

# Silicocene, $(C_5H_5)_2Si$ : A Highly Symmetric Sandwich Compound?

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**Abstract:** Ab initio quantum mechanical methods are employed in the study of several conformers of silicocene,  $(C_5H_5)_2Si$ . Specifically, fully optimized structures are obtained for  $C_s$ ,  $C_2$ ,  $D_{5h}$ ,  $C_{2v}$ , and  $D_{5d}$  isomers at the self-consistent-field (SCF) level of theory. Three different Gaussian basis sets ranging in size from a minimal STO-3G\* basis to one of double- $\zeta$  plus polarization (DZP) quality were used. The latter set consisted of 210 contracted basis functions. The effects of electron correlation were estimated using second-order perturbation theory (MP2) with the largest basis set. At the SCF DZP level of theory, silicocene is predicted to adopt a low-symmetry bent  $C_s$  structure. However, the difference in energy between the low-symmetry ( $C_s$ ,  $C_2$ ) and  $C_{2v}$  conformers is only 2.4 kcal/mol, with the  $D_{5d}$  conformer lying 8.8 kcal/mol higher in energy. Electron-correlation effects determined from MP2 energies at the SCF DZP optimized structures favor the higher symmetry species, with a  $C_{2v}$  conformer predicted to be 7.5 kcal/mol lower in energy than the  $C_s/C_2$  structures. It is shown that basis set augmentation, particularly the inclusion of polarization functions, favors the higher symmetry species. It is concluded that ab initio studies of  $\pi$ -bonded complexes, or sandwich compounds, require at least a DZP basis set to obtain reliable results. These studies do not conclusively determine the symmetry of the minimum energy conformer of silicocene. However, it is clear that the silicocene potential energy surface is flat with respect to motion of the cyclopentadienyl rings about the silicon atom and that if the high-symmetry  $D_{5d}$  or  $D_{5h}$  conformer is not a minimum, then it will not be significantly higher in energy than the true gas-phase minimum.

There has been considerable interest in the cyclopentadienyl sandwich compounds,  $Cp_2M$  ( $Cp = C_5H_5$ ) since a  $\pi$ -bonded  $D_{5d}$  structure was first suggested for ferrocene in 1952.<sup>1</sup> Contrary to the highly symmetric structure adopted by ferrocene, synthesis and structure determination of the group 14 sandwich compounds and the isoelectronic group 15 cations has shown that the majority of these compounds adopt a bent conformation with a subsequent variation in M-C bond distances. The first group 14 cyclopentadienyl sandwich compound to be synthesized was plumbocene in 1956 by Fischer and Grubert.<sup>2</sup> This compound is now understood to have a polymeric zigzag structure in the solid state with bridging cyclopentadienyl rings.<sup>3</sup> However, plumbocene is monomeric in the gas phase, with electron-diffraction measurements determining an angle between ring planes of  $45 \pm 15^\circ$  and a mean Pb-C distance<sup>4</sup> of 2.78 Å. Additionally, X-ray analysis of the full methyl derivative  $(C_5Me_5)_2Pb$  has determined a ring centroid-Pb-ring centroid angle of  $151^\circ$  with a range of Pb-C distances<sup>5</sup> from 2.69 to 2.90 Å.

Ascending the periodic table, preliminary electron-diffraction measurements showed stannocene,  $Cp_2Sn$ , to be bent with a ring centroid-Sn-ring centroid angle of  $\sim 125^\circ$  or an angle between ring planes<sup>4</sup> of  $\sim 55^\circ$ . Later, X-ray analysis determined this compound to be monomeric in the solid phase with two bent structures present in the crystal.<sup>5</sup> These structures were determined to have ring centroid-Sn-ring centroid angles<sup>5</sup> of  $148.0^\circ$  and  $143.7^\circ$  or, alternatively, angles between ring planes<sup>6</sup> of  $45.9^\circ$  and  $48.4^\circ$ . The analysis determined Sn-C distances of 2.58-2.75 and 2.56-2.85 Å, respectively. Electron-diffraction measurements on  $(C_5H_4Me)_2Sn$  show that this compound is also bent with an angle between ring planes of  $50 \pm 6^\circ$ .<sup>6</sup> An X-ray analysis of the fully methyl derivative,  $(C_5Me_5)_2Sn$ , gives two conformers with angles between ring planes of  $36.4^\circ$  and  $35.4^\circ$  and a corresponding range of Sn-C distances<sup>7</sup> of 2.57-2.78 and 2.56-2.85 Å. As noted by Almlöf et al.,<sup>6</sup> full methyl substitution favors a less bent structure as one would expect from consideration of steric effects. It is interesting to note that, although the angle between ring planes is decreased by full methyl substitution, the variation in Sn-C bond distances is virtually unaffected. Larger substituent groups on the cyclopentadienyl rings give a highly symmetric structure for decaphenyl stannocene,<sup>8</sup> which has five equivalent Sn-C bonds

to each ring (Sn-C = 2.689 Å) and a ring centroid-Sn-ring centroid angle of  $180.0^\circ$ .

Germanocene,  $(C_5H_5)_2Ge$ , was first synthesized in 1973 by Scibelli and Curtis.<sup>9</sup> The gas-phase structure of the unsubstituted molecule has not yet been determined, but the gas electron-diffraction (GED) structure of the dimethyl derivative  $(C_5H_4Me)_2Ge$  shows this compound to have an angle between ring planes<sup>6</sup> of  $34 \pm 7^\circ$ . X-ray studies of the unsubstituted parent molecule have determined a bent structure in the crystal with an angle between ring planes of  $50.4^\circ$  and a range of Ge-C distances<sup>10</sup> from 2.347 to 2.730 Å. Note that the parent germanocene exhibits a larger deviation from a parallel ( $D_{5d}$  or  $D_{5h}$ ) structure than does stannocene. The full methyl derivative  $(C_5Me_5)_2Ge$  has been synthesized,<sup>7</sup> but as yet no structural determination has been made.

The valence isoelectronic group 15 cations,  $(C_5Me_5)_2As^+$  and  $(C_5Me_5)_2Bi^+$  have been synthesized with an X-ray structural analysis having been reported for the arsenic compound.<sup>11</sup> This  $C_s$  symmetry cation is bent with an angle between ring planes of  $36.5^\circ$  and more significantly has a large range of As-C bond distances. The As-C distances vary from 2.188 to 2.667 Å in one cyclopentadienyl ring and from 2.261 to 2.742 Å in the second ring. Thus, this molecule can no longer be described as exhibiting bis- $\eta^5$  or  $\eta^5$  bonding (i.e. five equivalent M-C bonds) but rather  $\eta$  bonding to the first ring and  $\eta^2$  to the second.

In light of these observations it was interesting to note the recent synthesis and structural determination<sup>12</sup> of decamethyl silicocene,

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(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Si. This is the lightest of the group 14 sandwich compounds to be synthesized and, unlike decamethyl germanocene, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Si adopts a highly symmetric *D*<sub>5d</sub> structure (angle between rings of 0°) in the crystal. A second conformer, attributed by Jutzi, Kanne, and Krüger<sup>12</sup> to arise from crystal-packing effects, was found to have an angle between ring planes of 25.3° with an associated range of Si–C distances from 2.324 to 2.541 Å.

