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Geometric and Electronic Structure of Carbocene, $(C_5R_5)_2C$, versus Silicocene, $(C_5R_5)_2Si$ (R = H, Me)[†]

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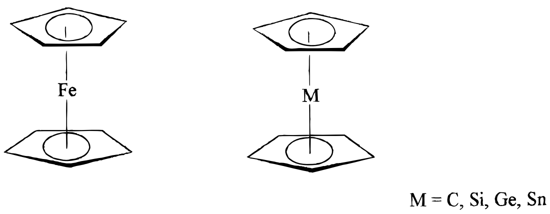
The electronic structures of carbocene and silicocene have been investigated by density functional calculations. Accordingly, carbocene behaves entirely different compared to silicocene. The former prefers a classical dicyclopentadienylcarbene structure, while the latter adopts a slightly distorted sandwich structure. Methyl substitution at the cyclopentadienyl unit does not exert a considerable effect on the resulting equilibrium structure. A detailed analysis of the electron distribution based on an analysis of the Laplacian of the charge density is given.

Introduction

Since the π-bonded D_{5d} structure was suggested for ferrocene (**1**; Chart 1) for the first time in 1952[1] considerable interest has arisen in the cyclopentadienyl sandwich compounds Cp_2M ($Cp = C_5H_5$) with M being a main-group element. With respect to the group 14 sandwich compounds the first representative was plumbocene, synthesized by Fischer and Grubert.[2] It possesses a polymeric zigzag structure in the solid state with bridging cyclopentadienyl rings.[3] In the gas phase it is monomeric, and electron-diffraction measurements determine an angle of 45 ± 15° between the ring planes and a mean Pb−C distance[4] of 2.78 Å. These principal bonding features are also preserved for the fully methylated derivative, $(C_5Me_5)_2Pb$.[5]

In contrast to the highly symmetric structure adopted by ferrocene, structure determinations of the group 14 sandwich compounds **2** (M = Sn, Ge, Si) have shown that the majority of these compounds take up a bent conformation with concomitant variation in the M−C bond distances; e.g., for the lower element homologue stannocene, Cp_2Sn, electron diffraction measurements have shown[4] a bent structure with a ring plane angle of ∼55°. Later X-ray analysis determined this compound to be monomeric in the solid phase with two bent structures in the crystal form.[5,6] Electron diffraction measurements were reported for $(C_5H_4CH_3)_2Sn$ and reveal this structure also to be bent at the central main-group atom.[6] An X-ray analysis of the permethyl derivative, $(C_5Me_5)_2Sn$, yields two conformers with ring plane angles of 36.4 and 35.4°.[7] It has been argued[6] that full methyl substitution favors a less bent structure with respect to the action of considerable steric effects between the methyl groups at the two ring systems. However, the variation in the Sn−C bond lengths is almost uneffected. Nevertheless, in decaphenylstannocene[8] the cyclopentadienyl rings are arranged in a highly symmetrical structure. Here the five Sn−C bonds are equivalent (2.689 Å) and the ring centroid−Sn−ring centroid angle is 180.0°.

Chart 1



1 **2**

Germanocene, $(C_5H_5)_2Ge$, first synthesized in 1973,[9] has been characterized as having a bent structure by X-ray analysis.[10] The angle between the ring planes is 50.4°, and a range of Ge−C distances from 2.347 to 2.730 Å has been observed. A structural determination for the fully methylated derivative $(C_5Me_5)_2Ge$[7] is available, and the dimethyl derivative of germanocene has been studied by electron diffraction in the gas phase.[6] All these investigations also reveal bent structures for germanocene. To this end the synthesis and structural investigation of decamethylsilicocene[11] is in line with the observations made for the higher main-group-element homologues of the metallocenes. $(C_5Me_5)_2Si$ adopts a highly symmetric D_{5d} structure in the crystal

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[†] Dedicated to Prof. P. Jutzi on the occasion of his 60th birthday.

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form. However, a second conformer, thought to arise from crystal-packing effects, was found with a bent structure. The Si−C distances range there from 2.34 to 2.55 Å. Experimental studies have also been reported on group 13 and group 15 element homologues (e.g., metallocene cations of arsenic and antimony[12]). The reader is referred to recent review articles which thoroughly cover these aspects.[13−15]

Quantum chemical investigations on main-group-element metallocenes have been carried out on the basis of semiempirical as well as ab initio calculations. Two semiempirical SCF studies on silicocene were reported.[16,17] The first study reports a global energy minimum with a D_{5d} structure, while the second favors a C_{2v} energy minimum. An ab initio quantum chemical study has been reported on unsubstituted germanocene.[6] However, the structure was not fully optimized. Furthermore, molecular mechanics calculations have been performed to study the bending mode in the metallocene sandwich structure.[18,19] The influence of bulky substituents was analyzed. It was stated that when the distance between the cyclopentadienyl rings is small, i.e., a central atom with a small radius, bulky substituents enforce a parallel arrangement of the two rings. Quantum chemical calculations of higher quality that consider the various possible conformations and utilize flexible basis sets have been reported only for the parent silicocene,[20] $(C_5H_5)_2Si$, and its related phosphocenium cation, $(C_5H_5)_2P^+$.[21]

