Trends in the Structures and Energetics of the Group 14 Metallocenes $(C_5H_5)_2M$ (M = Si−Pb): A Density Functional Theory Study

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The unsubstituted group 14 metallocenes $(C_5H_5)_2M$ (M = Si, Ge, Sn, Pb) were examined with density functional theory calculations. Geometries were optimized with a variety of functionals with pseudopotential basis sets, and eclipsed, staggered, and four bent conformations were considered for all compounds. The minimum energy structure for each metallocene is bent, but the preference for a bent over a linear geometry is slight and decreases from 3.1 kcal mol^{-1} for M = Si to 0.27 kcal mol^{-1} for M = Pb. The agreement between the calculated and experimental structures is generally good, but silicocene is predicted to be considerably more slipped than would be indicated by comparison with the experimentally available $(C_5Me_5)_2Si$; the discrepancy probably stems from differences between the $(C_5H_5)^-$ and $(C_5Me_5)^-$ ligands, rather than from a computational deficiency. Single-point energy calculations were performed on the two crystallographically independent molecules found in the solid-state X-ray structure of stannocene. The energy differences between them suggest that crystal packing forces on the complexes may be appreciable.

Introduction

When stannocene ($(C_5H_5)_2Sn$) and plumbocene ($(C_5H_5)_2Pb$) were first synthesized in 1956 by Fisher and Grubert,[1] the compounds were found to possess dipole moments in hexane solution. This suggested that they were "bent," with nonparallel cyclopentadienyl rings. Since that time, a host of metallocene derivatives of the group 14 elements (Si−Pb) have been structurally characterized with bent geometries in solution, the gas phase, and the solid state.[2] Wilkinson attributed the bending to a stereochemically active lone pair of *n*s valence electrons (Figure 1),[3] and this view has been widely adopted in interpreting the structures and reactions of the metallocenes.[4−7]

The expectation that group 14 metallocenes would always be found as bent molecules was first undermined by the report of the linear structure of $(C_5Ph_5)_2Sn$.[8] Although its linearity could be ascribed to the operation of intramolecular steric effects,[9] other substituted metallocenes with parallel rings have since been reported for which steric influences are less confidently invoked. These include $(C_5Me_5)_2Si$, which exists in both bent and linear forms in the solid state,[10] and the plumbocenes $[C_5Me_4(SiMe_2\text{-}t\text{-}Bu)]_2Pb$[11,12] and $[C_5(i\text{-}Pr)_3H_2]_2Pb$.[13] The closest intramolecular Me···Me′ contacts in the latter two compounds are >4.1 Å, and their linearity is not an obvious consequence of intramolecular steric crowding.

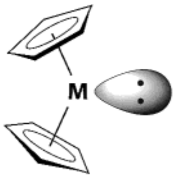

Figure 1. Prototypical group 14 metallocene, whose bending is attributed to a lone pair of metal valence electrons.

The structural role of the metal valence electrons in the group 14 metallocenes is further clouded by the bent metallocenes of the group 2 elements calcium, strontium, and barium,[14−16] whose M^{2+} centers possess noble

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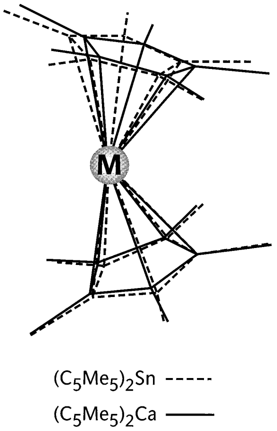

Figure 2. Superimposition of the solid-state structure of $(C_5Me_5)_2Sn$ and $(C_5Me_5)_2Ca$, demonstrating their geometric similarity.

gas electron configurations. The size of the heavier divalent group 14 elements is similar to that of the group 2 metals (e.g., $r_{Sn^{2+}} = 1.18$ Å, $r_{Pb^{2+}} = 1.19$ Å; cf. $r_{Sr^{2+}} = 1.18$ Å), and comparable group 2/group 14 metallocenes sometimes possess strikingly similar structures (Figure 2).[17]