This result was surprising since most of the previous group 15 dicyclopentadienyl sandwich compounds were found to adopt lower symmetry, bent conformations. Furthermore, an ab initio theoretical study of the valence isoelectronic phosphocanium cation, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>P<sup>+</sup>, predicted the minimum energy conformation to have C<sub>s</sub> symmetry, similar to the experimentally observed (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>As<sup>+</sup> compound. Moreover, the results of the unsubstituted group 15 compounds indicate that as the central atom becomes smaller (i.e., Pb → Sn → Ge), the angle between the Cp rings increases. Therefore, it is uncertain whether (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Si will also exhibit parallel Cp rings since (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Si may adopt *D*<sub>5d</sub> symmetry due solely to steric effects.

The aim of this study was to determine the structure and energetics of the different conformers of the parent silicocene, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Si, using ab initio theoretical methods. Previously, the ab initio self-consistent-field (SCF) method has been applied to the unsubstituted germanocene,<sup>6</sup> but the structure was not fully optimized. As already noted, the structure and energetics of several conformers of the isoelectronic cation, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>P<sup>+</sup>, were determined from full-geometry optimization using ab initio techniques.<sup>13</sup> Phosphocanium was predicted to have a global minimum energy structure of C<sub>s</sub> symmetry with η<sup>2</sup> bonding to one ring and η (or η<sup>3</sup>) bonding to the other, which is consistent with the results determined experimentally for the (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>As<sup>+</sup> cation. Two studies have reported MNDO results of silicocene.<sup>14,15</sup> These two studies are at odds with the first reporting a global minimum of *D*<sub>5h</sub> symmetry, and the second, reporting a C<sub>2v</sub> minimum structure. However, the second<sup>15</sup> study performed a more rigorous search of the silicocene potential energy surface. They found that the lower symmetry structure was favored by ~5.3 kcal/mol over the *D*<sub>5d</sub> structure using a constrained search for the low-symmetry species.

In the interest of quality, we decided to determine rigorously the structures of the *D*<sub>5d</sub>, *D*<sub>5h</sub>, C<sub>2v</sub>, C<sub>s</sub>, and C<sub>2</sub> conformers of silicocene, optimizing all variables within these symmetry constraints and categorizing the nature of the potential energy surface stationary point from analysis of the Hessian. The six silicocene conformers included in this study encompass all different reported equilibrium structures of the group 14 dicyclopentadienyl compounds and the isoelectronic group 15 cations. A description of each conformer will be given in the next section together with the full details of the theoretical approach. A discussion of the energetics of the six silicocene conformers and a discussion of the equilibrium structures are presented. The bonding present in the six conformers of silicocene is also discussed, followed by our concluding remarks.

### Theoretical Approach

Six conformers of silicocene were optimized at the SCF level of theory within the given symmetry constraints. An analytic gradient method was employed, and the structures were optimized such that all Cartesian gradients were less than 10<sup>-5</sup> au. The six models were chosen as follows:

(1) This is a *D*<sub>5d</sub> structure, which was investigated because the experimental information on decamethyl silicocene, indicated that the *D*<sub>5d</sub> structure was present in the crystal.<sup>12</sup> This conformer has the two Cp rings staggered. This conformer will be referred to as the *D*<sub>5d</sub> structure.

(2) This is a *D*<sub>5h</sub> structure, which an MNDO study<sup>15</sup> predicted to be of comparable energy to the *D*<sub>5d</sub> structure. The Cp rings are eclipsed in this conformer. This conformer will be referred to as the *D*<sub>5h</sub> structure.

(3) This is designated a "point-to-edge" structure using the notation of ref 13 since the two Cp rings approach most closely via a single carbon atom on one ring and two equivalent carbon atoms on the other ring. This conformer has only one plane of symmetry (C<sub>s</sub>) and the bonding to each Cp ring is inequivalent. This structure would result from relaxation of the parallel Cp rings in the *D*<sub>5d</sub> conformer. It is analogous to the lowest energy conformer reported for the isoelectronic (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>P<sup>+</sup> cation<sup>13</sup> and to the experimentally observed<sup>11</sup> (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>As<sup>+</sup>. This conformer will be referred to as the C<sub>s</sub> structure.

(4) This structure has a 2-fold rotation axis (i.e., C<sub>2</sub> symmetry), so that the bonding to the two Cp rings is equivalent. This type of structure was found to be the second lowest energy conformer<sup>13</sup> of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>P<sup>+</sup>. This conformer will be referred to as the C<sub>2</sub> structure.

(5) This is a C<sub>2v</sub> structure, labeled "edge-to-edge" since the two rings approach most closely via a C–C bond on each ring. This conformer will be referred to as the C<sub>2v</sub>(e–e) structure.

(6) This is a C<sub>2v</sub> structure, labeled "point-to-point" since the two rings approach most closely via a unique carbon atom on each ring. The latter two conformers, C<sub>2v</sub>(e–e) and C<sub>2v</sub>(p–p) were studied since these structures result from relaxation of the parallel Cp rings in the *D*<sub>5h</sub> species. This conformer will be referred to as the C<sub>2v</sub>(p–p) structure.

The structures were first optimized using an STO-3G basis set<sup>16</sup> augmented by a set of d functions on the central atom (α<sub>d</sub>(Si) = 0.5). This basis is designated STO-3G\*. Such basis sets are known to give improved structures, compared to experiment when considering second-row atoms,<sup>17</sup> than are their STO-3G counterparts. When the structural parameters and the associated analytic Hessians are used as a starting point, the conformers were then optimized with a double ζ-basis,<sup>18–20</sup> again augmented by a d function of exponent 0.5 on the central atom. This contracted basis, Si(11s7p1d/6s4p1d), C(9s5p/4s2p), H(4s/2s), is denoted DZd. Finally, to measure the importance of polarization functions on the orientation of the cyclopentadienyl rings, structures 1, 3, and 4 were optimized with the above double ζ-basis, but now incorporating one set of polarization functions on carbon (α<sub>d</sub>(C) = 0.85) and two sets of polarization functions on silicon (α<sub>d</sub>(Si) = 0.75; α<sub>d</sub>(Si) = 0.25). This basis set, Si(11s7p2d/6s4p2d), C(9s5p1d/4s2p1d), H(4s/2s) which includes 210 contracted Gaussian basis functions, is denoted DZP.

It is particularly important to use a large flexible basis set of at least DZP quality since there are several recent examples<sup>21–26</sup> for silicon compounds in which the ground-state structure was incorrectly predicted with smaller basis sets. In some of these studies<sup>23–25</sup> it has been demonstrated that more than one set of d polarization functions are necessary for the silicon atom. Furthermore, it is reasonable to expect that carbon d polarization functions will be very important in the description of a bis η<sup>5</sup> bonded sandwich compound. Therefore, on the basis of the flexibility of the DZP basis, we expect it to yield the most reliable results.

Analytic second derivatives were used to obtain the harmonic frequencies and infrared intensities for each basis set. Analytic methods are essential for such molecules, when considering both the number of atoms and the weak binding of the central atom to the Cp rings where real vibrational frequencies are less than 100 cm<sup>-1</sup>. The DZP basis C<sub>s</sub> structure of silicocene, for which there are 13 unique atoms, represents one of the largest systems for which SCF harmonic frequency analyses have been reported.

