70.1

[a] HF/6-31G* for M = C and Si. HF/DZ(d) for M = Ge and Sn. [b] The HF/DZ(d) values are 140.3 (Si_4H_4), 118.2 (Si_6H_6), and 99.1 (Si_8H_8) kcal/mol.

Chart 1
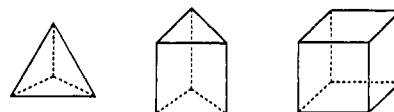
strained. For instance, the strain energies of tetrahedrane and cubane are evaluated to be as large as 140.0 and 154.7 kcal/mol, respectively.[7] Since no experimental value is available for the silicon analogues, their strain energies were calculated at the HF/6-31G* level from the homodesmotic reactions and, together with the calculated values for the carbon compounds, are given in Table 1.[8] The calculated strain energies of 141.4 and 158.6 kcal/mol for tetrahedrane and cubane are in close agreement with the experimental values[7] and are in contrast with those of the silicon compounds. Tetrasilatetrahedrane is as highly strained as tetrahedrane. As the number of four-membered rings increases (i.e., upon progressing to prismane and cubane), however, the strain of the

(1) For a review, see: Nagase, S, *Polyhedron* **1991**, *10*, 1299–1309.

(2) For the interesting properties of the cation systems, see: Kudo, T.; Nagase, S. *Rev. Heteroat. Chem.* **1993**, *8*, 122–142.

(3) For similarities and differences of chemical bonding between lighter and heavier main group elements, see: Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272–295.

(4) For a review of the double bond and ring systems, see: Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902–930.

(5) Calculations were carried out at the Hartree–Fock (HF) level with the ab initio effective core potentials and double-ζ (DZ) basis set augmented[5a] by a set of d-type polarization functions (d exponents 0.45 (Si), 0.246 (Ge), 0.183 (Sn), and 0.164 (Pb)). For carbon and silicon compounds, all-electron calculations were carried out with the split-valence d-polarized 6-31G*[5b] and 3-21G*[5c] basis sets. The effect of electron correlation was incorporated using non-local density functional theory at the BLYP level.[5d,e] The semiempirical AM1 method[5f] was employed for large systems. The Gaussian 92/DFT program was used. (a) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298. (b) Francl, M. N.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, M. S.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654–3665. (c) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039–5048. (d) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. (e) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, 37, 785–789. (f) Dewar, M. J. S.; Jie, C. X. *Organometallics* **1987**, *6*, 1486–1490.

(6) For a recent experimental review of the heavier polyhedranes, see: Sekiguchi, A; Sakurai, H. *Adv. Organomet. Chem.* **1995**, *37*, 1–38.

(7) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312–322.

(8) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60–62.

silicon compounds is significantly reduced while it increases in the carbon compounds. Hexasilaprismane is 32 kcal/mol less strained than prismane, while octasilacubane, which contains only four-membered rings, is 65 kcal/mol less strained than cubane. Consequently, it is not surprising that the first successful synthesis was of a derivative of octasilacubane.[9]

Also given in Table 1 are the strain energies of the still heavier germanium and tin compounds calculated at the HF/DZ(d) level.[10] Replacement by germanium and tin atoms has again little effect on the relief of strain in the tetrahedrane system. This is because three-membered germanium and tin rings are as highly strained as three-membered silicon rings, as is apparent from the strain energies of cyclotrigermane (39.4 kcal/mol) and cyclotristannane (36.6 kcal/mol),[10] which differ only slightly from that of cyclotrisilane (38.9 kcal/mol);[8] all of these strain energies are larger than that of cyclopropane (28.7 kcal/mol).[8] However, the strain energies of hexasilaprismane and octasilacubane containing four-membered rings are further decreased upon replacement of the silicon atoms by germanium and tin atoms: for example, the strain energy of octastannacubane is only 70.1 kcal/mol. Such relief of strain in the prismane and cubane systems reflects the fact that the strain energies of four-membered rings decrease successively in the order cyclobutane (26.7 kcal/mol)[8] > cyclotetrasilane (16.7 kcal/mol)[8] > cyclotetragermane (15.2 kcal/mol)[10] > cyclotetrastannane (12.2 kcal/mol):[10] these values agree within 1 kcal/mol with the strain energies per four-membered ring of the cubane system, suggesting the additivity of strain in this system.

Generally, the strain of polyhedral compounds is progressively relieved as the skeletal atoms become heavier and the number of four-membered rings increases.[10] This finding has greatly stimulated the synthesis of the heavier cubic skeletons. Thus, an octastannacubane derivative (Sn_8R_8, R = 2,6-$Et_2C_6H_3$) was successfully synthesized and its structure was determined by X-ray diffraction.[11] This was followed by the syntheses and X-ray structural determination of octagermacubane (Ge_8R_8, R = 2,6-$Et_2C_6H_3$ and $CMeEt_2$)[12] and octasilacubane (Si_8R_8, R = 2,6-$Et_2C_6H_3$,[12] CMe_2CHMe_2,[13] and t-Bu[14]) derivatives. Likewise, hexagermaprismane (Ge_6R_6, R = $CH(SiMe_3)_2$)[15] and hexasilaprismane (Si_6R_6, R = 2,6-i-$Pr_2C_6H_3$)[16] derivatives were also synthesized and their structures determined, so that only hexastannaprismane derivatives (Sn_6R_6) are still missing in this series. The relative stability of the valence isomers is noteworthy: whereas benzene is much more stable than prismane, the prismane skeleton becomes drastically more stable than the benzene skeleton as the skeletal atoms become heavier.[1,17-19]

Chart 2

A successive decrease in strain due to replacement by the heavier atoms is also applicable to bicyclo[2.2.0]-hexane[20] and [2.2.2]propellane systems[1,21] consisting of four-membered rings (Chart 2). The derivatives of bicyclo[2.2.0]hexasilane[22] and bicyclo[2.2.0]hexastannane[23] have been synthesized recently and their structures determined by X-ray diffraction. However, the heavier analogues of [2.2.2]propellane have not yet been synthesized.