In the present quantum chemical study we present a structural investigation of the experimentally hitherto unknown carbocene, $(C_5H_5)_2C$. We will compare our results with corresponding investigations on silicocene, $(C_5H_5)_2Si$. Finally, the fully methylated derivatives will be energy-optimized at the DFT level. Their structures have been determined without any geometrical constraints in the energy optimizations. Thus our results allow us to predict the experimental structures, i.e., the permethylated derivatives of these metallocenes. The basis of our investigations are calculations of double-ζ and triple-ζ quality for the basis sets within the density functional formalism.[22,23] The latter method was chosen in order to account for the electron correlation contribution within these molecular structures. In the interest of quality we determined rigorously the structures of D_{5d}, D_{5h}, C_{2v}, C_s and C_2 conformers of (parent) carbocene and silicocene. All variables within these symmetry constraints were optimized, and the nature of the various stationary points on the electronic hypersurfaces was characterized by analysis of the Hessian matrixes. The various conformers of carbocene and silicocene properly encompass all different reported equilibrium structures of the group 14 dicyclopentadienyl compounds.

Theoretical Procedure

All of the structures were calculated first at the SCF level of theory and then refined by energy optimization within the density functional formalism. For the latter we used the three-parameter functional of Becke[23] with the nonlocal correlation contributions provided by the LYP expression.[24] Analytical gradients were employed throughout. Since the resulting electronic hypersurfaces appear very flat, tight optimization criteria had to be used. The structures were optimized such that all Cartesian gradients were less than 10^{-6} au. For the cases at hand it is particularly important to use flexible basis sets in the calculations. We have chosen in all calculations the 6-31g(d) basis set,[25−26] which is of double-ζ quality. In addition it is augmented by a single set of polarization functions at the heavy atoms.[27] On the optimized geometries single-point calculations were performed for the parent compounds with a triple-ζ basis[28,29] and two sets of polarization functions at the heavy atoms (6-311g(2d,1p)). The importance of electron correlation on the energy balances of the various structures was additionally analyzed at a MP2[30,31] and a CCSD(t)[32] level of sophistication, utilizing the density functional (DFT) optimized geometries. On this basis we ensured that the DFT method accounts in a proper way for the different amounts of electron correlation contributions in the various structures. All of the quantum chemical calculations were performed with the Gaussian set of programs.[33]

Results and Discussion

(a) Qualitative Considerations. We begin the discussion with a consideration of the molecular orbitals of D_{5d}-symmetrical carbocene. In a simplified manner[34] the molecule can be partitioned into Cp_2^{2-} (A) and C^{2+} (B) units. The nodal characteristics and phase relationships of the Cp units (A) with respect to the central carbon atom (B) are illustrated in a shorthand notation, as shown in Chart 2. A corresponding interaction diagram is depicted in Figure 1.

We note that Figure 1 accounts for a staggered conformation (D_{5d} symmetry), which is the least sterically hindered arrangement of Cp units. The Cp_2^{2-}

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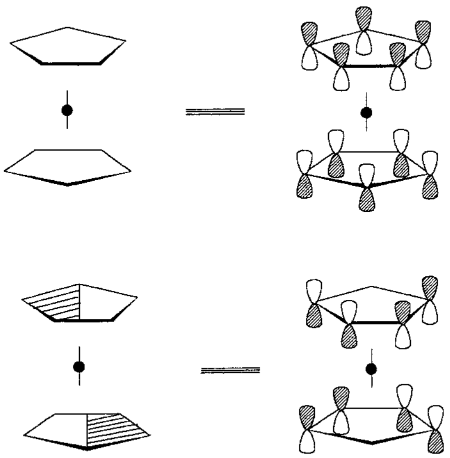
Chart 2



molecular orbitals interact in a different manner with the orbitals at the central atom. The a_{1g} orbital (fragment A) interacts with the s orbital at the central carbon atom (B). Most strongly pronounced is the interaction of the p_z orbital (at B) with the a_{2u} molecular orbital of the Cp_2 fragment (A). The overlap among the e_{1u} orbitals is rather weak; it is caused by a subfrontier orbital interaction with the construction of a π bond.[34,35] For symmetry reasons there is no interaction of the e_{1g} orbitals at A with the orbitals at fragment B. This is an essential difference in the construction of bonding with (classical) ferrocene. As indicated in Chart 3, within D_{5d} symmetry the d orbitals split into the components $a_g(d_{z^2})$, $e_{2g}(d_{x^2-y^2},d_{xy})$, and $e_{1g}(d_{xz},d_{yz})$.