To account for electron-correlation effects, second-order perturbation theory (MP2)<sup>27</sup> energies were determined using the DZP basis set at the SCF equilibrium geometries for the conformers C<sub>2v</sub>(e–e), C<sub>2v</sub>(p–p), C<sub>s</sub>, C<sub>2</sub>, and *D*<sub>5d</sub>. In order to assess the reliability of perturbation theory (MP2) to incorporate correctly the effects of electron correlation, configuration interaction energies<sup>28</sup> including all single and double excitations

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Table I. Absolute Energies (hartrees) and Relative Energies (kcal/mol) for the (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Si Structures Using the STO-3G\* and DZd Basis Sets

structure	SCF/STO-3G* <sup>a</sup>			SCF/DZd <sup>b</sup>		
	absolute	relative	negative eigenvalues	absolute	relative	negative eigenvalues
C <sub>2</sub>	-665.393 23	0.0	0	-673.202 43	0.0	0
C <sub>s</sub>	-665.393 26	-0.02	0	-673.200 28	1.4	1
D <sub>5d</sub>	-665.337 78	34.8	2	-673.174 17	16.8	2
D <sub>5h</sub>	-665.337 74	34.8	3	-673.174 16	16.8	3
C <sub>2v</sub> (e-e)	-665.379 05	8.9	2	-673.190 68	7.4	2
C <sub>2v</sub> (p-p)	-665.389 62	2.3	2	-673.198 09	2.7	2

<sup>a</sup>Energies are given for the geometries optimized at the SCF STO-3G\* level of theory. <sup>b</sup>Energies are given for the geometries optimized at the SCF DZd level of theory.

from the reference wave function (CISD) were determined with the DZd basis at the SCF DZd equilibrium geometries. However, it is important to realize that the essentially nonpolarized DZd basis is inappropriate for the inclusion of *quantitative* dynamic electron-correlation effects. The effects of size-consistency were considered with the Davidson correction<sup>29</sup> (CISD+Q) and with the more rigorous coupled-pair functional<sup>30,31</sup> (CPF) method. In the CISD and CPF computations, the silicon (1s2s2p) and carbon (1s) corelike molecular orbitals remained doubly occupied in all configurations and the corresponding virtual orbitals were deleted. This generated 1 383 321, 1 381 801, 692 253, and 692 249 (C<sub>2h</sub>) configurations for the C<sub>s</sub>, C<sub>2</sub>, C<sub>2v</sub>, and D<sub>5d</sub> conformers, respectively. All electrons and molecular orbitals were allowed to be active when determining the MP2 electronic energy. The SCF and MP2 theoretical predictions reported in this study were obtained with the Cambridge Analytic Derivatives Package (CADPAC).<sup>32</sup>

The DZP basis (210 basis functions) is the smallest basis that has sufficient correlating functions to determine reliably the optimized geometries of the conformers of silicocene at a correlated level of theory. For the simplest electron-correlation method (MP2), we estimate that a single gradient calculation with current state-of-the-art programs and computational facilities (CRAY XMP-48) would take 6 h of cpu time for the C<sub>s</sub> conformer, for which 29 unique nuclear coordinates have to be optimized. Due to the cost, this option was not available. Optimization of a D<sub>5d</sub> structure (in C<sub>2h</sub> symmetry) would be somewhat less expensive, but in the absence of the MP2 energies for the optimized C<sub>s</sub> or C<sub>2</sub> structures, the more expensive MP2 Hessian would be required to determine whether this conformer was a minimum on the potential energy surface. Even then, it would not determine whether this was the global energy minimum. For the other electron-correlation methods mentioned here (CPF, CISD), the cost of such computations would be significantly more expensive. Thus, given the computational facilities at our disposal, the geometries of the silicocene conformers were not optimized at a correlated level of theory.

**Energetics of the Six Conformers of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Si.** The absolute and relative energies of the six conformers predicted at the SCF level with the STO-3G\* and DZd basis sets are given in Table I, together with a characterization of each stationary point in terms of the number of negative eigenvalues<sup>33</sup> of the second-derivative matrix. The C<sub>s</sub> and C<sub>2</sub> conformers are both minima on the potential energy surface at the STO-3G\* level of theory, with the C<sub>s</sub> structure being fractionally lower in energy. The more symmetric conformers, however, are high-order transition states having 2 (C<sub>2v</sub>(e-e)), 2 (C<sub>2v</sub>(p-p)), 2 (D<sub>5d</sub>), and 3 (D<sub>5h</sub>) imaginary frequencies, and they lie 2.3, 8.9, 34.8, and 34.8 kcal/mol higher in energy than the C<sub>2</sub> conformer, respectively.

When the DZd basis is considered, the C<sub>2</sub> conformer is the only genuine minimum on the potential energy surface, with the smallest vibrational frequency being only 45 cm<sup>-1</sup>. The C<sub>s</sub> structure is a transition state (one negative eigenvalue of the Hessian). Thus, the STO-3G\* and DZd basis sets give a slightly different description of the surface with respect to the C<sub>2</sub> and C<sub>s</sub> conformers. Previous studies have shown that due to the inflexibility of a minimal basis set, a STO-3G\* potential energy surface may yield more minima than does a larger basis set.<sup>34</sup> The C<sub>2v</sub>(e-e), C<sub>2v</sub>(p-p), D<sub>5d</sub>, and D<sub>5h</sub> structures are again high-order transition states (2, 2, 2, and 3 negative eigenvalues of the Hessian, respectively). The relative energetics at the SCF DZd level of theory correlates with the characterization of the stationary points, such that the energies rel-

Table II. Absolute Energies (hartrees) and Relative Energies (kcal/mol) for the (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Si Structures Using the DZP Basis Set

structure	SCF <sup>a</sup>			MP2 <sup>b</sup>	
	absolute	relative	negative eigenvalues	absolute	relative
C <sub>2</sub>	-673.362 78	0.0	1	-674.936 40	0.0
C <sub>s</sub>	-673.363 25	-0.3	0	-674.936 46	-0.04
D <sub>5d</sub>	-673.345 34	10.9	3	-674.943 97	-4.7
C <sub>2v</sub> (e-e)	-673.360 42	1.5	1	-674.948 39	-7.5
C <sub>2v</sub> (p-p)	-673.359 42	2.1	2	-674.943 82	-4.7

<sup>a</sup>Energies are given for the geometries optimized at the SCF DZP level of theory. <sup>b</sup>Single-point energies determined at the SCF DZP optimized geometries.

ative to the C<sub>2</sub> conformer are all increasingly positive with values of 1.4 (C<sub>s</sub>), 2.7 (C<sub>2v</sub>(p-p)), 7.4 (C<sub>2v</sub>(e-e)), and 16.8 kcal/mol (D<sub>5d</sub>, D<sub>5h</sub>). It is important to note that the larger DZd basis set has halved the energy difference between the lower symmetry species and the highest symmetry conformers (D<sub>5d</sub>, D<sub>5h</sub>), compared to the STO-3G\* basis set results, although the energies of the C<sub>2v</sub> conformers relative to the C<sub>2</sub> structure are little affected.

The energetic results obtained with the largest DZP basis at the SCF DZP optimized geometries are presented in Table II. The zero-point vibrational energies affect the relative energetics very little and thus are not included in this discussion. At the SCF level of theory, the C<sub>s</sub> and C<sub>2</sub> conformers are again very close in energy, with the C<sub>s</sub> being the lower by 0.3 kcal/mol. In this case, it is the imaginary frequency of 62.8 cm<sup>-1</sup> for the C<sub>2</sub> conformer that indicates a breaking of symmetry to C<sub>1</sub> whereas, at the SCF DZd level of theory, it is an imaginary frequency of 142.6 cm<sup>-1</sup> for the C<sub>s</sub> structure that is associated with a normal mode, which breaks symmetry and leads to a C<sub>1</sub> configuration. This mode could indicate motion toward the C<sub>2</sub> conformer since there is no element of symmetry linking the C<sub>s</sub> and C<sub>2</sub> structures. Judging from the small magnitude of the imaginary frequencies, the silicocene potential energy surface appears to be very flat with respect to interconversion between the C<sub>2</sub> and C<sub>s</sub> conformers at both the SCF DZd and SCF DZP levels of theory. The MP2 DZP single-point energies support this hypothesis since the two conformers are separated by only 0.04 kcal/mol.