With the availability of the heavier prismane and cubane ([4]prismane) derivatives, interest in the larger members of the [n]prismane family ($M_{2n}H_{2n}$, n > 4) as synthetic targets is increasing. In carbon chemistry, [5]prismane is the largest prismane that has ever been synthesized.[24] Although the synthesis of the next larger [6]prismane was attempted, it is not yet successful except for the related compound, secohexaprismane.[25] As is clearly shown in Figure 1,[1,18] the heavier [n]prismanes are much less strained than the corresponding carbon compounds, and more so as M becomes heavier. As a consequence, the strain energies of perstanna[n]prismanes are 76.1 (n = 5), 98.1 (n = 6), and 188.4 (n = 8) kcal/mol smaller than those of the carbon counterparts.

The [n]prismane skeletons are composed of n four-membered rings and two n-membered rings. As Figure 1 shows, the strain decreases when n increases from 2 to 5, because the number of four-membered rings increases and the bond angles in the n-membered rings at the top and bottom approach the ideal tetrahedral angle of 109.5°. However, the strain increases greatly with a further increase in n from n = 5, despite the increasing number of four-membered rings. This is due to the increasing derivation of the bond angles in the n-membered rings from the tetrahedral angle: they are 120.0° for n = 6 and 135.0° for n = 8. As a result, the strain energy is the smallest in perstanna[5]prismane. Thus, the first successful synthesis and X-ray structural study were of its derivative ($Sn_{10}R_{10}$, R = 2,6-$Et_2C_6H_3$).[26] Furthermore, a persila[5]prismane derivative may be soon synthesized as the first silicon example of the polyhedral system.[27]

(9) Matsumoto, H.; Higuchi, K.; Hoshino, Y.; Koike, H.; Naoi, Y.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1083–1084.

(10) Nagase, S. Angew. Chem., *Int. Ed. Engl.* **1989**, *28*, 329–330.

(11) Sita, L. R.; Kinoshita, I. *Organometallics* **1990**, *9*, 2865–2867.

(12) Sekiguchi, A.; Yatabe, T.; Kamatani, H.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6260–6262.
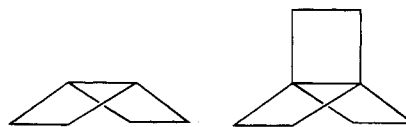
(13) Matsumoto, H.; Higuchi, K.; Kyushin, S.; Goto, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1354–1356.

(14) Furukawa, K.; Fujino, M.; Matsumoto, N. *Appl. Phys. Lett.* **1992**, *60*, 2744–2745.

(15) Sekiguchi, A.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 55–56.

(16) Sekiguchi, A.; Yatabe, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 5853–5854.

(17) (a) Nagase, S.; Kudo, T.; Aoki, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1121–1122. (b) Nagase, S.; Teramae, H.; Kudo, T. *J. Chem. Phys.* **1987**, *86*, 4513–4517.

(18) Nagase, S.; Kobayashi, K.; Kudo, T. *Main Group Metal Chem.* **1994**, *17*, 171–181.

(19) For a similar trend for group 15 elements, see: (a) Nagase, S.; Ito, K. *Chem. Phys. Lett.* **1986**, *126*, 43–47. (b) Kobayashi, K; Miura, H.; Nagase, S. *J. Mol. Struct. (Theochem)* **1994**, *311*, 69–77.

(20) (a) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1988**, 54–56. (b) Nagase, S.; Nakano, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1077–1079. (c) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1990**, 630–632.

(21) (a) Nagase, S.; Kudo, T. *Organometallics* **1987**, *6*, 2456–2458. (b) Nagase, S. Unpublished data.

(22) Matsumoto, H.; Miyamoto, H.; Kojima, N.; Nagai, Y.; Goto, M. *Chem. Lett.* **1988**, 629–632.

(23) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 3769–3770.

(24) Eaton, P. E.; Or, Y. S.; Branca, S. J.; Shankar, B. K. R. *Tetrahedron* **1986**, *42*, 1621–1631.

(25) Mehta, G.; Padma, S. *J. Am. Chem. Soc.* **1987**, *109*, 2212–2213.

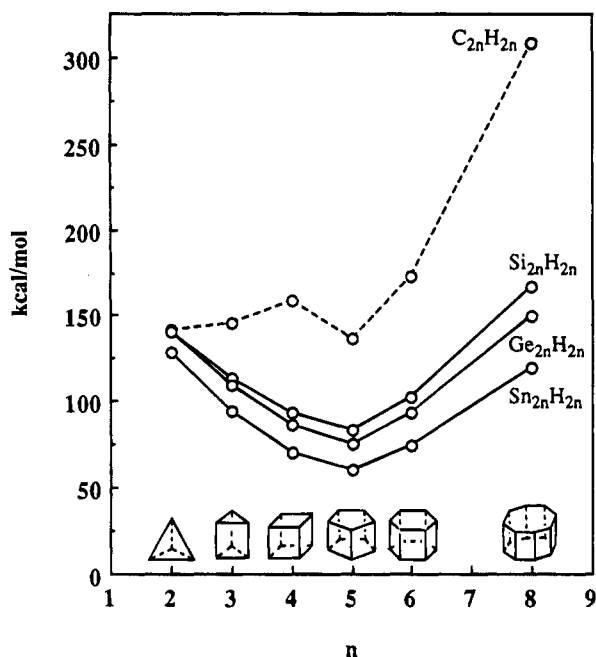(26) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1991**, *113*, 1856–1857.