The degenerate e_{1g} set is capable of forming strong π-bonds with the Cp units. Such an interaction is absent for the main-group metallocenes. On this basis ferrocene adopts a more tightly bound sandwich structure than those of metallocenes having heavier main-group elements as the central atom. It is in conformity with the experimental observations that group IV metallocenes tend to reduce their D_{5d} structure to lower symmetry. This allows a stronger mingling of the orbitals at A with those at B. A more detailed analysis of the electron density distributions in the various metallocenes (vide infra) supports this view.

(b) Parent Carbocene versus Silicocene. To put the discussion on firmer ground, we first performed quantum chemical calculations at an ab initio level on the parent carbocene and silicocene, with assumption of various symmetry constraints for the structures. The various structures obtained from the optimization of carbocene and silicocene are depicted in Figure 2. The corresponding structural parameters (bond lengths in Å and bond angles in degrees) are collected in Tables 1−3.

The corresponding relative energies at the various quantum chemical levels of sophistication are listed in Table 4.

In the investigations the highly symmetrical sandwich structure (D_{5d} symmetry) is taken as a reference. At the b3lyp/6-31g* level of sophistication the C−C distances between the central carbon and the peripheral Cp carbon atoms amount to 2.242 Å. This may be compared with D_{5d} symmetry optimized parent silicocene with a C−Si distance of 2.519 Å. We note that corresponding D_{5h}-symmetrical structures for carbocene and silicocene are slightly higher in energy (2 kcal/mol) at the b3lyp/6-31g* level of optimization.[36]

Table 1. Predicted Geometry Parameters for the C_{2v} Structure of Carbocene (M = C) and Silicocene (M = Si, in Parentheses)

type	bond length (Å), bond angle (deg)
M−C(1)	1.871 (2.280)
M−C(2)	2.516 (2.639)
M−C(3)	2.828 (2.837)
C(1)−C(1′)	1.446 (1.435)
C(1)−C(2)	1.423 (1.422)
C(2)−C(3)	1.401 (1.407)
∠C(1)MC(1)	110.4 (97.4)
∠MC(1)C(2)	98.7 (87.7)
∠ MC(1)C(1′)	67.3 (71.7)

Table 2. Predicted Geometry Parameters for the C_s Structure of Carbocene (M = C) and Silicocene (M = Si, in Parentheses)

type	bond length (Å), bond angle (deg)
M−C(1)	1.730 (2.268)
M−C(2)	2.475 (2.647)
M−C(3)	2.844 (2.855)
M−C(4)	1.543 (2.201)
M−C(5)	2.459 (2.448)
M−C(6)	3.317 (2.796)
C(1)−C(1′)	1.454 (1.437)
C(1)−C(2)	1.427 (1.422)
C(2)−C(3)	1.398 (1.407)
∠C(1)MC(4)	107.0 (97.2)
∠MC(1)C(2)	102.8 (88.6)
∠MC(1)C(1′)	65.1 (71.5)
∠MC(4)C(5)	107.2 (81.8)

Table 3. Predicted Geometry Parameters for the C_2 Structure (^{1}A State) of Carbocene (M = C) and Silicocene (M = Si, in Parentheses)

type	bond length (Å), bond angle (deg)
M−C(1)	1.501 (2.223)
M−C(2)	2.204 (2.329)
M−C(3)	2.456 (2.573)
M−C(4)	3.068 (2.715)
M−C(5)	3.187 (2.848)
∠C(1)MC(1′)	111.1 (97.7)
∠MC(1)C(2)	93.7 (75.7)
∠MC(1)C(3)	109.8 (86.8)

It is apparent from the quantum chemical results on the parent systems that carbocene and silicocene are structurally different species, although they are valence isoelectronic. Essential differences in bonding are mainly due to the different sizes of the central main-group element, silicon versus carbon. A more detailed analysis on the basis of electron density differences will be given in section d of this paper. For both structures the vibrational analysis predicts two imaginary frequencies. These refer to two degenerate bending motions. For carbocene symmetry reduction causes a considerable drop in energy. The most stable structure (^{1}A state) refers to C_2 symmetry. It corresponds to a carbene with

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(36) Rapidly rotating rings have been established for the related ferrocene. The energy barrier to ring rotation is estimated to be 1−3 kcal/mol.[14]