The energetics of the high-symmetry conformers relative to the low-symmetry species (C<sub>2</sub>, C<sub>s</sub>) change significantly at the SCF DZP level of theory when compared to the values determined with the smaller basis sets. For example, the energy difference between the C<sub>2</sub> and D<sub>5d</sub> conformers decreases significantly from 16.8 (SCF DZd) to 10.9 kcal/mol (SCF DZP). The addition of the polarization functions to the carbon atoms and the larger span of the d functions on the silicon atom offer more flexibility for the highly symmetric D<sub>5d</sub> π-bonded structure compared to the C<sub>s</sub> and C<sub>2</sub> conformers.

The energy difference, ΔE(C<sub>2v</sub>(e-e) - C<sub>2</sub>), also decreases from 7.4 (DZd) to 1.5 kcal/mol (DZP) whereas the energy of the C<sub>2v</sub>(p-p) structure remains consistently at 2-3 kcal/mol above the C<sub>2</sub> structure. Thus the C<sub>2v</sub>(e-e) conformer is now slightly lower in energy (0.6 kcal/mol) than the C<sub>2v</sub>(p-p) species. The imaginary frequency for the C<sub>2v</sub>(e-e) conformer determined with the DZP basis is greatly reduced in magnitude (62.6 cm<sup>-1</sup>) from the DZd values (194.8 and 176.7 cm<sup>-1</sup>) in agreement with the energetic results. The C<sub>2v</sub>(p-p) conformer remains a second-order transition state on going from the DZd to the DZP basis set, with imaginary frequencies of similar magnitude (55.1 and 43.8 cm<sup>-1</sup>, DZP; 71.1 and 35.2 cm<sup>-1</sup>, DZd). The D<sub>5d</sub> conformer is again a high-order transition state at the SCF DZP level of theory, with three negative eigenvalues of the Hessian. A degenerate pair with an imaginary frequency of 105.0 cm<sup>-1</sup> represents a motion toward a bent structure, as was the case with the smaller basis sets. The third imaginary mode (frequency 6.0 cm<sup>-1</sup>) represents a motion that destroys the symmetry relation

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**Table III.** Absolute Energies (hartrees) and Relative Energies (kcal/mol) for the  $(C_5H_5)_2Si$  Structures Using the CPF, CISD, and MP2 Methods with the DZd Basis Set

	CPF <sup>a</sup>		CISD <sup>a</sup>		CISD+Q <sup>a</sup>		MP2 <sup>a</sup>	
	absolute	relative	absolute	relative	absolute	relative	absolute	relative
$C_2$	-674.204 00	0.0	-673.939 24	0.0	-674.093 70	0.0	-674.113 35	0.0
$C_3$	-674.202 23	1.1	-673.938 33	0.6	-674.092 90	0.5	-674.116 50	-2.0
$D_{5d}$	-674.178 90	15.8	-673.915 11	15.1	-674.070 99	14.3	-674.107 48	3.7
$C_{2v}(e-e)$	-674.193 11	6.8	-673.930 53	5.5	-674.085 32	5.3	-674.115 88	-1.6
$C_{2v}(p-p)$	-674.198 76	3.3	-673.934 26	3.1	-674.088 61	3.2	-674.108 53	3.0

<sup>a</sup>Single-point energies determined at the SCF DZd optimized geometries.

of the two rings. This type of motion is consistent with a  $C_3$  minimum.

The relative energies of the conformers determined with methods that include electron correlation in conjunction with the DZd basis are presented in Table III, and the MP2 DZP energies are given in Table II. At this point it should be stressed that the DZd basis is not adequately flexible to quantitatively incorporate the effects of dynamic electron correlation but was used to compare the CPF and CISD results with those of MP2. Thus, while we expect that the trends between the various dynamic electron-correlation techniques will be reliably reproduced with the DZd basis,<sup>35</sup> the absolute magnitude of the differences will certainly change when a more complete one particle basis set is used. The DZP basis, which includes a set of polarization functions on C and two sets of polarization functions on Si, is probably the smallest basis set that could reliably include the effects of dynamic electron correlation.

Analysis of the relative energies presented in Table III indicates that electron correlation favors the high-symmetry species over the low-symmetry species. For example, the relative energy of the  $C_{2v}(e-e)$  conformer ( $\Delta E(C_{2v}(e-e) - C_2)$ ) is lowered by 0.6 (CPF), 1.9 (CISD), 2.1 (CISD+Q), 9.0 (MP2 DZd), and 9.0 (MP2 DZP) kcal/mol from the corresponding SCF prediction. Similarly, the relative energy of the  $D_{5d}$  conformer is also lowered, by 1.0 (CPF), 1.7 (CISD), 2.5 (CISD+Q), 13.1 (MP2 DZd), and 15.6 (MP2 DZP) kcal/mol, compared to the SCF values. However, comparison of the DZd results for the different electron-correlation methods suggests that second-order perturbation theory may overestimate the effects of electron correlation. Nevertheless, the trend that favors the high-symmetry species relative to the  $C_3$  and  $C_2$  conformers is likely to become more pronounced on increasing the flexibility of the basis set at all the correlated levels of theory. It is the combined effect of the flexible one-particle basis set and electron correlation that predicts the energies of the  $C_{2v}(e-e)$ ,  $C_{2v}(p-p)$ , and  $D_{5d}$  conformers relative to the  $C_2$  species to be -7.5, -4.7, and -4.7 kcal/mol, respectively, at the MP2 DZP level of theory. Although the effect of electron correlation as measured by the CISD/CPF methods is smaller, a small effect is all that is required to make the  $C_{2v}(e-e)$  conformer a minimum on the potential energy surface, since at the SCF DZP level of theory, the difference in energy between the  $C_{2v}(e-e)$  and  $C_3$  conformers is only 1.8 kcal/mol. It should be reiterated that the small DZd basis set may considerably underestimate the effects of dynamic electron correlation, due to the lack of correlating functions.<sup>35</sup> Thus, the only conclusion that can be drawn from the energetic results of Table III is that MP2 probably overestimates the effects of electron correlation, but the magnitude of this overestimation is not discernable. These results do suggest that a conformer adopting higher symmetry than  $C_2$  or  $C_3$  may be the minimum energy gas-phase structure of  $(C_5H_5)_2Si$ . Such a result would be consistent with the experimental findings for decamethyl silicocene,  $(C_5Me_5)_2Si$ , and would demonstrate that the  $D_{5d}$  symmetry of decamethyl silicocene is due in part to the electronic structure and not solely the repulsive steric interaction of the methyl groups.

Highly accurate relative energies of the conformers of  $(C_5H_5)_2Si$  are difficult to predict given the obvious importance of electron correlation. Full-geometry optimization at a correlated level of theory followed by an analytic second-derivative determination will possibly lead to a different global minimum energy structure. Such determinations would require large basis sets of triple- $\zeta$  plus double-polarization quality to be quantitative, and although current theoretical methods are capable of full-geometry optimizations at the MP2 DZP level of theory, the cost and available computational facilities make them impractical. Because both basis set augmentation and electron correlation favor the high-symmetry conformers of silicocene, experience<sup>21-25</sup> suggests that the gas-phase minimum energy structure adopts  $D_{5d}$ ,  $D_{5h}$ , or at least  $C_{2v}$  symmetry. However, since a vast quantity of ab initio results on molecules of this size do not exist, we feel that the only definitive conclusion that may be drawn is that the silicocene potential energy surface is very flat with respect to movement of the two Cp rings.