Figure 1. The strain energies of the tetrahedrane and [n]-prismane systems ($M_{2n}H_{2n}$) calculated at the HF/6-31G* level for M = C and Si and at the HF/DZ(d) level for M = Ge and Sn.

Figure 2. Two isomers of the heavier bicyclic compounds containing two three-membered rings.

The physical and chemical properties of the derivatives synthesized up to now are summarized in a recent review.[6] It is interesting to note that the X-ray structures are in reasonably close agreement with those calculated for the parent compounds.

Compounds Consisting of Only Three-Membered Rings. We are now capable of providing insight into the difference between four-membered and three-membered rings. The size of the valence 2s atomic orbital of a carbon atom is almost equal to that of the 2p atomic orbitals, as measured by the atomic radii (r) of maximal electron density, $r_s = 0.646$ Å and $r_p = 0.644$ Å. However, the valence s and p atomic orbitals differ successively in size for the heavier atoms: $r_p - r_s = 0.203$ (Si), 0.249 (Ge), 0.285 (Sn), and 0.358 (Pb) Å.[28] Therefore, the heavier atoms have a lower tendency to form s–p hybrid orbitals with high p character, and they tend to maintain the ns^2np^2 electronic valence configuration even in their compounds.[1,10,29] Apparently, this property of the heavier atoms is favorable for making ca. 90° bond angles with low strain in the four-membered rings, as already pointed out. In contrast, formation of three-membered rings with bond angles of ca. 60° becomes unfavorable since hybrid orbitals with sufficiently high p character are essential for a description of the bent bond orbitals.

It could be argued that the bond lengths in three-membered rings are shorter than those in four-membered rings: for instance, 2.341 Å (cyclotrisilane) vs 2.373 Å (cyclotetrasilane) and 2.314 Å (tetrasilatetrahedrane) vs 2.396 Å (octasilacubane) at the HF/6-31G* level,[8,30] and this trend is further enhanced in the heavier compounds. However, bond lengths are not always correlated with bond strengths, and the bonds in three-membered rings are calculated to be

weaker than those in four-membered rings.[1,31] This is because the heavier atoms are forced to hybridize to a considerable extent in order to achieve and maintain the three-membered skeletons of a given symmetry, at the expense of large energy loss. To compensate for this energy loss, the bond lengths between skeletal atoms shorten in order to form bonds as effectively as possible. However, the cost for hybridization is too large to be offset just by bond shortening, leading to higher strain and weaker bonds in the three-membered rings.

Consequently, the heavier polyhedral compounds consisting of only three-membered rings easily undergo bond stretching or bond breaking because of the high strain and the weak bonds. For example, the heavier analogues (M_4H_6) of bicyclo[1.1.0]butane consisting of two fused three-membered rings are subject to "bond stretch" isomerism. In the case of M = Si[20a,32] and Ge,[20b] two distinctly different structures are located as minima, as shown in Figure 2. The isomers with a longer central bond are more stable than those with a normal bond length. In the case of M = Sn and Pb,[33] the located minima are only bond stretch isomers where the central bond lengths are severely stretched and the interflap angles between three-membered rings are increased to 144° and 152°, respectively. However, the central bonds have fairly small singlet diradical character, despite the bond stretching.[33] A noteworthy point in Figure 2 is that two bridgehead hydrogens approach one another closely in the bond stretch isomers with M–M–H bond angles of 93° (M = Si) to 86° (M = Pb). This suggests that bulky substituents cannot be accommodated at the bridgeheads of bond stretch isomers. Indeed, up to now, only a bicyclo[1.1.0]tetrasilane derivative with a short central bond of 2.373 Å has been successfully synthesized by introducing bulky *t*-Bu groups at the bridgeheads.[34]

The heavier analogues of [1.1.1]propellane consisting of three fused three-membered rings also undergo bond stretching in the central bonds.[35] However, the singlet states are at least 1 eV lower in energy than

(27) Sekiguchi, A. Private communication.

(28) Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, *12*, 311–406.

(29) For a similar trend for group 15 elements, see: Nagase, S. In *The Chemistry of Organic Arsenic, Antimony, and Bismuth Compounds*; Patai, S., Ed.; Wiley: New York, 1994; Chapter 1, pp 1–24.

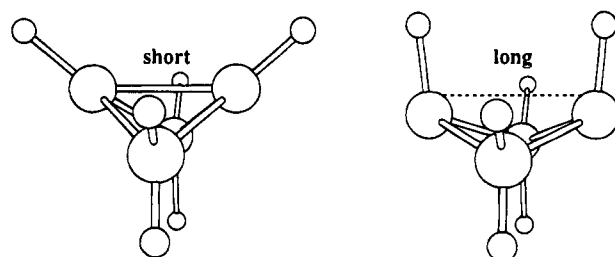(30) See also the experimental and calculated data cited in ref 4.

(31) For an argument based on the bond paths of maximum electron density between bonded ring atoms, see: Cremer, D.; Gauss, J.; Cremer, E. J. *Mol. Struct. (Theochem)* **1988**, *169*, 531–561. A strong bending of the Si–Si bonds leads to a decrease in the bond energies. However, it seems unclear why the Si–Si bond lengths in three-membered rings are shorter.

(32) (a) Schleyer, P. v. R.; Sax, A. F.; Kalcher, J.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364–366. (b) Dabisch, T.; Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1986**, 896–898. (c) Schoeller, W. W.; Dabisch, T.; Busch, T. *Inorg. Chem.* **1987**, *26*, 4383–4389. (d) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 2888–2891. (e) Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 3408–3414.

(33) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1992**, *96*, 9189–9194.