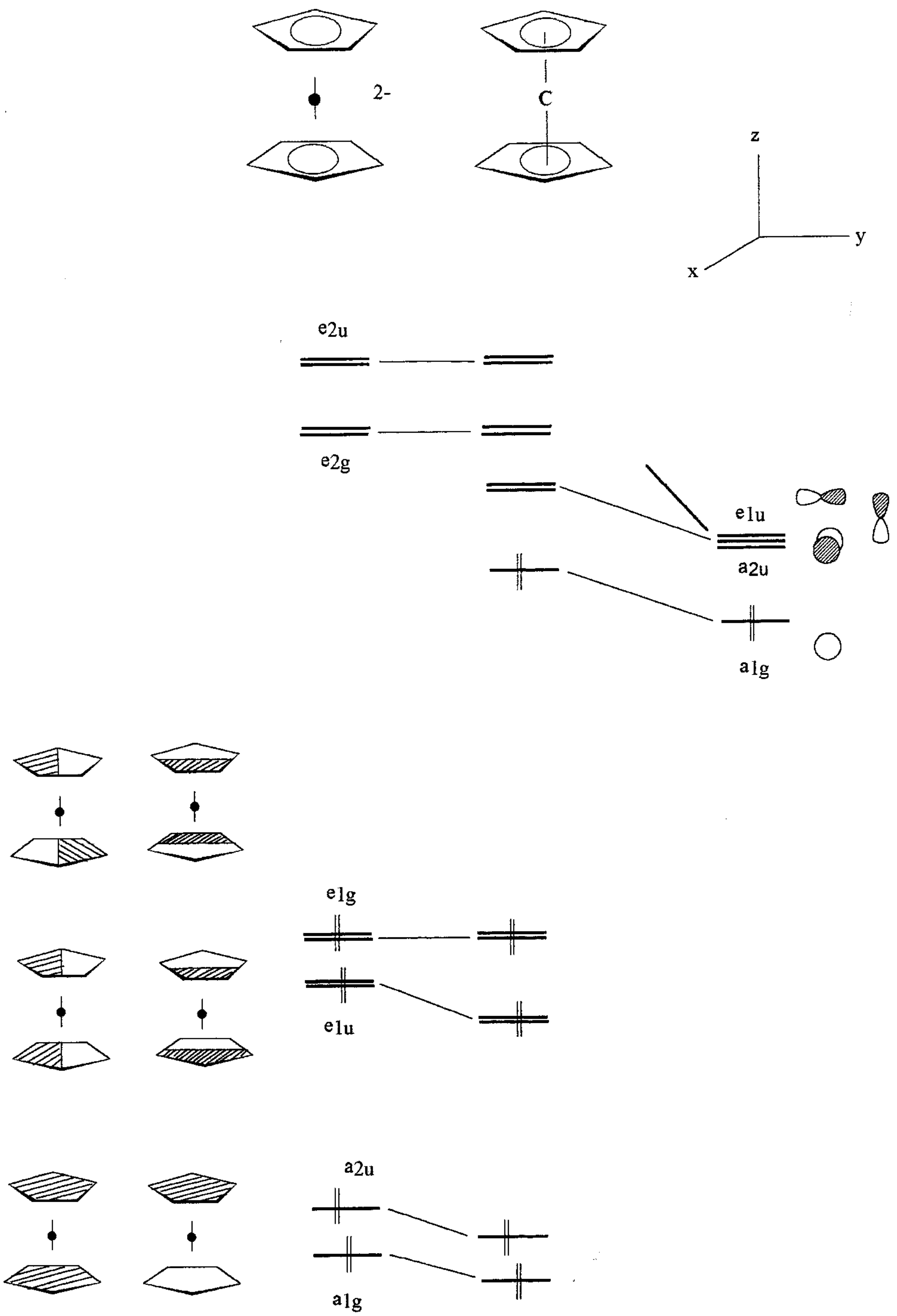

Figure 1. Construction of the molecular orbitals of carbocene from Cp_2^{2-} (A) and C^{2+} (B).

two almost exclusively η^1-bonded Cp rings. A triplet state (^{3}B) is 4 kcal/mol less stable than the singlet state. In the singlet state the central carbon atom tends to adopt a weak η^3 coordination. For carbocene the lowest energy species is in fact a structural isomer, the phenylcyclopentadiene which results from carbene rearrangement. It is 160.7 kcal/mol lower in energy than the D_{5d} structure. A plot with the Molden program[37] of the two energy lowest relevant isomers is shown in Figure 3.

Interestingly, the C_2-symmetrical structure is predicted to be an energy minimum on the electronic hypersurface. The calculations predict unequal bond lengths (2.2, 2.5 Å) from the central to the geminal carbon atoms at the Cp units. Thus, it would be of interest to design corresponding experiments to analyze in more detail the bonding situation of dicyclopentadienylcarbene. Although our calculations predict phenylcyclopentadiene to be much lower in energy (>100 kcal/mol) than the D_{5d} carbocene, our results do not make any prediction about the energy barrier which separates these two species.

In comparison, the parent silicocene does not tend to gain considerable energy by symmetry reduction. The drop in energy from D_{5d} symmetry amounts to −4.0 (C_s) and −4.1 kcal/mol (C_2). This is in agreement with the experimental X-ray analysis on decamethylsilicocene.[11]