**Table IV.** Predicted Geometrical Parameters for the  $C_3$  Structure of  $(C_5H_5)_2Si^a$ 

	STO-3G*	DZd	DZP
Si-ring 1 centroid ( $X_1$ )	2.701	2.661	2.534
Si-ring 2 centroid ( $X_2$ )	2.124	2.345	2.266
$X_1$ -Si- $X_2$ angle $\theta$	149.2	149.1	152.4
ring normal-Si-ring normal angle $\phi$	72.7	74.7	89.3
angle between Cp rings	107.3	105.3	90.7
Si-C Distances <sup>b</sup>			
Si-C <sub>6</sub> ( $C_3$ )	1.911 (2.880)	1.969 (3.127)	2.003 (2.992)
Si-C <sub>4</sub> ( $C_2$ )	2.755 (2.585)	2.732 (2.803)	2.650 (2.704)
Si-C <sub>5</sub> ( $C_1$ )	3.539 (2.016)	3.467 (2.158)	3.269 (2.159)
Si-C <sub>5'</sub> ( $C_{1'}$ )	3.539 (2.016)	3.467 (2.158)	3.269 (2.159)
Si-C <sub>4'</sub> ( $C_2'$ )	2.755 (2.585)	2.732 (2.803)	2.650 (2.704)
C-C Distances <sup>b</sup>			
C <sub>6</sub> -C <sub>4</sub>	1.512 (1.391)	1.496 (1.404)	1.475 (1.398)
C <sub>4</sub> -C <sub>5</sub>	1.326 (1.415)	1.358 (1.421)	1.357 (1.414)
C <sub>5</sub> -C <sub>5'</sub>	1.475 (1.459)	1.460 (1.460)	1.447 (1.442)
C <sub>5</sub> -C <sub>4'</sub>	1.326 (1.415)	1.358 (1.421)	1.357 (1.414)
C <sub>4</sub> -C <sub>6</sub>	1.512 (1.391)	1.496 (1.404)	1.475 (1.398)
C-H Distances <sup>b</sup>			
C <sub>6</sub> -H	1.087 (1.078)	1.081 (1.068)	1.081 (1.073)
C <sub>4</sub> -H	1.081 (1.083)	1.071 (1.069)	1.075 (1.074)
C <sub>5</sub> -H	1.081 (1.077)	1.070 (1.070)	1.075 (1.074)
C <sub>5'</sub> -H	1.081 (1.077)	1.070 (1.070)	1.075 (1.074)
C <sub>4'</sub> -H	1.081 (1.083)	1.071 (1.069)	1.075 (1.074)

<sup>a</sup>Bond lengths are given in angstroms and angles in degrees. See Figure 1 for the numbering of the carbon atoms. <sup>b</sup>Values in parentheses refer to the second ring.

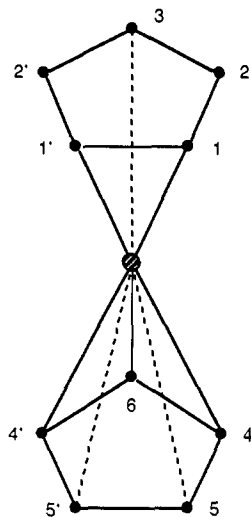
**Table V.** Predicted Geometrical Parameters for the  $C_2$  Structure of  $(C_5H_5)_2Si^a$ 

	STO-3G*	DZd	DZP
Si-ring centroid (X)	2.615	2.576	2.386
X-Si-X angle $\theta$	142.8	146.6	152.3
ring normal-Si-ring normal angle $\phi$	51.3	64.7	90.2
angle between Cp rings	128.7	115.3	89.8
Si-C Distances			
Si-C <sub>1</sub>	3.483	3.417	3.131
Si-C <sub>2</sub>	2.784	2.792	2.675
Si-C <sub>3</sub>	1.887	1.967	2.032
Si-C <sub>4</sub>	2.589	2.542	2.403
Si-C <sub>5</sub>	3.383	3.287	2.980
C-C Distances			
C <sub>1</sub> -C <sub>2</sub>	1.328	1.361	1.368
C <sub>2</sub> -C <sub>3</sub>	1.506	1.484	1.455
C <sub>3</sub> -C <sub>4</sub>	1.515	1.497	1.461
C <sub>4</sub> -C <sub>5</sub>	1.329	1.365	1.375
C <sub>5</sub> -C <sub>1</sub>	1.472	1.455	1.431
C-H Distances			
C <sub>1</sub> -H	1.080	1.069	1.074
C <sub>2</sub> -H	1.081	1.070	1.074
C <sub>3</sub> -H	1.087	1.080	1.078
C <sub>4</sub> -H	1.081	1.071	1.074
C <sub>5</sub> -H	1.082	1.070	1.075

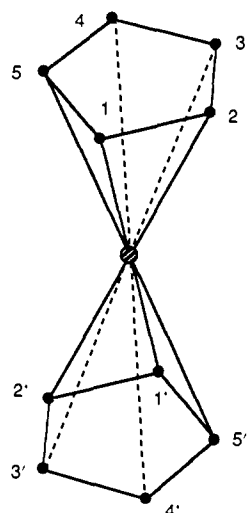
<sup>a</sup>Bond lengths are given in angstroms and angles in degrees. See Figure 2 for the numbering of the carbon atoms.

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The possibility of silicocene possessing a triplet ground state was also investigated. However, the highest occupied molecular orbital and the



**Figure 1.** Pictorial representation of the  $C_s$  conformer of silicocene. Note that the two cyclopentadienyl rings are not symmetry related in this isomer. Symmetry-related atoms are primed.

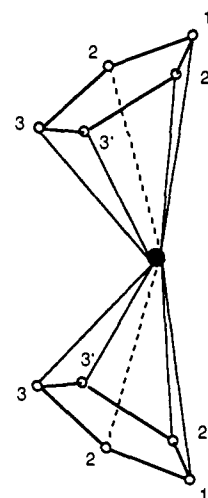


**Figure 2.** Pictorial representation of the  $C_2$  conformer of silicocene. Note that the two cyclopentadienyl rings are symmetry related in this isomer. Symmetry-related atoms are primed.

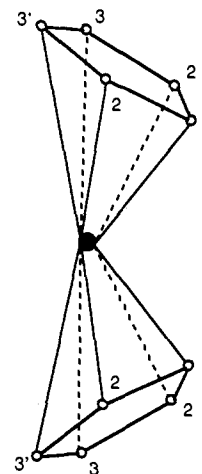
lowest unoccupied molecular orbital for the high-symmetry conformers are both doubly degenerate and so such a triplet state would have to distort to lower symmetry by the Jahn-Teller theorem. Test SCF energies with the DZd basis set for the low-symmetry triplet states were at least 80 kcal/mol higher in energy than the lowest SCF singlet. Therefore, further investigations of triplet states were deemed unnecessary.