Given the ambiguous link that exists between their geometric conformations and electronic structures, the group 14 metallocenes offer an attractive forum for computational investigations of metal-centered lone electron pairs in organometallic compounds. There have in fact been repeated studies of the complexes using molecular mechanics, semiempirical, and HF-SCF methods. The results from semiempirical MO calculations suggest that σ-bound geometries (i.e., $(\eta^1\text{-}C_5H_5)_2M$ or $(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)M$) are the lowest energy forms for some of the metallocenes.[10,18,19] Those calculations that do favor π-bound cyclopentadienyl rings usually indicate that bent structures enjoy large energetic preferences over their linear counterparts, with predicted linearization energies as high as 110 kJ mol^{-1} for $(C_5H_5)_2Ge$[20] and 100 kJ mol^{-1} for $(C_5H_5)_2Sn$.[21] These early estimates have been substantially reduced with the use of computational methods of greater sophistication, particularly as electron correlation effects are taken into account (e.g., with Møller−Plesset treatments and density functional theory (DFT) approaches).[1,22−24]

DFT calculations have been shown to provide accurate geometries for main-group molecules with lone pairs of electrons.[25] As an investigation of the entire series of the unsubstituted group 14 metallocenes using a common method has not previously appeared, we were interested in determining what insights a DFT analysis would provide into the similarities and differences in the structures and energetics of the compounds.

While this work was in progress, a DFT analysis of $(C_5H_5)_2C$, $(C_5H_5)_2Si$, and $(C_5Me_5)_2Si$ was described,[26] and a related examination of $[C_5Me_4(SiMe_2\text{-}t\text{-}Bu)]_2M$ (M = Ge, Sn, Pb) and $(C_5H_5)_2Ge$ was reported.[12] These studies had aims different from those of the present work, viz., whether $(C_5H_5)_2C$ should be a π-bound metallocene, how its bonding differs from that of $(C_5H_5)_2Si$ and $(C_5H_5)_2Fe$,[26] and why the three $[C_5Me_4(SiMe_2\text{-}t\text{-}Bu)]_2M$ metallocenes are linear.[12] In contrast to these reports, the present contribution examines the unsubstituted metallocenes $(C_5H_5)_2M$ (Si−Pb) (the hypothetical $(C_5H_5)_2C$ is not a metallocene[26]) and gives specific attention to the effect of DFT functionals on the calculated geometries.

Computational Details

Calculations were performed using the Gaussian 98W suite of programs.[27] Molecular orbitals were visualized using the Chem3D Pro program.[28] Tests were made of a variety of functionals, including the BP86 functional of Becke and Perdew,[29,30] the BLYP functional of Becke[29] and Lee, Yang, and Parr,[31,32] the PW91 functional of Perdew and Wang,[33] the B3LYP hybrid functional of Becke and Lee, Yang, and Parr,[34] and the B3PW91 hybrid functional of Becke, Perdew, and Wang.[33,34] Ultimately the B3PW91 functional, which incorporates Becke's three-parameter exchange functional[34] with the 1991 gradient-corrected correlation functional of Perdew and Wang,[33] was chosen as giving the most consistent reproduction of experimental geometries. Although all-electron basis sets exist for the group 14 elements, computational efficiency required the use of effective core potentials (ECP); those of the Stuttgart/Bonn group were chosen for the metals. These are "small core" ECPs for Ge, Sn, and Pb; that is, the $(n-1)$-spd shell is considered part of the valence space, and the valence basis sets are supplemented with polarization functions; for Ge, the valence basis set is (12s12p9d)/[6s6p4d], and for Sn and Pb, (12s12p9d3f2g)/[6s6p4d3f2g].[35] For Si, the valence basis set ((4s,4p)/[2s,2p])[36] was supplemented with a

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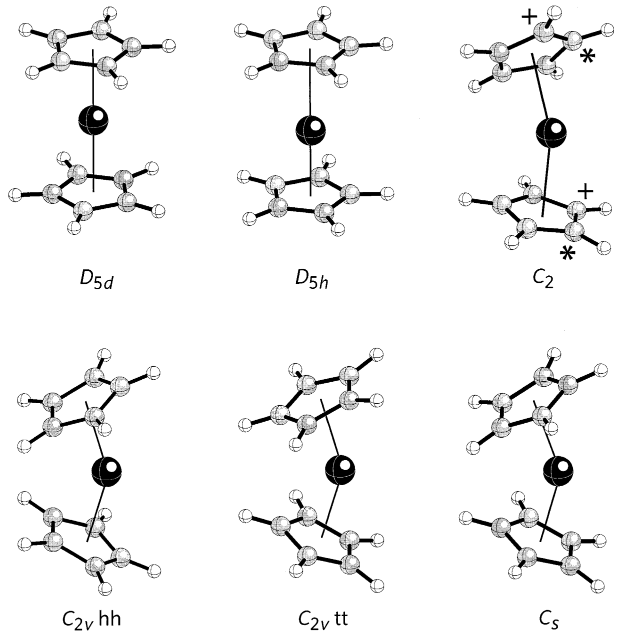