(34) (a) Masamune, S.; Kabe, Y.; Collins, S.; Williams, D. J.; Jones, R. *J. Am. Chem. Soc.* **1985**, *107*, 5552–5553. (b) Jones, R.; Williams, D. J.; Kabe, Y.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 173–174.
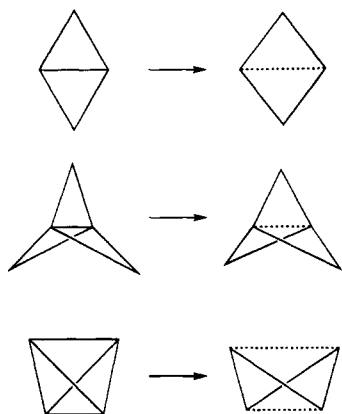
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Figure 3. Schematic description of bond stretch in the heavier compounds consisting of only three-membered rings.

Table 2. Effect of Substituents on the Strain Energies (kcal/mol) Calculated at the HF/6-31G* Level

	R = H	R = Me	R = SiH₃
cyclopropane (c-C₃R₆; D_{3h})	28.7	35.5	34.8
cyclotrisilane (c-Si₃R₆; D_{3h})	38.9	37.6	28.1
tetrasilatetrahedrane (Si₄R₄; T_d)	140.9	134.6	114.5
hexasilaprismane (Si₆R₆; D_{3h})	113.8	105.6	95.7
octasilacubane (Si₈R₈; O_h)	93.5	88.9	77.9

the triplet states.[35d] In the singlet ground states, the diradical character is only slightly increased upon going from [1.1.1]propellane to its heavier analogues,[1,35d] although the bonding interaction between the central atoms decreases.[35d] The theoretical prediction of central bond stretching has been corroborated by the X-ray structure of a pentastanna[1.1.1]-propellane derivative (Sn₅R₆, R = 2,6-Et₂C₆H₃).[36] On the other hand, computation of the heavier analogues of tetrahedrane, consisting of four three-membered rings, shows that they collapse almost without a barrier by the breaking of the two skeletal bonds to an isomer having one four-membered ring of tetraradical character.[37]

As schematically summarized in Figure 3, it is a general trend that bond stretching and bond breaking take place so as to decrease the number of three-membered rings and instead increase the number of less strained four-membered rings.

Substituent Effects

In order to enrich the chemistry of the heavier polyhedral compounds, it is important to clarify the role of substituents on the properties of the systems. For this purpose, methyl and silyl groups were first investigated as representative substituents. As already mentioned, the strain energy of cyclotrisilane (c-Si₃H₆) is ca. 10 kcal/mol larger than that of cyclopropane (c-C₃H₆). As Table 2 shows,[38,39] the strain energy decreases only by 1.3 kcal/mol when the H atoms are substituted by Me groups. In contrast, substitution by SiH₃ groups remarkably decreases the strain energy, c-Si₃(SiH₃)₆ being 11 kcal/mol less strained than the parent c-Si₃H₆, and makes the strain as low as that of c-C₃H₆.

The heavier three-membered rings have been regarded as unsuitable as building blocks for polyhedral compounds. However, Table 2 indicates that the

effects of substituents are also remarkable in polyhedral compounds, the effect of the SiH₃ group being again larger than that of the Me group. Mulliken charge analyses show that the SiH₃ group acts as an electropositive substituent while the Me group is electronegative.[38–40] The advantage of electron-donating substituents over electron-accepting ones in the relief of strain is ascribed to the fact that the increased negative charges on the skeletal atoms decrease the size difference between valence s and p atomic orbitals and make s–p hybridization favorable; the s–p promotion energies also decrease by the increased negative charges.[41] This important electronic effect of the substituents has been usually disregarded. Thus, it is not surprising that the strain energy of octastannacubane (Sn₈H₈) is successively decreased as the hydrogens are substituted by the electropositive SiH₃, GeH₃, and SnH₃ groups.[38]

In the successful syntheses and isolation of the heavier polyhedral compounds, it has been emphasized that the choice of bulky substituents is of crucial importance.[6] In a recent Account, it has been claimed that there are some discrepancies between the X-ray structures of the synthesized derivatives and our calculated structures of the parent compounds, due to severe nonbonding interactions between bulky substituents.[42] In an attempt to provide systematically qualitative insight on these points, octasilacubanes (Si₈R₈) bearing alkyl, aryl, and silyl substituents of various sizes were calculated at the AM1 level (Table 3).[43] X-ray structures are available for R = 2,6-Et₂C₆H₃,[12] CMe₂CHMe₂,[13] and t-Bu.[14] Both the calculated and the X-ray structures show almost perfect cubic skeletons. In addition, the experimental skeletal Si–Si bond lengths are reasonably well reproduced, taking into account the overestimation by ca. 0.05 Å in calculation at the AM1 level. As Table 3 shows, the O_h symmetry of Si₈H₈ is lowered as the substituents become bulky. Nevertheless, all of the calculated structures still show symmetry, in contrast with the available experimental structures in crystals. This suggests that packing forces significantly affect the favorable conformations of bulky substituents around the skeleton, since the energy loss due to the conformational changes is very small. However, the overall structural features hold even in crystals.

As Table 3 shows, the skeletal bond lengths increase by 0.02–0.05 Å upon substitution by alkyl and aryl groups. This bond lengthening is somewhat enhanced

(35) For Si, see: (a) Nagase, S.; Kudo, T. *Organometallics* **1987**, *6*, 2456–2458. (b) Schleyer, P. v. R.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1267–1268. For Ge, see: (c) Nagase, S.; Kudo, T. *Organometallics* **1988**, *7*, 2534–2536. For Sn, see ref 1 and see: (d) Gordon, M. S.; Nguyen, K. A.; Carroll, M. T. *Polyhedron* **1991**, *10*, 1247–1264. (e) Gallego-Planas, N.; Whitehead, M. A. *J. Mol. Struct. (Theochem)* **1992**, 419–432.