**Structures of the Six Conformers of  $(C_5H_5)_2Si$ .** The geometric parameters for the  $C_s$  and  $C_2$  conformers of silicocene are given in Tables IV and V, respectively. For these species, the cyclopentadienyl plane was defined as the "best" plane in terms of a least-squares fit of the carbon atom positions. This procedure was used previously for the structural analysis of the phosphocenium cation.<sup>13</sup> Also note that X defines the centroid of these least-squares fit planes. The greek letter  $\theta$  represents the angle  $X_1-Si-X_2$  or ring one centroid-Si-ring two centroid. The angle  $\phi$  is defined as the supplement to the angle between the two Cp rings. See Figure 1 for the numbering of the carbon atoms for the  $C_s$  structure and Figure 2 for identifying the carbon atoms of the  $C_2$  isomer.

Considering first the  $C_s$  and  $C_2$  conformers, it is evident that as the basis set is improved the two cyclopentadienyl rings become less skewed toward one another, approaching a more symmetric structure. Two independent structural parameters support this conclusion. The angle  $\theta$  increases from 149.2° (STO-3G\*) to 152.4° (DZP) and from 142.8° (STO-3G\*) to 152.3° (DZP) for the  $C_s$  and  $C_2$  conformers, respectively. Even more significant, though, is the large decrease in the angle between the Cp rings. For the  $C_s$  structure this angle ranges from 107.3° (STO-3G\*) to 105.3° (DZd) to 90.7° (DZP). The  $C_2$  species exhibits an even larger change, with this angle varying from 128.7° (STO-3G\*) to 115.3°



**Figure 3.** Pictorial representation of the  $C_{2v}(e-e)$  conformer of silicocene. Note that the two cyclopentadienyl rings are symmetry related in this isomer. Symmetry-related atoms are primed.



**Figure 4.** Pictorial representation of the  $C_{2v}(p-p)$  conformer of silicocene. Note that the two cyclopentadienyl rings are symmetry related in this isomer. Symmetry-related atoms are primed.

(DZd) to 89.8° (DZP). Note, that for both conformers the addition of polarization functions on the carbon atoms and two sets of polarization functions on the silicon atom is vitally important for the proper determination of this angle.

A second interesting basis set effect is the decrease in the range of the Si-C bond distances as the basis is improved. When the STO-3G\* basis is used, the  $C_s$  conformer Si-C bond distances range from 1.911 to 3.539 Å for one cyclopentadienyl ring and 2.016 to 2.880 Å for the other, while for the  $C_2$  conformer the Si-C bond distances range from 1.887 to 3.483 Å (two equivalent rings). The analogous DZP results are 2.003-3.269 and 2.159-2.992 Å for the  $C_s$  structure and 2.032-3.131 Å for the  $C_2$  species. The reduction in the range of the Si-C bond distances together with the decrease in the angle between the Cp rings is indicative of a movement toward a more symmetric structure. When Tables IV and V are examined, it is also evident that the greatest reduction in the range of Si-C distances occurs between the DZd and DZP basis sets, again emphasizing the importance of polarization functions for the proper description of sandwich compounds. After making the above observations, it should not be surprising that the range of C-C bond distances also decreases in going from the STO-3G\* basis set to the much larger DZP basis. In particular, the range of C-C bond distances decreases from 1.328-1.515 (STO-3G\*) to 1.368-1.461 Å (DZP) for the  $C_2$  conformer.

Another interesting feature of the  $(C_5H_5)_2Si$  potential energy surface is the similarity between the  $C_s$  and  $C_2$  structures with increasing theoretical sophistication. For example, the angle  $\theta$  takes the values 149.1° and 146.6° with the DZd basis for the  $C_s$  and  $C_2$  structures, respectively. However, with the larger DZP basis,  $\theta$  has the values 152.4° and 152.3°, respectively. A better example is given by the angle between the Cp rings where the appropriate values are 105.3° ( $C_s$ ; DZd), 115.3° ( $C_2$ ; DZd),

**Table VI.** Predicted Geometrical Parameters for the  $C_{2v}(e-e)$  Structure of  $(C_5H_5)_2Si^a$ 

	STO-3G*	DZd	DZP
Si-ring centroid (X)	2.118	2.337	2.260
$X_1-Si-X_2$ angle $\theta$	155.6	152.5	153.5
ring normal-Si-ring normal angle $\phi$	108.1	103.0	112.3
angle between Cp rings	71.9	77.0	67.7
Si-C Distances			
Si-C <sub>1</sub>	2.815	3.034	2.901
Si-C <sub>2</sub>	2.560	2.764	2.670
Si-C <sub>3</sub>	2.073	2.236	2.239
C-C Distances			
C <sub>1</sub> -C <sub>2</sub>	1.391	1.406	1.400
C <sub>2</sub> -C <sub>3</sub>	1.411	1.420	1.413
C <sub>3</sub> -C <sub>3'</sub>	1.448	1.450	1.433
C-H Distances			
C <sub>1</sub> -H	1.078	1.068	1.074
C <sub>2</sub> -H	1.081	1.069	1.074
C <sub>3</sub> -H	1.076	1.069	1.073

<sup>a</sup> Bond lengths are given in angstroms and angles in degrees. See Figure 3 for the numbering of the carbon atoms.

**Table VII.** Predicted Geometrical Parameters for the  $C_{2v}(p-p)$  Structure of  $(C_5H_5)_2Si^a$ 

	STO-3G*	DZd	DZP
Si-ring centroid (X)	2.635	2.594	2.297
$X_1-Si-X_2$ angle $\theta$	152.1	156.5	158.4
ring normal-Si-ring normal angle $\phi$	58.8	76.2	112.2
angle between Cp rings	121.2	103.8	67.8
Si-C Distances			
Si-C <sub>1</sub>	1.893	1.978	2.119
Si-C <sub>2</sub>	2.704	2.677	2.474
Si-C <sub>3</sub>	3.458	3.356	2.899
C-C Distances			
C <sub>1</sub> -C <sub>2</sub>	1.511	1.490	1.436
C <sub>2</sub> -C <sub>3</sub>	1.328	1.364	1.392
C <sub>3</sub> -C <sub>3'</sub>	1.472	1.451	1.410
C-H Distances			
C <sub>1</sub> -H	1.086	1.078	1.073
C <sub>2</sub> -H	1.081	1.071	1.074
C <sub>3</sub> -H	1.081	1.070	1.073

<sup>a</sup> Bond lengths are given in angstroms and angles in degrees. See Figure 4 for the numbering of the carbon atoms.

90.7° ( $C_3$ ; DZP), and 89.8° ( $C_2$ ; DZP). Further evidence suggesting the increasing similarity of the  $C_2$  and  $C_3$  conformers is given by the decrease in the magnitude of the imaginary frequency of the transition state with basis set improvement. Specifically, the imaginary frequency with the DZd basis is 142.6  $cm^{-1}$  ( $C_3$  conformer) while with the DZP basis set it is only 62.8  $cm^{-1}$  ( $C_2$  conformer).