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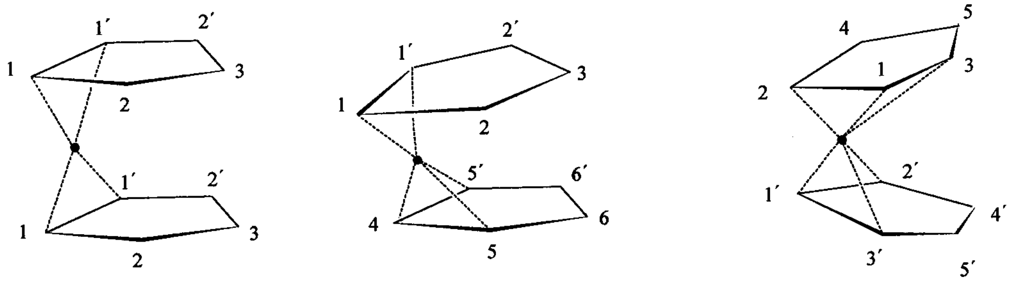
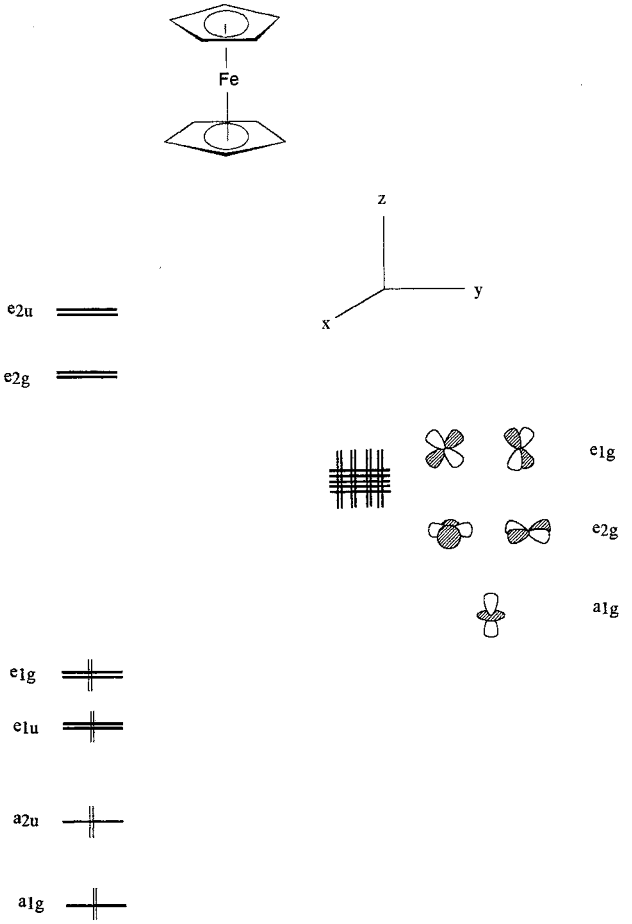
[37] The Molden program was written by G. Schaftonaar.



(C2v) (Cs) (C2)

Figure 2. Pictorial representation of the various conformers of the parent carbocene (silicocene).

Chart 3



The view that silicocene has only a relatively weak deformation potential from high symmetry (D_{5d}) to lower symmetry (C_s, C_2) has been further substantiated by single-point calculations with the optimized geometries at a higher computational level, DFT2 and CCSD(t), as summarized in Table 4. For carbocene corresponding calculations at an improved level were not attempted.

(c) Permethyl Substitution. One may question the influence of the methyl groups on the actual hapticities of silicocene and carbocene. In fact, on the basis of semiempirical calculations it has been argued that the substituents play an essential role.[18] Hitherto the ab initio calculations reported on silicocene[20] have been restricted to an analysis of bonding of the experimentally unknown parent compound. Thus, more accurate quantum chemical calculations on the permethyl-substituted metallocenes are lacking.

Table 4. Relative Energies (in kcal/mol) of Various Conformers and Negative Eigenvalues (*N*), at Various Levels of Sophistication[a]

structure	sym	DFT1[b]	DFT2[c]	CCSD[d]	*N*[e]
$\eta^5-\eta^5$	D_{5d}	0.0	0.0	0.0	2
		0.0	0.0	0.0	2
$\eta^2-\eta^2$	C_{2v}	−22.9			2
		−3.8	−4.1	−4.0	2
$\eta^2-\eta^1$	C_s	−42.3			1
		−4.0	−4.4	−4.3	0
$\eta^3-\eta^3$	C_2 (^{1}A)	−49.4			0
		−4.1	−4.4	−4.4	0
	C_2 (^{3}B)	−45.4			0

[a] The first entry given for each structure and symmetry is for carbocene, and the second entry is for silicocene. [b] b3lyp/6-31g(d). [c] b3lyp/6-311g(2d,1p)//b3lyp/6-31g(d). [d] CCSD(t)/6-31g(d)//b3lyp/6-31g(d). [e] Number of imaginary eigenvalues in the vibrational analysis (harmonic approximation).