Figure 3. The six geometries used for optimization. The linear forms include both eclipsed (D_{5d}) and staggered (D_{5h}) versions, whereas the bent forms include those directly derived from the linear conformations (C_s, C_{2v}tt, C_{2v}hh) and another (C_2) that is obtained by applying a "twist" to the C_s form. In the C_2 drawing, two pairs of symmetry-related atoms are marked by (*) and (+); the other atoms are similarly related.

single set of d functions with $\alpha = 0.45$. Dunning's correlation-consistent basis sets cc-pVDZ were used on carbon ((9s4p1d)/[3s2p1d]) and hydrogen ((4s1p)/[2s1p]),[37] and the aug-cc-pVTZ set for Si ((16s10p3d2f)/[6s5p3d2f])[38] was used for comparisons with the ECP basis.

Geometry optimizations were performed on six different conformations of each metallocene, including two linear (D_{5d}, D_{5h}) and four bent forms (C_s, C_2, C_{2v}hh ("heel-to-heel"), and C_{2v}tt ("toe-to-toe")) (Figure 3). Stationary points were characterized by the calculation of vibrational frequencies for all geometries, and zero-point corrections were applied to the energies of the final geometries.

Results and Discussion

To determine the manner in which different DFT methods modeled experimental bond distances in the group 14 metallocenes, we conducted a survey using both pure and hybrid (with HF exchange) functionals. These computational approaches were then applied to the staggered (D_{5d}) linear geometries for each metallocene. The variation in M−C bond lengths with different DFT functionals is included as Table 1. It should be noted that solid-state structures of the unsubstituted metallocenes are known experimentally for $(C_5H_5)_2Ge$[39] and $(C_5H_5)_2Sn$[40] only; the decamethylmetallocenes of silicon and lead were used as references for $(C_5H_5)_2Si$[10] and $(C_5H_5)_2Pb$.[40] The difficulties of using $(C_5Me_5)_2Si$ as a reference for silicocene will be examined in detail below.

Table 1. Variation in M−C Distances (Å) for $(C_5H_5)_2M$ under D_{5d} Symmetry

functional	$(C_5H_5)_2Si$	$(C_5H_5)_2Ge$	$(C_5H_5)_2Sn$	$(C_5H_5)_2Pb$
BP86	2.511	2.572	2.738	*a*
PW91	2.500	2.562	2.723	*a*
BLYP	2.544	2.607	2.778	*a*
B3LYP	2.518	2.581	2.749	2.814
B3PW91	2.489	2.551	2.718	2.781

[a] Geometry would not converge with the "pure" DFT functionals.

Survey of DFT Functionals. All the DFT functionals generated M−C distances that were within 0.06 Å of each other for a given metal, yet there were subtle systematic differences between them. The B3PW91 and PW91 functionals generated essentially identical results (within 0.01 Å) that were consistently closest to the experimental reference geometries. Slightly longer bonds were generated by BP86, B3LYP, and BLYP, in that order.

These results seem to indicate that whether a DFT functional is pure or hybrid is not as important to the geometry of these molecules as is the identity of the correlation functional. This finding is interestingly paralleled by results from the electron affinity calculations of Martin et al.,[41] who found that of the exchange and correlation functionals, the former played a greater role in providing accurate results for first-row atoms, whereas the latter proved more important for second-row atoms. In addition, the LYP correlation functional was found to generate better results for the first-row atoms, whereas the PW91 correlation functional was superior for the second-row species. The fact that similar computational approaches are effective for both the calculation of electron affinities of isolated atoms and the structures of the metallocenes indicates that the treatment given to the metal centers in the metallocenes (which are second row and heavier) is critical to their final geometries.

Trends in Potential Energy Surfaces. Table 2 lists all the conformations, their relative energies, and number of imaginary vibrational frequencies for the group 14 metallocenes. Several patterns are evident in the zero-point corrected energies and symmetries, although it is also clear that the potential energy surfaces for these molecules (especially in the bent forms) are in general *extremely* flat and that the differences between conformations is often energetically miniscule. In several cases, the change from a structure with no imaginary frequencies (a true minimum) to a higher order saddle point involves energy changes of less than 10^{-4} hartree and is not chemically meaningful.