(36) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454–6456.

(37) Nagase, S.; Nakano, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1081–1083.

(38) Nagase, S.; Kobayashi, K.; Nagashima, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1302–1304.

(39) Nagase, S. *Pure Appl. Chem.* **1993**, *65*, 675–682.

(40) The view is also confirmed by using the natural population analysis (Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899) at the HF/6-31G* level. The natural charges on the skeletal Si atoms of c-Si₃R₆ change from 0.330 (R = H) to 0.855 (R = Me) and −0.186 (R = SiH₃) while those of Si₈R₈ change from 0.155 (R = H) to 0.424 (R = Me) and −0.095 (R = SiH₃). This trend of the charge changes due to substitution agrees well with those obtained previously at the same level from the Mulliken charge analysis.[38,39]

(41) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 1061–1073.

(42) Sita, L. R. *Acc. Chem. Res.* **1994**, *27*, 191–197.

(43) Kobayashi, K.; Nagase, S. To be published.

Table 3. Symmetries, Si–Si Bond Lengths, Charges, and HOMO Energies of Various Octasilacubane Derivatives (Si_8R_8) Calculated at the AM1 Level[a]

R	sym	Si–Si (Å)[b]	charge[c]	HOMO (eV)
H	O_h	2.421	0.045 (0.068)	−9.70 (−8.13)
alkyl groups				
Me	O_h	2.437	0.255 (0.343)	−8.68 (−6.65)
t-Bu	D_2	2.445	0.264 (0.481)	−8.68 (−6.71)
CMe_2CHMe_2	D_2	2.462	0.242 (0.435)	−8.54 (−6.51)
aryl groups				
Ph	D_2	2.446	0.366 (0.393)	−8.26 (−6.27)
$2,6\text{-}Et_2C_6H_3$	C_2	2.470	0.343 (0.389)	−8.22 (−6.31)
silyl groups				
$Si(SiH_3)_3$	D_2	2.414	0.021 (0.054)	−9.22 (−7.99)
SiH_3	O_h	2.402	−0.216 (−0.115)	−9.48 (−8.14)
$SiMe_2CHMe_2$	D_2	2.408	−0.324 (−0.188)	−8.48 (−7.08)
$SiMe_3$	O_h	2.395	−0.343 (−0.185)	−8.47 (−7.09)
SiF_3	O_h	2.391	−0.539 (−0.313)	−9.81 (−10.89)

[a] In parentheses are the HF/3-21G* values calculated on the AM1 optimized structures. [b] Average skeletal bond lengths. [c] Average Mulliken charges on skeletal atoms.

as the substituents become bulky: e.g., 2.446 Å (R = Ph) vs 2.470 Å (R = $2,6\text{-}Et_2C_6H_3$). However, it should be noted that there is also a good correlation between the bond lengthening and the increased positive charges on the skeletal atoms (Table 3): the skeletal bonds are lengthened even on substitution by the small Me group. It appears that both steric and electronic effects are responsible for the skeletal bond lengthening, although emphasis has been put, in the past, only on the former effect. It is noteworthy that substitution by alkyl and aryl groups raises the HOMO (localized on the skeletons) levels and increases the reactivities. This makes the presence of bulky groups very important since they can fully protect the cubane skeletons, as clearly shown in Figure 4.

Table 3 reveals that the skeletal bond lengths tend to shorten with an increase in the negative charges on the skeletal atoms due to silyl substituents, regardless of their bulk. This is also confirmed by the geometrical optimization with the ab initio calculations at the HF/3-21G* level, as shown in Table 4.[43] The most electropositive SiF_3 group provides the shortest skeletal bond lengths and the lowest HOMO level while the $SiMe_3$-substituted octasilacubane has a relatively high HOMO level. To our knowledge, there has been only one synthetic example with R = $SiMe_2Bu\text{-}t$, although its structural data is not yet available for comparison.[9]

The heavier tetrahedrane skeleton has long been sought, and we have suggested that it can be synthesized if properly substituted by silyl groups.[38,39] As already pointed out, tetrasilatetrahedrane (Si_4R_4) collapses with no significant barrier to a "two-bond broken" isomer when R = H, the latter being 37.3 kcal/mol more stable at the BLYP/6-31G* level.[43] This energy difference is decreased by 8.9 kcal/mol with R = Me, but the two bonds still remain broken. When R = SiH_3, however, the bond stretch isomer becomes only 10.4 kcal/mol more stable with only one bond stretched, as shown in Figure 5. The resultant structural feature resembles closely that of the bond stretch isomer of bicyclo[1.1.0]tetrasilane shown in Figure 2. It is therefore expected that a tetrasilatetrahedrane derivative can be prepared by placing bulky
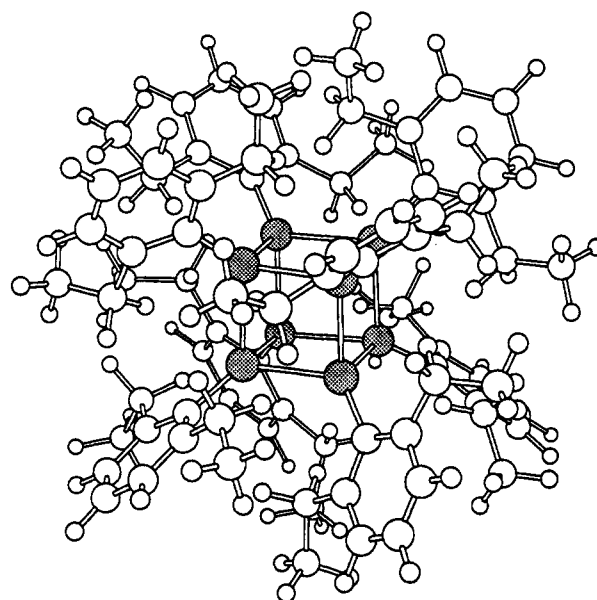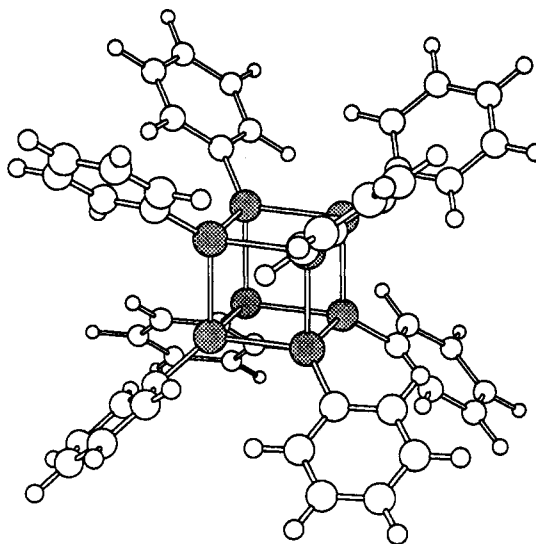
Figure 4. Examples of the steric protection of the cubic silicon skeleton by phenyl and 2,6-diethylphenyl groups. The bulk of 2,6-diethylphenyl groups is apparently more effective for steric protection.