The geometric parameters for the  $C_{2v}$  conformers are given in Tables VI and VII. See Figures 3 and 4 for the numbering of the carbon atoms. The two  $C_{2v}$  structures show markedly dissimilar behavior with respect to augmentation of the basis set. Like the lower symmetry structures, the  $C_{2v}(p-p)$  conformer exhibits a large decrease in the angle between Cp rings (121.2°, STO-3G\*; 67.8°, DZP), a reduction in the range of Si-C distances (1.565 Å, STO-3G\*; 0.780 Å, DZP), and a reduction in the range of C-C bond lengths (0.183 Å, STO-3G\*; 0.044 Å, DZP). Note that these trends are again indicative of movement toward a more

symmetric structure. The structural parameters of the  $C_{2v}(e-e)$  conformer do not change significantly on going from the STO-3G\* basis to the DZP basis, unlike those for the  $C_{2v}(p-p)$  conformer. However, the DZP geometries of both the  $C_{2v}$  conformers show many similarities. For example, both have a very similar angle between ring planes (67.7°,  $C_{2v}(e-e)$ ; 67.8°,  $C_{2v}(p-p)$ ), range in Si-C distances (0.780 Å,  $C_{2v}(p-p)$ ; 0.662 Å,  $C_{2v}(e-e)$ ), and range in C-C bond lengths (0.044 Å,  $C_{2v}(p-p)$ ; 0.030 Å,  $C_{2v}(e-e)$ ).

Although the  $C_{2v}(p-p)$  equilibrium structure changes significantly with respect to basis set enlargement, its energy relative to the lowest symmetry conformers does not change dramatically. Conversely, the  $C_{2v}(e-e)$  equilibrium structure is little affected by improvements in the basis set, but the relative energetics are considerably altered on going from the DZd to the DZP basis set. This may be understood by considering the angle between ring planes determined for the  $C_{2v}(e-e)$ ,  $C_{2v}(p-p)$ , and  $C_2$  conformers with the DZd and DZP basis sets. The difference between this angle for the  $C_{2v}(p-p)$  and  $C_2$  conformers is 11.5° and 22.0° for the DZd and DZP basis sets, respectively, whereas the corresponding differences between the  $C_{2v}(e-e)$  and  $C_2$  conformers are 38.3° (DZd) and 22.1° (DZP). The larger relative change and the direction of the change for the  $C_{2v}(e-e)$  conformer could thus explain the drop of 5.9 kcal/mol between the relative energies of the  $C_{2v}(e-e)$  and  $C_2$  structures on going from the DZd to the DZP basis set.

The structural similarities between the  $C_{2v}(e-e)$  and  $C_{2v}(p-p)$  conformers at the DZP level results in the imaginary frequencies of the two structures now having the same order of magnitude (62.6  $cm^{-1}$ ,  $C_{2v}(e-e)$ ; 71.1 and 35.2  $cm^{-1}$ ,  $C_{2v}(p-p)$ ), corresponding to motions to a lower symmetry structure (62.6 and 71.1  $cm^{-1}$ ) and to a "pseudorotation" of one ring relative to the other for the  $C_{2v}(p-p)$  conformer (35.2  $cm^{-1}$ ). Furthermore, the energetics determined at the SCF DZP level of theory show that the  $C_3$ ,  $C_2$ ,  $C_{2v}(e-e)$ , and  $C_{2v}(p-p)$  conformers lie within a range of 2.4 kcal/mol, indicating that the potential surface is very flat in this region.

The  $D_{5h}$  and  $D_{5d}$  optimized structural parameters are listed in Table VIII. The obvious difference between the high-symmetry species and the lower symmetry conformers is the large reduction in the number of independent nuclear degrees of freedom. Namely, the  $D_{5h}$  and  $D_{5d}$  structures have only four unique nuclear coordinates as compared to the  $C_3$  and  $C_2$  conformers, which have 29 unique coordinates.

The most notable basis set effect found for the  $D_{5h}$  and  $D_{5d}$  conformers is the increase in the Si-C distance. In particular, the Si-C distance changes from 2.339 (STO-3G\*) to 2.523 Å (DZP) for the  $D_{5d}$  species. However, this increase is due to the larger *s,p* basis set as shown by the slight decrease in the Si-C distance in going from the DZd (2.568 Å) to the DZP (2.523 Å) basis set. This parameter may alternatively be represented by the Si-ring centroid distance, 2.010 (STO-3G\*), 2.266 (DZd), and 2.219 Å (DZP).

For comparison, the  $D_{5d}$  MNDO optimized structural parameters<sup>14</sup> of  $(C_5H_5)_2Si$  and the reported structural parameters<sup>12</sup> of  $(C_5Me_5)_2Si$  are also listed in Table VIII. The MNDO structure is quite different from the DZP ab initio structure, with the Cp rings being significantly closer to the silicon atom yielding a Si-C distance of only 2.198 Å. The DZP SCF Si-C and Si-X distances are quite similar to those determined experimentally for the full methyl derivative. For both quantities, the ab initio values are approximately 0.1 Å larger. The ab initio and experimental C-C bond lengths are not as comparable since the experimental value represents an average of the  $D_{5d}$  and bent structures.

**Bonding in  $(C_5H_5)_2Si$ .** Labeling a cyclopentadienyl ring as  $\eta^5$ ,  $\eta^2$ , or  $\eta^n$  bonded to the central silicon atom is necessarily somewhat arbitrary. One standard of comparison would be to compare a typical Si-C bond length with the Si-C distances in  $(C_5H_5)_2Si$ . This method was utilized in the study of the phosphocanium cation.<sup>13</sup> However, from comparison of the experimental Si-C bond length in methylsilane,  $H_3CSiH_3$ , of 1.867 Å<sup>36,37</sup> and the corresponding SCF DZP value of 1.880 Å<sup>38</sup> with the

**Table VIII.** Predicted Geometrical Parameters for  $D_{5h}$  and  $D_{5d}$  Structures of  $(C_5H_5)_2Si^a$ 

	STO-3G*		DZd		DZP	MNDO <sup>b</sup>	expt <sup>c</sup>
	$D_{5h}$	$D_{5d}$	$D_{5h}$	$D_{5d}$	$D_{5d}$	$D_{5d}$	$D_{5d}$
Si-ring centroid (X)	2.010	2.010	2.266	2.267	2.219	1.826	2.11
Si-C distance	2.339	2.339	2.568	2.568	2.523	2.198	2.42
C-C distance	1.405	1.405	1.419	1.419	1.410	1.438	1.394
C-H distance	1.078	1.078	1.068	1.068	1.074		
Si-X-H angle	89.4	89.4	90.7	90.7	90.1		

<sup>a</sup> Bond lengths are given in angstroms and angles in degrees. <sup>b</sup> From ref 15. <sup>c</sup> Experimental data for decamethyl silococene from ref 12.

**Table IX.** Mulliken Orbital Populations of the Silicon Atom in the C<sub>s</sub>, C<sub>2</sub>, and D<sub>5d</sub> Conformers of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Si Using the DZP Basis Set