Excluding the all-electron $(C_5H_5)_2Si$ calculation, the highest energy conformation for all the metallocenes is of D_{5d} symmetry, which represents a second-order saddle point ($N_{imag} = 2$). Lower in energy (but by as little as 1.8×10^{-5} hartree (0.01 kcal mol^{-1}) for $(C_5H_5)_2Pb$) is the conformation with D_{5h} symmetry and the bent geometries, which in some cases are minima and in other cases represent higher order saddle points (e.g., C_{2v}hh is a minimum for $(C_5H_5)_2$(Si,Ge,Sn) but represents a transition state ($N_{imag} = 1$) for $(C_5H_5)_2Pb$). The $(C_5H_5)_2Ge$ and $(C_5H_5)_2Sn$ metallocenes are the most similar to

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Table 2. Zero-Point Corrected Energies of Optimized Structures for $(C_5H_5)_2M$

	relative energy[a] and number of imaginary vibrational frequencies (in brackets)				
symmetry	$(C_5H_5)_2Si$[b]	$(C_5H_5)_2Si$[c]	$(C_5H_5)_2Ge$	$(C_5H_5)_2Sn$	$(C_5H_5)_2Pb$
D_{5d}	0.004878 (3.1); [2]	0.006524 (4.1); [2]	0.001330 (0.83); [2]	0.002418 (1.5); [2]	0.000424 (0.27); [2]
D_{5h}	0.004799 (3.0); [3]	0.006539 (4.1); [3]	0.001283 (0.81); [2]	0.002334 (1.5); [2]	0.000406 (0.25); [2]
C_{2v}hh	0.000411 (0.26); [0]	0.000530 (0.33); [1]	0.000130 (0.082); [0]	0.000057 (0.036); [0]	0.000042 (0.026); [1]
C_{2v}tt	0.000769 (0.48); [2]	0.001076 (0.68); [2]	0.000146 (0.092); [2]	0.000218 (0.14); [2]	0.0 (0.0); [2]
C_s	0.0 (0.0); [1]	0.0 (0.0); [1]	0.0 (0.0); [0]	0.0 (0.0); [0]	0.000005 (0.003); [0]
C_2	0.000077 (0.048); [0]	0.000100 (0.063); [0]	0.000037 (0.023); [0]	0.000055 (0.034); [0]	0.000426 (0.27); [2]

[a] Energies in hartrees; energies in parentheses are kcal mol^{-1} equivalents. The lowest absolute energies (au) for each metallocene are as follows: Si, −390.631332; Ge, −676.201697; Sn, −601.202045: Pb, −579.780213. [b] With pseudopotential basis set on Si. [c] With all-electron basis set (aug-cc-pVTZ) on Si.

each other, whereas the location of minima and transition structures for $(C_5H_5)_2Si$ and $(C_5H_5)_2Pb$ often differ from each other and from the germanocene/stannocene pair. Details for the individual molecules are summarized below.

Geometry Optimization of $(C_5H_5)_2Si$. In the optimized C_s structure of $(C_5H_5)_2Si$, the average Si−(C_5H_5) ring centroid distance is 2.189 Å, with Si−C bond distances ranging from 2.278 to 2.754 Å ($\Delta = 0.48$ Å). The ring centroid−Si−ring centroid angle is 155.3°, with an angle between the planes of 53.6°. For comparison, the C_2 structure, which has no imaginary frequencies and is negligibly higher in energy (0.05 kcal mol^{-1}), has a Si−(C_5H_5) ring centroid distance of 2.190 Å, with Si−C bond distances ranging from 2.245 to 2.744 Å ($\Delta = 0.50$ Å). The ring centroid−Si−ring centroid angle in this geometry is 154.9°, with an angle between the planes of 53.5°. The difference in the geometries reflects a change in position of the silicon atom relative to the rings, whose angle is essentially the same in the C_s and C_2 structures. Although structurally distinct, at this level of theory one of these geometries cannot be said to be the absolute lowest in energy. Complicating the picture further, a second minimum structure is calculated with the C_{2v}hh geometry at 0.21 kcal mol^{-1} above the C_2 form. This geometry is not a minimum with the all-electron basis set calculation, however.

The bond lengths and bending angles may be compared with the geometric parameters of the bent form of $(C_5Me_5)_2Si$:[10] the experimental Si−(C_5Me_5) centroid distance is 2.121 (av) Å, with a range of Si−C distances of 2.323−2.541 Å ($\Delta = 0.22$ Å), a ring centroid−Si−ring centroid angle of 167.4°, and an angle between the planes of 25.4°. The relatively poor fit between $(C_5H_5)_2Si$ and $(C_5Me_5)_2Si$ is evident in Figure 4.