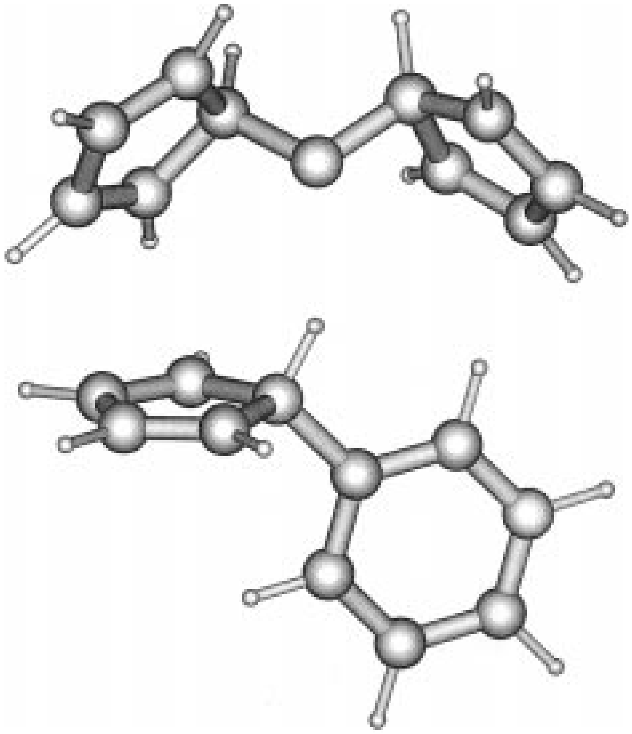


Figure 3. Molden plots of the singlet state of dicyclopentadienylcarbene (C_2 symmetry; top) and of phenylcyclopentadiene (C_1 symmetry; bottom).

To remedy this situation, we performed additional quantum chemical calculations on decamethyl-substituted carbocene and silicocene. The energy optimizations were performed without any symmetry restrictions (C_1 symmetry) at the DFT1 level of sophistication.

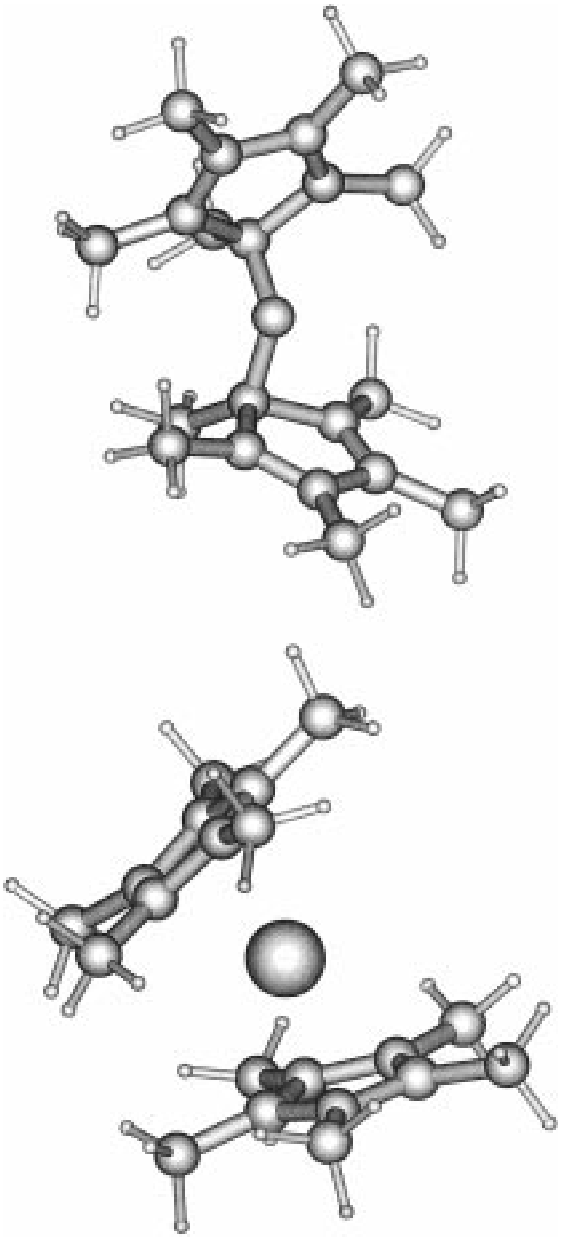


Figure 4. Molden plots for decamethylcarbocene (top) and -silicocene (bottom).

The resulting equilibrium geometries are shown in Figure 4.

For silicocene the computed structure is in perfect agreement with the X-ray analysis.[11] The Si−C(ring) distances range from 2.4 to 2.6 Å. The structural plot evidences a slightly bent metallocene structure. For decamethylcarbocene the bonding situation is different. A carbene-like structure (sharpest angle at the central carbon atom 125.1°) comes to the fore. We note that our investigations were restricted to the evaluation of a singlet structure. A Ψ-C_2 symmetrical structure is adopted; i.e., the closest C−C distances from the central carbon to the geminal ring carbon atoms are 2.2 and 2.4 Å. These values are similar to those in the parent carbocene (see Table 3). Similar values are taken up for the C−C distances from the central carbon to the neighboring carbon atoms (1.5 Å). Thus, our elaborate ab initio calculations at the DFT1 level indicate that the methyl substituents do not exert considerable changes in the geometries of the investigated metallocenes.