Table 4. Calculated Data for Octasilacubane Derivatives (Si_8R_8) Optimized at the HF/3-21G* Level

R	sym	Si–Si (Å)	charge[a]	HOMO (eV)
H	O_h	2.386	0.065	−8.23
Me	O_h	2.391	0.328	−7.05
SiH_3	O_h	2.383	−0.112	−8.31
$SiMe_3$	O_h	2.390	−0.169	−7.45
SiF_3	O_h	2.369	−0.373	−10.42

[a] Mulliken charge.

silyl groups on the stretched atoms. This has recently been beautifully realized with R = $Si(Bu\text{-}t)_3$: the X-ray study corroborates the presence of a tetrahedral silicon skeleton.[44] Whereas the successful synthesis may be simply ascribed to the stabilizing effect of silyl groups,

(44) Wiberg, N.; Finger, C. M. M.; Polborn, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1054–1056.
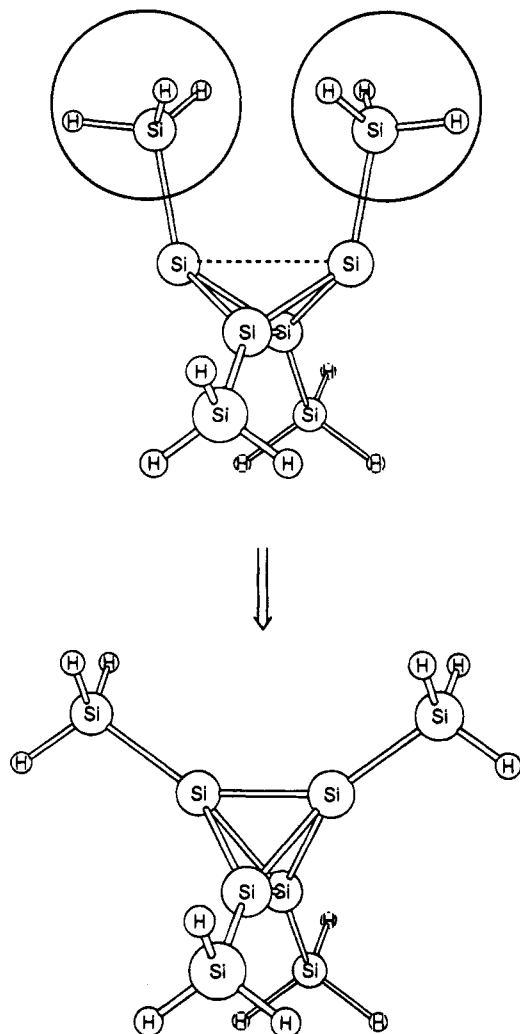
Figure 5. Possible conversion of the bond stretch isomer to a tetrahedral structure upon replacement of the substituents in circles by more bulky silyl groups.

it should be emphasized that the bulk of these groups also plays an important role by preventing the collapse of the skeleton and protecting it against reactive reagents.

Electropositive substituents are also effective in stabilizing the heavier unsaturated compounds since they make hybridization favorable.[38,39] Thus, the first unsaturated three-membered germanium compounds, cyclotrigermenes (c-Ge_3R_4, R = Si(t-Bu)$_3$ and Ge(t-Bu)$_3$), have been synthesized recently.[45] This is also the first example of compounds which contain a "planar" Ge=Ge doubly bonded part, since no planar structure of digermenes ($R_2Ge=GeR_2$) has been heretofore reported.

Spherical Cage Compounds Consisting of Pentagons and Hexagons

According to Figure 1, the strain energies of [n]-prismanes strongly increase with an increase in n. In the [10]prismanes ($M_{20}H_{20}$) shown in Figure 6, the bond angles in the 10-membered rings at the top and bottom become as large as 144.0°. This great deviation from the ideal tetrahedral angle is reflected in the strain energies of $Si_{20}H_{20}$, $Ge_{20}H_{20}$, and $Sn_{20}H_{20}$,

(45) Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H.; Nagase, S. *J. Am. Chem. Soc.* **1995**, *117*, 8025–8026.