The geometry of silicocene has been investigated repeatedly over the last two decades.[17] Owing to the flat potential surfaces that relate the different ring conformations, it might be expected that its structure should be highly sensitive to the computational method used. A low symmetry (C_2[26] or C_s[42]) geometry is found as the potential energy minimum with HF-SCF or DFT methods, but it has not been possible to reproduce in $(C_5H_5)_2Si$ the relatively narrow range of Si−C bond lengths displayed in $(C_5Me_5)_2Si$. At one time, improvements in the level of theoretical treatment (especially with basis sets) were expected to reduce and perhaps eliminate the discrepancy between the structures.[42] For example, estimates of Δ_{Si-C} from HF-SCF calculations decrease from 1.66 Å (with a minimal STO-3G(*) basis set)[42] to 1.07 Å (with 3-21G(*)). Enlarging the basis set further, however, produces only modest change (e.g., $\Delta_{Si-C} = 1.00$ Å with HF/6-311G(d,p)).[43] Using a DFT approach and the B3LYP/6-31G(d) combination, Schoeller et al.[26] determined that the range of predicted Si−C bond lengths should be 2.223−2.848 Å ($\Delta = 0.63$ Å); our calculation with the B3PW91 functional and an ECP basis set reduces the spread only slightly, to 0.53 Å. In a further test, we found that using a large all-electron basis set with additional diffuse and polarization functions on silicon made only small changes to the optimized geometry, and the range of Si−C bond lengths (under C_2 symmetry) was still wide (2.212−2.772 Å; $\Delta_{Si-C} = 0.56$ Å). It appears that, as in the Hartree−Fock analysis, a point of diminishing returns is reached with DFT methods; within the limits of these approaches, $(C_5H_5)_2Si$ appears irreducibly slipped.

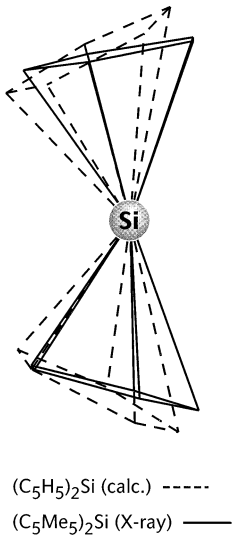

Figure 4. Comparison of the optimized structure of $(C_5H_5)_2Si$ (C_2) with that of the cyclopentadienyl ring framework of $(C_5Me_5)_2Si$ (CH_3 groups omitted).

Decamethylsilicocene may not be a good basis for comparison with calculations on the parent compound. In fact, Schoeller discovered that $(C_5Me_5)_2Si$ optimized at the B3LYP/6-31G(d) level displays Si−C distances ranging from 2.4 to 2.6 Å ($\Delta = 0.2$ Å), which not only is a near match for the experimental values but also represents a reduction in the Si−C bond length spread by 0.4 Å from that calculated for $(C_5H_5)_2Si$. Thus the presence of the methyl groups strongly regularizes the geometry of $(C_5Me_5)_2Si$. This cannot be solely a steric effect, as the closest Me···Me′ contacts in the linear form

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of $(C_5Me_5)_2Si$ are >4.5 Å, which is outside the sum of the van der Waals' radii for two methyl groups (4.0 Å).[44] A similar regularizing effect of the pentamethylcyclopentadienyl ligand in a main-group complex containing a small metal center is evident in the structure of decamethylberyllocene, $(C_5Me_5)_2Be$. Whereas the parent beryllocene Cp_2Be[45] and even $(C_5Me_4H)_2Be$ possess one η^5-ring and η^1-slipped ring,[46] the presence of five methyl groups on each ring produces the relatively symmetrical $(\eta^5\text{-}C_5Me_5)_2Be$, which has parallel rings and a narrow range of Be−C distances ($\Delta_{Be-C} = 0.15$ Å).[46] In this molecule, there are Me···Me′ contacts as close as 3.63 Å, so that it is not possible to dismiss steric influences entirely. Nevertheless, it is clear that the structure of $(C_5Me_5)_2Si$ has been strongly affected by the presence of the methyl groups; we believe it is no longer advisable to use the decasubstituted metallocene as the experimental reference for the parent compound.