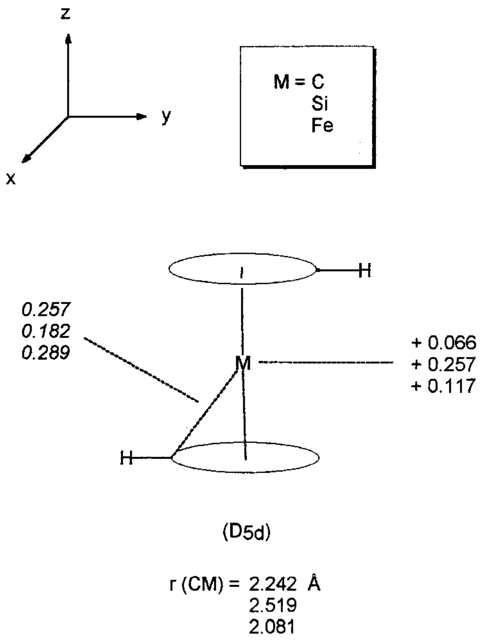


Figure 5. NBO charges and Wiberg bond indices (in italics) for carbocene, silicocene, and ferrocene (D_{5d} symmetry).

(d) Electron Density Distributions. Of particular interest are the electron distributions in the metallocene structures. We have evaluated these on the basis of various partitioning schemes for the total electron density distributions, utilizing natural bond orbital analysis,[38] Bader's method of "atoms in molecules",[39] and also an analysis of the electron localization function.[40] For completeness we included in our considerations ferrocene,[41] in which the central element is not a p-block element (C, Si, etc.) but a d^6 transition-metal element (Fe). A first, very informative insight is given by a NBO analysis of the D_{5d}-symmetrical structures. A pictorial description of charge densities and Wiberg bond indices (in italics) is given in Figure 5.

The values from top to bottom refer to carbocene (M = C), silicocene (M = Si), and ferrocene (M = Fe), with a D_{5d} structure imposed. Accordingly, silicocene possesses the most positive central atom. This is in agreement with the fact that nucleophilic addition reaction at the central atom can easily occur.[42] The silicocene possesses also the weakest covalent bond between the central atom and the Cp units. A further bisection of the individual populations of the valence orbitals is collected in Table 5.

The p-block metallocenes differ from the d-block metallocene (ferrocene) in that for the former only s and

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Table 5. NBO Partitioning of Valence Orbital Occupation Numbers of Carbocene, Silicocene, and Ferrocene (D_{5d} Symmetry)

s, p, d orbital	occupation no.		
	M = C	M = Si	M = Fe
s	1.994	1.996	0.181
p_x	0.757	0.461	0.004
p_y	0.757	0.461	0.004
p_z	0.412	0.196	0.008
d_{xy}	0.000	0.000	1.861
d_{xz}	0.001	0.007	0.975
d_{yz}	0.001	0.007	0.975
$d_{x^2-y^2}$	0.000	0.000	1.861
d_{z^2}	0.001	0.004	1.949

p orbitals are incorporated in bonding. The s and p orbital populations in the carbocene are in general larger than in silicocene. In other words, the central atom in the former is more electronegative than in the latter structure. As a consequence, more electron density is donated toward the peripheral Cp rings in the silicocene. The p_z orbital donates in both cases more electron density toward the Cp rings than do the p_x and p_y orbitals. In the ferrocene the essential bonding is constituted by the d orbitals. The dominant bonding is achieved by contributions arising from the d_{xz} and d_{yz} orbitals. They refer to the e_{1g} set of d orbitals and are responsible for the π-bonding contribution in the d-block metallocene.

A further insight into bonding within these three different metallocene types are supplied by a analysis of the Laplacian of the electron densities, as determined by the Bader approach of atoms in molecules.[39] Corresponding plots of the electron densities and the Laplacian of the electron densities are given in Figure 6. The plots view the course of the electron densities from the central atom (C, Si, Fe) to one edge of the Cp ring.