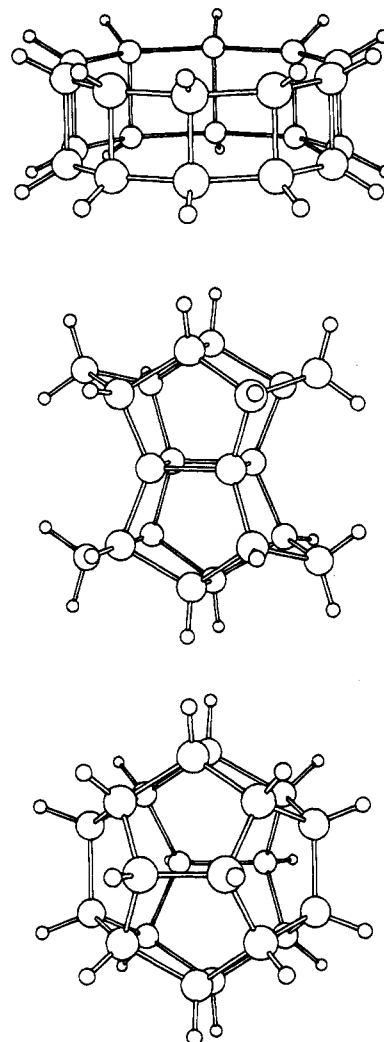**Figure 6.** Three isomers of $M_{20}H_{20}$ with prismane, pagodane, and dodecahedrane structures.

Table 5. Relative Energies (kcal/mol) of the $M_{20}H_{20}$ Isomers

	[10]prismane	[1.1.1.1]pagodane	dodecahedrane
$C_{20}H_{20}{}^a$	0.0	−404.9	−448.5
$Si_{20}H_{20}{}^a$	0.0	−200.1	−219.8
$Ge_{20}H_{20}{}^b$	0.0	−172.3	−194.3
$Sn_{20}H_{20}{}^b$	0.0	−140.0	−159.1

^{a} HF/6-31G*. ^{b} HF/DZ(d).

which are 252.1, 223.6, and 180.1 kcal/mol, respectively, although these values are much smaller than that of 492.1 kcal/mol for $C_{20}H_{20}$.[18] As Table 5 shows, the isomeric [1.1.1.1]pagodane structures containing the less strained rings are much more stable than the [10]prismane structures. In the $M_{20}H_{20}$ system, the most fascinating are the dodecahedral cage structures with high I_h symmetry. The construction of the carbon skeleton was long considered as the "Mount Everest of alicyclic chemistry" until the successful synthesis.[46] As Table 5 shows, the dodecahedrane structures are more stable than the pagodane structures. In these dodecahedrane structures, each skeletal atom can form bond angles close to the ideal tetrahedral value and consequently the strain energies become as small as 32.3 ($Si_{20}H_{20}$), 29.3 ($Ge_{20}H_{20}$), and 21.0 ($Sn_{20}H_{20}$) kcal/mol.[18] These values are half of the value of 43.6

(46) Paquette, L. A. *Chem. Rev.* **1989**, *89*, 1051–1065.

kcal/mol for $C_{20}H_{20}$. It may be an interesting challenge to find proper precursors of the heavier dodecahedranes.

In view of the great progress in the chemistry of fullerenes (which are hollow spherical cage clusters (C_n) consisting of five-membered and six-membered rings), the heavier analogues are of current interest. It has been suggested that silicon clusters (Si_n) also have a strong tendency to take on fullerene-like structures as the cluster size increases, as do carbon clusters.[47] Furthermore, the preference of "pseudo-fullerene-like" cages containing additional four-membered rings is suggested even for smaller silicon clusters $(n = 14-24)$,[48] although direct experimental evidence is lacking.

On the other hand, derivatives of C_{60} and C_{70} having silicon and germanium rings were successfully synthesized by the additions of silylenes, disiliranes, and digermiranes to the fullerene cages.[49] The additions of disiliranes and digermiranes take place only photochemically. A very recent important finding is that endohedral metallofullerenes (fullerenes with a metal or metals inside the cage) such as La@C_{82}, Gd@C_{82}, and La$_2$@C_{80} also can be functionalized by the additions of disiliranes and digermiranes in a thermal as well as a photochemical way,[50] because of the unique electronic properties due to metal doping.[51] It is expected that these remarkable successes will trigger more experimental work on the heavier atom-containing fullerenes.

Unusually Short Phantom Bonds

As mentioned above, the central bonds of the heavier [1.1.1]propellanes are stretched. In contrast, we have found that the lengths become drastically short in the novel propellane-like structures of M_2X_3 (M = Si,[20a,52] Ge,[35c] Sn,[1] and Pb[1]) when X = O: they are even further shortened upon ionization[2] (Chart 3). The lengths between the M atoms, which are compa-
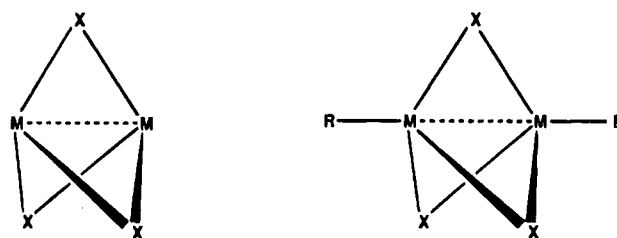
Chart 3

rable to Si—Si triple and Sn—Sn and Pb—Pb double bond lengths, are the shortest known since neither triply bonded silicon compounds nor double bonds (significantly shorter than single bond lengths) for tin and lead compounds have been successfully synthesized up to now. In addition, it has been found that the M—M lengths are rather shortened in the bicyclo-[1.1.1]pentane system $(M_2X_3R_2)$, despite the separations between formally nonbonded atoms.[1,35c,52,53] These remarkable findings have greatly stimulated the theoretical study of the nature of bonding[54] as well as successful synthesis.[55] It has been discussed that no significant bond exists between the M atoms and that M_2X_3 has considerable diradical character in the ground singlet state.[54c,d] On the other hand, the syntheses and X-ray studies of $Si_2Se_3R_2$, $Si_2S_3R_2$, and $Ge_2Se_3R_2$ have been successful, although the approach to the most exciting $M_2O_3R_2$ is still in progress.[55]