Geometry Optimization of $(C_5H_5)_2Ge$. In the lowest energy optimized structure of $(C_5H_5)_2Ge$ (C_s), the Ge−(C_5H_5) ring centroid distance is found to be 2.25 Å, with Ge−C bond distances ranging from 2.405 to 2.718 Å ($\Delta = 0.31$ Å). The ring centroid−Ge−ring centroid angle is 165.4°, with an angle between the planes of 36.6°. For comparison, the crystal structure of $(C_5H_5)_2Ge$ (with crystallographically imposed C_2 symmetry) has a Ge−ring centroid distance of 2.23 Å, Ge−C bond distances of 2.347−2.730 Å ($\Delta = 0.38$ Å), a ring centroid−Ge−ring centroid bending angle of 152.4°, and a 50.4° angle between the ring planes.[39] It should be noted that the calculated geometry matches the experimental structure more closely than does the $(C_5H_5)_2Si/(C_5Me_5)_2Si$ pair.

Geometry Optimization of $(C_5H_5)_2Sn$. In the lowest energy optimized structure of $(C_5H_5)_2Sn$ (C_s), the Sn−(C_5H_5) ring centroid distance is 2.425 Å, with Sn−C bond distances ranging from 2.577 to 2.863 Å ($\Delta = 0.29$ Å). The ring centroid−Sn−ring centroid angle is 162.1°, with an angle between the ring planes of 46.8°. The geometry agrees reasonably well with experimental data. The solid-state structure of $(C_5H_5)_2Sn$ consists of two crystallographically independent molecules, one of which has approximate C_{2v}hh symmetry, with Sn−ring centroid distances of 2.38 and 2.45 Å, Sn−C bond distances ranging from 2.56 to 2.84 Å ($\Delta = 0.28$), with a ring centroid−Sn−ring centroid bending angle of 143.7° and an angle between the ring planes of 46.7°. The other has C_{2v}tt symmetry, with a Sn−ring centroid distance of 2.41 Å to both rings, Sn−C bond distances of 2.58−2.75 Å ($\Delta = 0.18$ Å), a ring centroid−Sn−ring centroid bending angle of 148.0°, and an angle between the ring planes of 46.3°.[40] The geometric differences between the two conformers in the solid state (e.g., Δ_{Sn-C} values of 0.28 Å in one molecule and 0.18 Å in the other) provide an estimate of the influence of crystal packing forces (see below).

Geometry Optimization of $(C_5H_5)_2Pb$. The C_s and C_{2v}tt structures of $(C_5H_5)_2Pb$ are indistinguishable in energy ($\Delta = 0.003$ kcal mol^{-1}), but the C_s form has no imaginary frequencies, indicating it is a true minimum on the potential energy surface. In contrast, there are two imaginary frequencies associated with the C_{2v}tt structure. In the C_s structure, the Pb−(C_5H_5) ring centroid distance (2.50 Å) has increased only slightly over that of stannocene. The Pb−C bond distances range from 2.685 to 2.852 Å ($\Delta = 0.17$ Å), with a ring centroid−Pb−ring centroid angle of 156.1° and an angle between the ring planes of 34.0°. The C_{2v}tt structure also has a Pb−(C_5H_5) ring centroid distance of 2.50 Å, with Pb−C bond distances ranging from 2.686 to 2.852 Å ($\Delta = 0.16$ Å), a ring centroid−Pb−ring centroid angle of 156.5°, and an angle between the ring planes of 33.8°. These geometries are essentially structurally identical; ring rotation around the Pb−ring centroid vector is all that is responsible for the difference in imaginary frequencies. Both structures agree well with experimental data on $(C_5Me_5)_2Pb$, which has a Pb−ring centroid distance of 2.48 Å, Pb−C bond distances of 2.69−2.90 Å ($\Delta = 0.21$ Å), a ring centroid−Pb−ring centroid bending angle of 151.4°, and an angle between the ring planes of 33.3°.[40]

Preferences for Bending. To maximize the calculated preferences for bending in the metallocenes, we define it as the difference in energy between the highest energy linear forms and the lowest energy bent forms. Even so, the values for the metallocenes are small: 3.1, 0.83, 1.5, and 0.27 kcal mol^{-1}, for $(C_5H_5)_2Si$, $(C_5H_5)_2Ge$, $(C_5H_5)_2Sn$, and $(C_5H_5)_2Pb$, respectively (Table 2). With the all-electron basis set on $(C_5H_5)_2Si$, the difference increases to 4.1 kcal mol^{-1}. Only silicocene, and perhaps stannocene, can be said to have a chemically significant, if small, preference for bending; that for the other molecules is close to the "noise" level of these calculations (approximately 1−2 kcal mol^{-1}),[47] so that their linear and bent forms are essentially equienergetic.