	C <sub>s</sub>	C <sub>2</sub>	C <sub>2v</sub> (e-e)	C <sub>2v</sub> (p-p)	D <sub>5d</sub>
s	5.98	5.98	6.01	6.00	6.00
p <sub>x</sub> + p <sub>y</sub>	5.13	5.15	5.09	5.09	4.86
p <sub>z</sub>	2.38	2.35	2.30	2.33	2.29
d	0.08	0.08	0.17	0.15	0.34
Total Atomic Population					
Si	13.57	13.56	13.58	13.57	13.51

experimental Si-C distance in decamethyl silicocene (2.42 Å), this approach seems inappropriate in this case. An alternative method would be to use the Si-C distance of the SCF DZP high-symmetry D<sub>5d</sub> conformer as the standard of comparison, since this structure certainly exhibits η<sup>5</sup> bonding between the Cp rings and the central silicon atom. This distance defined by the SCF DZP level of theory is within 0.1 Å of the experimental determination for (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Si. Therefore, we discuss the bonding in the C<sub>s</sub>, C<sub>2</sub>, and C<sub>2v</sub> conformers based on an upper limit of 2.523 Å, the Si-C distance for the D<sub>5d</sub> conformer (SCF DZP). The C<sub>2</sub> structure is then defined to have η<sup>2</sup> bonding to each ring (Si-C = 2.03 and 2.40 Å) comparable to the C<sub>2</sub> conformer of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>P<sup>+</sup>. The C<sub>s</sub> structure exhibits η bonding to one ring (Si-C = 2.00 Å) and η<sup>2</sup> bonding to the other ring (Si-C = 2.16 and 2.16 Å), similar to the C<sub>s</sub> conformers of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>P<sup>+</sup> and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>As<sup>+</sup>. Both rings of the C<sub>2</sub> structure and the ring of the C<sub>s</sub> structure, which is η bonded to the Si atom and most closely approaches the Si atom via a unique carbon atom, display a reasonable degree of alternation of C-C bond lengths, namely, 1.455, 1.368, 1.431, 1.375, and 1.461 Å for the C<sub>2</sub> conformer and 1.475, 1.357, 1.447, 1.357, and 1.475 Å for the C<sub>s</sub> conformer. The second ring of the C<sub>s</sub> conformer, which is η<sup>2</sup> bonded to the silicon atom, displays much less bond alternation. We note, however, that if the SCF STO-3G\* C-C bond lengths were used in this analysis, then a different picture of the bonding in the cyclopentadienyl rings would emerge. Namely, there is significantly greater bond alternation in these rings, leading to a view of the cyclopentadienyl rings as having very localized single and double bonds. Therefore, it is important to stress the necessity of using large basis sets in ab initio studies of loosely bound π-bonded complexes in order to obtain a reliable description of the bonding.

On the basis of our model, the C<sub>2v</sub>(e-e) conformer exhibits η<sup>2</sup> bonding to each Cp ring (Si-C = 2.24 and 2.24 Å) while the C<sub>2v</sub>(p-p) structure shows η<sup>2</sup> bonding to each Cp ring (Si-C = 2.12, 2.47, and 2.47 Å), similar to the analogous conformers of the phosphocenium cation.<sup>13</sup> The C-C bonding in the rings of the C<sub>2v</sub> conformers is much more equivalent than for the C<sub>2</sub> and C<sub>s</sub> conformers, with a maximum range of 0.044 Å. Moreover, the average C-C distance in the C<sub>2v</sub> structures (1.413 Å, C<sub>2v</sub>(p-p); 1.412 Å, C<sub>2v</sub>(e-e)) closely approaches the C-C bond distance in the D<sub>5d</sub> conformer (1.410 Å). Thus, the Cp rings are best viewed as having a delocalized π structure around the ring.

Comparing the DZP SCF Si-C distances for the C<sub>s</sub>, C<sub>2</sub>, and C<sub>2v</sub> structures with the Si-C distance for the D<sub>5d</sub> conformer, we note that the C<sub>2v</sub>, C<sub>2</sub>, and C<sub>s</sub> conformers exhibit maximum deviations of 16, 24, and 30%, respectively. Therefore, it should not be surprising that the C<sub>2v</sub> conformers exhibit a greater degree of π bonding to the Cp rings. As a final note concerning the extent of π bonding present in the different silicocene conformers, we point out that had this analysis been performed with only the SCF STO-3G\* data, different conclusions would have resulted. For example, the C<sub>2v</sub>(p-p) structure would have been labeled as η bonded for each Cp ring. Therefore, we again emphasize the necessity of including in the basis set a minimum of one set of polarization functions on the carbon atom and two sets of polarization functions on the silicon atom.

Mulliken population analyses are reported in Table IX for the C<sub>s</sub>, C<sub>2</sub>, C<sub>2v</sub>(e-e), C<sub>2v</sub>(p-p), and D<sub>5d</sub> conformers at the SCF DZP level of theory. It must be realized that these values are somewhat arbitrary since they are based on a nonunique partitioning scheme,<sup>39</sup> however, the trends

between the different isomers at the same level of theory should be reproducible and give insight into the bonding present in the different conformers of silicocene. On the basis of the data in Table IX, it is clear that the relative importance of d functions changes between the various isomers. As the system becomes more symmetric, the d function population increases: 0.08 (C<sub>s</sub>), 0.08 (C<sub>2</sub>), 0.15 (C<sub>2v</sub>(p-p)), 0.17 (C<sub>2v</sub>(e-e)), and 0.34 (D<sub>5d</sub>). It is well established that silicon has energetically low-lying d orbitals, and from these studies it would appear that symmetric structures allow more d function participation in the bonding. Electron correlation should also favor the highly symmetric forms since inclusion of electron-correlation effects generally increases the polarization function participation in the molecular bonding.

Comparison of the total silicon electron populations, which are 13.57 (C<sub>s</sub>), 13.56 (C<sub>2</sub>), 13.58 (C<sub>2v</sub>(e-e)), 13.57 (C<sub>2v</sub>(p-p)), and 13.51 (D<sub>5d</sub>), shows that the moderate amount of charge transfer from the silicon atom to the two Cp rings remains fairly constant for all the structures and, therefore, should not have a large differential effect on the conformations of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Si.

### Concluding Remarks

We have presented results of the first ab initio study of the dicyclopentadienyl sandwich compound silicocene. The simplest ab initio method (SCF STO-3G\*) predicts silicocene to adopt a low-symmetry, bent structure. The trends in energetics on increasing the basis set from STO-3G\* to DZP at the SCF level for the C<sub>s</sub>, C<sub>2</sub>, and C<sub>2v</sub> conformers of silicocene indicate that the effect of enlarging the basis set stabilizes the C<sub>2v</sub> conformers relative to the C<sub>s</sub> and C<sub>2</sub> conformers. There is also a dramatic lowering in energy of the D<sub>5d</sub> structure relative to the C<sub>s</sub> and C<sub>2</sub> structures.

Accepting that a unique partitioning scheme for the atomic orbital analysis of SCF electronic wave functions does not exist and that any method used is in some way biased, we have performed atomic orbital population analyses of the DZP SCF electronic wave functions using the well-known Mulliken approach. These analyses demonstrate that the Si d orbital population of the D<sub>5d</sub> and C<sub>2v</sub> symmetry species is larger than for the C<sub>s</sub> and C<sub>2</sub> conformers. Thus, since the symmetric conformers have more silicon d orbital participation in the bonding, this trend in energetics is likely to continue with augmentation of basis set, particularly including a complete span of polarization functions. Furthermore, the effects of dynamic electron correlation appear to lower the symmetric species relative to the C<sub>2</sub> and C<sub>s</sub> conformers. Thus, the reason silicocene may adopt a high-symmetry conformation is due to the low-lying d orbitals of silicon and because the more symmetric structures increase the Si d orbital participation in the bonding.

Although, the C<sub>2v</sub> structures are closer energetically to the C<sub>2</sub> and C<sub>s</sub> structures, the geometric parameters show many similarities with a more highly symmetric species. For the C<sub>2v</sub>(e-e) conformer, the range in Si-C distances is much reduced from that determined for the C<sub>2</sub> and C<sub>s</sub> conformers and lies within 15% of the D<sub>5d</sub> Si-C bond distance with an associated range in C-C bond lengths of only 0.030 Å. It remains to be seen whether the effects of larger basis sets and electron correlation will reduce the angle between ring planes by the 68° required to make the D<sub>5d</sub> or D<sub>5h</sub> conformer a global energy minimum on the potential energy surface.

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