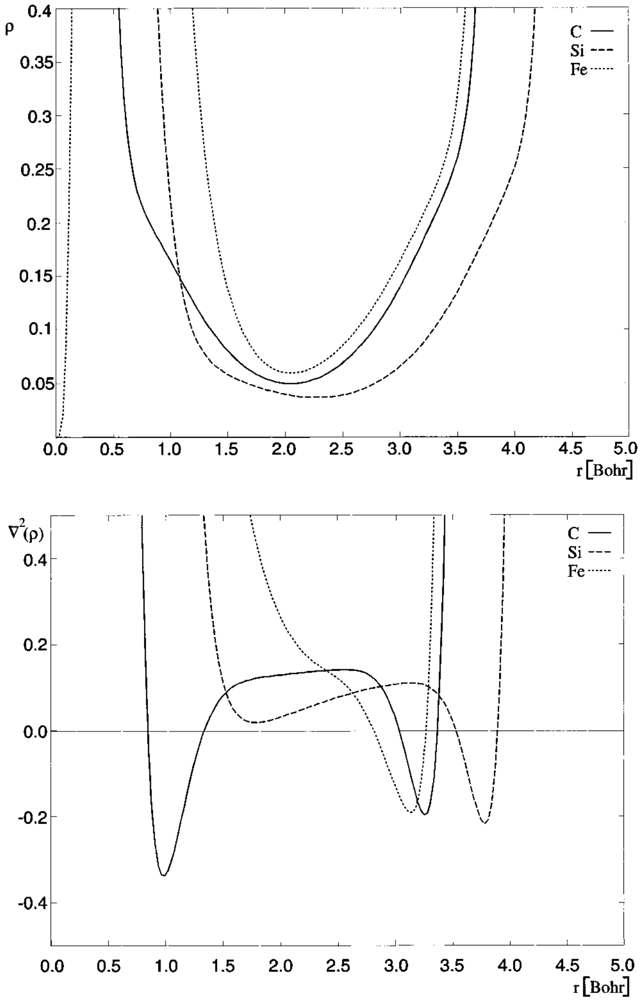

Figure 6. Electron densities (top; ρ, bohr^{-3}) and Laplacian of the electron densities (bottom; $\nabla^2(\rho)$, bohr^{-5}) of carbocene, silicocene, and ferrocene. The values are plotted from the central atom ($r = 0.0$) to one ring carbon atom (r in bohr); $\nabla^2(\rho) < 0.0$ local charge concentration.

Accordingly, there is no charge concentration ($\nabla^2\rho(r) < 0$) in the binding region between the central atom and the ring atoms. This is a common feature of bonding in the metallocenes. However, there is an essential difference between the metallocenes constituted of p-block elements (C, Si) versus the d-block case (ferrocene). In case of carbocene the electron density is most strongly concentrated at the central atom. This may be attributed to the strong electronegativity of carbon (compared to silicon) and the smaller orbital expansion of the participating s and p orbitals. For silicon a larger orbital expansion is expected, and this is also witnessed in the Laplacian contribution. A different case is determined for ferrocene. Electron density is here more continuously spread to the Cp ring(s). This is a consequence of the more diffuse nature of the d orbitals as compared with the p orbitals. However, the bonding situation in carbocene is not essentially different from that in silicocene, besides the fact that the p orbitals for silicon are larger in extension (3p) than in carbon (2p). Consequently, bonding of the central atom toward the Cp ring systems can be enhanced. A further aspect may be noted here. Silicon, as a higher main-group element when compared with carbon, is more reluctant to form strong hybrid orbitals.[43] As a consequence, the tendency of carbocene to prefer "classical" carbene structures is more strongly pronounced.

We note that the electron density distribution of ferrocene was obtained from quantum chemical calculations at the effective core potential level.[41] There the core orbitals are taken into consideration by an effective potential. This may somewhat affect the overall shape of the Laplacian of the electron density distribution. However, we think that the principal considerations, i.e., the stronger participation of d orbitals in bonding toward the Cp rings, are not altered.

Conclusions

The results of our investigations can be summarized as follows.

(1) Carbocene is different from silicocene in the way that it easily rearranges to carbene-like structures. The driving force for rearrangement is fairly large (approximately 50 kcal/mol). However, the most stable species is phenylcyclopentadiene, which would result from carbene rearrangement of the carbene structure with C_2 symmetry.

(2) Dicyclopentadienylcarbene possesses a triplet state fairly close in energy to the lowest energy singlet state.

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(43) Schoeller, W. W. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O., Eds.; Thieme: Stuttgart, Germany, 1990, and references cited therein.

The latter adopts predominantly a η^1 coordination of the two Cp rings with a small tendency for η^3 coordination.

(3) In contrast, silicocene tends also to be distorted from an ideal sandwich geometry (D_{5d}) to a bent structure, but to a much smaller extent. The matter is substantiated by density functional calculations at various levels of sophistication and also at the CCSD(t) level.

(4) An investigation of the electron distributions within the sandwich structures makes the difference in bonding between metallocenes constituted of p-block elements (C, Si) and d-block elements (Fe) apparent. In the former the p orbitals and in the latter the d orbitals take part in bonding with the Cp ligands. For carbocene the orbital extensions at the central atom are essentially smaller than for silicocene. This indicates a decreased capability to keep the Cp ligands bound. For ferrocene electron density donation ($Cp^- \rightarrow Fe^{2+}$) is counteracted by back-donation ($Fe(d)^{2+} \rightarrow Cp^-$) of electron densities. However, for main-group metallocenes the electron donation is restricted to $Cp^- \rightarrow Si^{2+}$, since back-donation is not possible. Such a view, however, rests on the assumption that two electrons are localized on a central Si^{2+} atom (in its standard state).

(5) Elaborate density functional calculations were also performed for the decamethyl derivatives of carbocene and silicocene. In comparison with those for their parent systems, these calculations do not indicate essential differences in bonding caused by the electronic and/or steric influences of the methyl groups.

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