In an earlier study of $(C_5H_5)_2Si$ with double-ζ-quality basis sets, the relative energies of the SCF/HF-optimized geometries were computed with various forms of CI (CISD and CISD+Q) and MP2 perturbation approaches.[42] Inclusion of electron correlation consistently reduced the preference for the bent vs linear structures, and MP2 corrections in fact inverted the relative stabilities of some of the geometries. For example, the preference for C_2 over D_{5d} dropped from 16.8 kcal mol^{-1} (HF/SCF) to 15.1, 14.3, and finally 3.7 kcal mol^{-1} with CISD, CISD+Q, and MP2 approaches, respectively. Enlargement of the basis sets on Si and C with additional polarization functions actually placed the MP2 energy of the D_{5d} form 4.7 kcal mol^{-1} below that of the C_2 geometry. At this level of theory, however, the C_{2v}hh geometry was 2.8 kcal mol^{-1} below the D_{5d} form, so that a bent structure was still favored. It should be noted that the structures themselves were not optimized with the various methods designed to account for electron correlation. It is therefore not completely straightforward to compare the relative stabilities of the various conformations with our DFT results. The ca. 3 kcal mol^{-1} preference for a bent geometry at the MP2 level, however, is in line with the DFT calculations.

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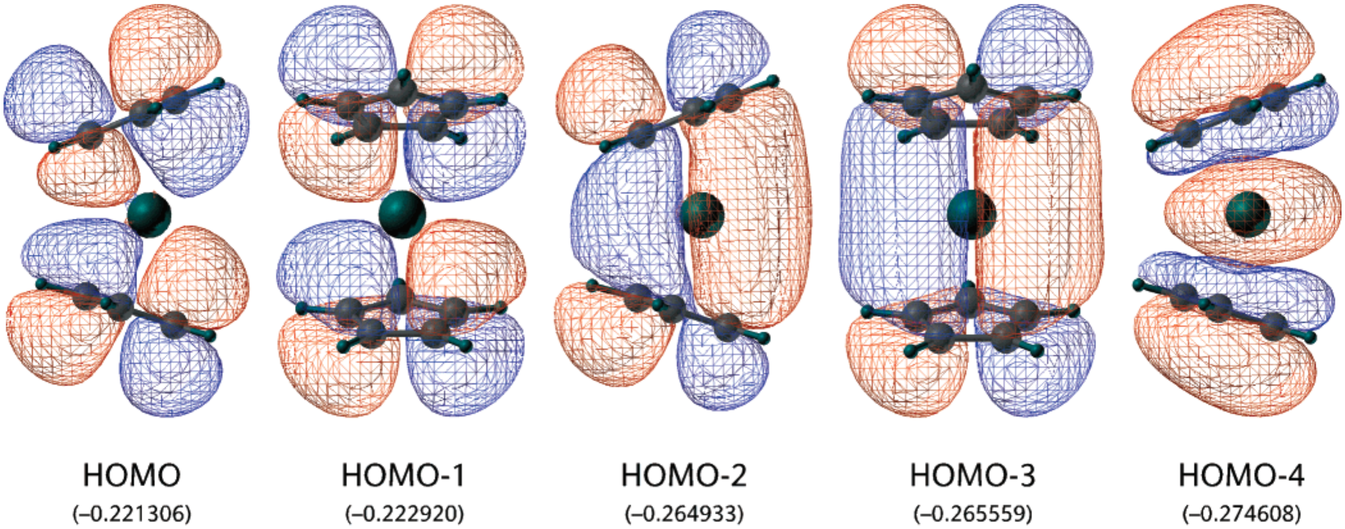

Figure 5. Graphical representation of the HOMO-*n* ($n = 0-4$) orbital of $(C_5H_5)_2Ge$, showing the symmetric shape of the metal-centered lone pair in the HOMO-4 orbital. The numbers below the orbitals are energies in hartrees.

Our results with the heavier metallocenes can be contrasted with a recent ab initio HF-SCF study;[6] in every case, the DFT results suggest a smaller preference for bending: i.e., 0.81, 1.5, and 0.27 kcal mol^{-1} (DFT) versus 6.4, 4.0, and 0.66 kcal mol^{-1} (HF) for $(C_5H_5)_2Ge$, $(C_5H_5)_2Sn$, and $(C_5H_5)_2Pb$, respectively. The HF values were not corrected for zero-point energy, which might reduce the differences between the DFT and HF methods.