Compounds Containing the Heaviest Lead Atoms

The difference in the sizes of valence s and p orbitals becomes largest for the lead atom. This is due to the contraction of the 6s orbital, which mostly originates from the so-called relativistic effect.[56] As a result, the lead atom is most reluctant to form hybrid orbitals with highly directional p character, also known as the inert 6s pair effect (i.e., core-like nature of the 6s electrons). Therefore, the lead atom has the strongest tendency to be divalent with $6s^26p^2$ and forms nonrigid skeletons. Reflecting this, cyclotetraplumbane[1] and bicyclo[2.2.0]hexaplumbane[20c] tend to form skewed C_{4h} and C_2 structures, respectively, unlike their lighter analogues. This trend is further enhanced in three-membered rings; the skewed C_{3h} structure of cyctro-triplumbane (represented as a weak complex of three plumbylenes) is 10 kcal/mol more stable than the normal trigonal D_{3h} structure.[1] Thus, triplumbaprismane containing two three-membered rings easily collapses into a less strained six-membered monocycle. Even in octaplumbacubane, two bonds tend to be stretched in order to create two six-membered rings, as shown in Figure 7. However, it is expected that a cubic skeleton can be recovered in the presence of

(47) (a) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1991**, *187*, 291–294. (b) Reference 39. (c) Nagase, S.; Kobayashi, K. *Fullerene Sci. Technol.* **1993**, *1*, 299–308. (d) Kobayashi, K.; Nagase, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3334–3338. (e) Slanina, Z.; Lee, S.-L.; Kobayashi, K.; Nagase, S. *J. Mol. Struct. (Theochem)* **1994**, *312*, 175–178.

(48) Kobayashi, K.; Nagase, S. To be published.

(49) (a) Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 1605–1606. (b) Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *Fullerene Sci. Technol.* **1993**, *1*, 339–349. (c) Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 10366–10367. (d) Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359–1363. (e) Akasaka, T.; Mitsuhida, E.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 2627–2628. (f) Akasaka, T.; Mitsuhida, E.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Chem. Soc., Chem. Commun.*, in press. (g) Akasaka, T.; Mizushima, T.; Ando, W.; Kobayashi, K.; Nagase, S.; Suzuki, T.; Wälchli, M.; Erata, T. Submitted for publication.

(50) (a) Akasaka, T.; Kato, T.; Kobayashi, K.; Nagase, S.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Nature* **1995**, *374*, 600–601. (b) Akasaka, T.; Nagase, S.; Kobayashi, K.; Suzuki, T.; Kato, T.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1343–1344. (c) Akasaka, T.; Nagase, S.; Kobayashi, K.; Suzuki, T.; Kikuchi, K.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Angew. Chem., Int. Ed. Engl.*, in press. (d) Akasaka, T.; Kato, T.; Nagase, S.; Kobayashi, K.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Tetrahedron*, in press.

(51) (a) Nagase, S.; Kobayashi, K.; Kato, T.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *201*, 475–480. (b) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1993**, *214*, 57–63. (c) Nagase, S.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1837–1838. (d) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1994**, *228*, 106–110. (e) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1994**, *231*, 319–324. (f) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Nakao, Y.; Achiba, Y.; Kobayashi, K.; Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1094–1096.

(52) Nagase, S.; Kudo, T.; Kurakake, T. *J. Chem. Soc., Chem. Commun.*, **1988**, 1063–1064.

(53) For related compounds containing boron atoms, see: (a) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591–599. (b) Liang, C. L.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1878–1884.

(54) (a) Streitwieser, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1261–1262. (b) Kabe, Y.; Kawase, T.; Okada, J.; Yamashita, O.; Goto, M.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 794–796. (c) Schmidt, M. W.; Nguyen, K. A.; Gordon, M. S.; Montgomery, J. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 5998–6001. (d) Nguyen, K. A.; Carroll, M. T.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 7924–7929.

(55) (a) Yoshida, H.; Takahara, Y.; Erata, T.; Ando, W. *J. Am. Chem. Soc.* **1992**, *114*, 1098–1100. (b) Choi, N.; Asano, K.; Ando, W. *Organometallics* **1995**, *14*, 3146–3148. (c) Choi, N.; Watanabe, S.; Ando, A. To be published.

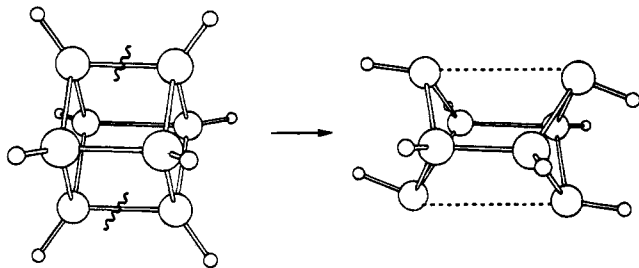(56) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563–594.

Figure 7. Bond stretch isomerism in octaplumbacubane (Pb_8H_8).

bulky electropositive substituents, as in the case of tetrasilatetrahedrane.

Concluding Remarks

Polyhedral compounds consisting of the heavier group 14 elements were once thought to be synthetically inaccessible. This view has been drastically changed in the last few years through a close interplay of theoretical predictions and experimental tests. Many new types of heavier polyhedral compounds have been synthesized, characterized, and isolated, showing novel structures and properties which are often unexpected from the carbon counterparts. These accomplishments have greatly enhanced our understanding of the bonding nature in the heavier systems. The compounds synthesized so far also serve as precursors of newer types of compounds. It is expected that the theoretical interpretations and predictions presented in this Account, although still incomplete, will be of help in planning the fruitful synthesis of new derivatives of the heavier group 14 elements.