The trend toward smaller bending forces with the heavier metals correlates with the expected increase in the ionicity of the bonding with the heavier metals. The change in bonding is also reflected in subtle ways in the optimized geometries. For example, the spread in M−C bonds decreases in the order 0.53, 0.31, 0.29, and 0.16 Å for $(C_5H_5)_2Si$, $(C_5H_5)_2Ge$, $(C_5H_5)_2Sn$, and $(C_5H_5)_2Pb$, respectively. The change in the Δ_{M-C} values means that the cyclopentadienyl ring is more nearly perpendicular to the metal−ring centroid vector in the heavier metallocenes. Such perpendicularity is typically found in ionic metallocenes and is expected on the basis of an electrostatic interpretation of the bonding (cf. the Δ_{M-C} value of 0.057 Å in $(C_5Me_5)_2Ca$[15]).

Estimation of Intermolecular Forces. Owing to the low energy difference between the bent and linear forms of the metallocenes, the effect of crystal packing forces on their structures could be substantial. Recent attempts to quantify the effects of crystal packing in organotin structures have been made by Tiekink et al.,[48] who have proposed that the magnitude of packing forces can be estimated by comparing calculated energies for structures in the gas phase to those in the solid state. Such comparisons cannot directly give an indication of the multiple intermolecular forces that constitute crystal packing, however, since they are limited to the behavior of a single molecule.

A somewhat different analysis can be made with $(C_5H_5)_2Sn$, however. There are two crystallographically independent molecules in its solid-state structure with slightly different geometries; the C−C bond lengths in the two conformations, for example, vary over a 0.15 Å range. At the B3PW91/Sn(ECP) level, the two conformations are found to differ in energy by 44 kcal mol^{-1}. This variance is more than an order of magnitude greater than that between the optimized bent and linear forms of $(C_5H_5)_2Sn$. The large difference in energies suggests that the small intramolecular influence of the metal-centered lone pair (<2 kcal mol^{-1}) could easily be overcome by intermolecular lattice forces.

Electronic Structures. As previously found from HF-SCF calculations on $(C_5H_5)_2$(Ge,Sn,Pb),[6] the HOMO and HOMO-1 for all four metallocenes are primarily ring-based and π-antibonding in nature. The HOMO-2 is localized on the silicon center in $(C_5H_5)_2Si$; this represents the conventional “lone pair”. For the three heavier metallocenes, the HOMO-2 and HOMO-3 are combinations of ligand π orbitals and metal s and p orbitals. Only at HOMO-4 is the primarily metal-localized orbital reached (Figure 5). Cowley et al. also determined that the lone pair of stannocene is not the HOMO (it was identified as the HOMO-2 orbital on the basis of SW-Xα calculations) and noted that this was consistent with the experimental irreversibility of its electrochemical oxidation.[5a]

Examination of the energy of the lone pair orbital in $(C_5H_5)_2Si$ (all-electron basis set) indicates a stabilization in energy by 1.7 kcal mol^{-1} upon bending from a D_{5d} to C_s configuration. This difference represents only a portion of the total energy change upon bending (4.1 kcal mol^{-1}); thus reduction of the energy of the lone pair MO does not alone account for the conformational preference. It should also be noted that the bending *angle* in the metallocenes does not correlate with their bending *preference*; $(C_5H_5)_2Pb$ is the most bent, for example, despite its gaining the least energy on bending. There is likely a change in the driving force for the bending with the increase in atomic number. The structure of silicocene reflects the “carbene-like” character of the metal center, but this will be less important with the heavier metals. Other mechanisms for bending, such as the core polarization effects that have been proposed to be active with the bent group 2 metallocenes,[49] may well be involved with stannocene and plumbocene.

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Conclusions

Ab initio calculations with density functional theory methods have confirmed that, at least in their isolated, monomeric form, the group 14 metallocenes are most stable as slipped sandwich compounds with π-bound cyclopentadienyl rings. The difference in energy between the linear and bent forms for the metallocenes is small (ca. 0.3−3 kcal mol^{-1}), and the stereochemical influence of the metal-centered lone pair of electrons is relatively slight. The metallocenes' conformational floppiness means that the magnitude of ring slippage is difficult to model and could be strongly affected by ring substituents and solid-state packing forces. The fact that the heavier metallocenes are still strongly bent even though there is little energetic push from the metal-centered lone pair suggests that other bending mechanisms, such as core polarization, should be considered for these molecules.

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