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The Nature of the Tin Lone Pair and Phenyl Ring Packing in Decaphenylstannocene

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Fenske–Hall molecular orbital calculations are reported for decaphenylstannocene (S_{10} symmetry) and for stannocene (C_{2v} symmetry). The results predict that the tin lone pair in decaphenylstannocene resides in the HOMO, a Sn 5s-like orbital, and is not delocalized onto the ring system of the ligands. The calculated Mössbauer isomer shift 4.09 mm s^{-1} is larger than that calculated for stannocene (3.56 mm s^{-1} at a Cp–Sn–Cp angle of 146°) and close to the experimental isomer shift of 3.74 mm s^{-1} (Zuckerman, J. J., personal communication). Computer graphics are used to show that the experimental structure minimizes steric repulsion by placing the phenyl rings on the cyclopentadienyl ligands in a nearly perpendicular orientation.

Introduction

X-ray crystal structures for most $(\eta^5\text{-}R_5C_5)_2E$ derivatives, E = Ge,[1] Sn,[2,3] and Pb,[2,4] reveal a severely bent Cp–Sn–Cp geometry with angles between 143° and 148°. However, in decaphenylstannocene the cyclopentadiene rings are exactly parallel.[5] Thus, the molecule violates the valence-shell electron-pair repulsion model. Heeg, Janiak, and Zuckerman[5] raised the question of where the lone pair resides now that it is not stereochemically active. They suggested[5] that the tin lone pair might be delocalized into the phenyl rings in this high-symmetry structure. However, the Fenske–Hall molecular orbital (MO) calculations,[6] reported here, reveal that the lone pair resides in the Sn 5s-like orbital of decaphenylstannocene. The lone pair shows no tendency to delocalize into either the phenyl groups or the cyclopentadiene rings. The calculated Mulliken populations predict a Mössbauer isomer shift of 4.09 mm s^{-1} for decaphenylstannocene and 3.56 mm s^{-1} for stannocene. MO calculations were also carried out for stannocene, varying the Cp–Sn–Cp angle from 180° to 120°. A comparison between stannocene with parallel Cp rings and decaphenylstannocene suggested that the structure of the latter is primarily steric in origin. This was confirmed by molecular modeling calculations on decaphenylstannocene in which various orientations of the phenyl rings were examined.

Results and Discussion

Nature of the Tin Lone Pair. The results for decaphenylstannocene are shown in the MO diagram in Figure 1. The lowest unoccupied molecular orbital (LUMO) is the $2e_{1u}$. The highest occupied molecular orbital (HOMO) $2a_g$ is a doubly occupied antibonding combination of the tin 5s and the Cp a_1 orbitals. The $1e_{1g}$ orbital is a nonbonding pair of Cp π orbitals, and the $1e_{1u}$ is a pair of bonding orbitals made up of Cp π e_1 and tin $5p_{x,y}$ orbitals.

Calculations on stannocene at various Cp–Sn–Cp angles show a similar order for the MO's. This order is in agreement with previous extended Hückel calculations.[3] However, recent Xα-SW[7] and MNDO[8] calculations on stannocene and photoelectron (PE) spectroscopic studies[7,9,10] place the $2a_g$ (HOMO) below the $1e_{1g}$ and $1e_{1u}$. At 180° the a_1 orbital is primarily 5s in character. As the Cp rings are bent back, the $5p_z$ stabilizes the a_1 orbital and the orbital becomes a 5s–5p hybrid. The energies of the orbitals below the HOMO remain fairly constant until about 150° when they begin to increase. The increase is due to the steric repulsion between the Cp rings and is responsible for halting the decrease in angle brought about by the decreasing HOMO energy.

Although orbital energies from Fenske–Hall calculations have shown good agreement with PE spectra in the past, the orbital energies of cyclic π systems are usually predicted to be too low.[7] Thus, the order of the $2a_g$ and the $1e_{1g}$, $1e_{1u}$ pairs in decaphenylstannocene could be inverted from the order shown in Figure 1. However, since the $2a_g$ is destabilized as the Cp rings are made parallel, it could be the HOMO in decaphenylstannocene even though it is not the HOMO in stannocene. For the results discussed here this order is unimportant.

Mössbauer spectroscopy has been useful in determining the population of metal valence s orbitals. Mössbauer spectra for a host of Sn(II) and Sn(IV) compounds have been reported.[12–16] The isomer shifts of Sn(IV) compounds are typically below 2, and Sn(II) are usually above 2.5 mm s^{-1}, with respect to $BaSnO_3$. The Mössbauer spectrum of stannocene[17] shows an isomer shift of 3.73 mm s^{-1} and a quadrupole splitting of 0.65 mm s^{-1}. The high isomer shift indicates that most of the Sn lone pair is localized in the 5s orbital with some delocalization of the electrons into the 5p orbitals to give the observed small quadrupole splitting. The isomer shift determined[18] from

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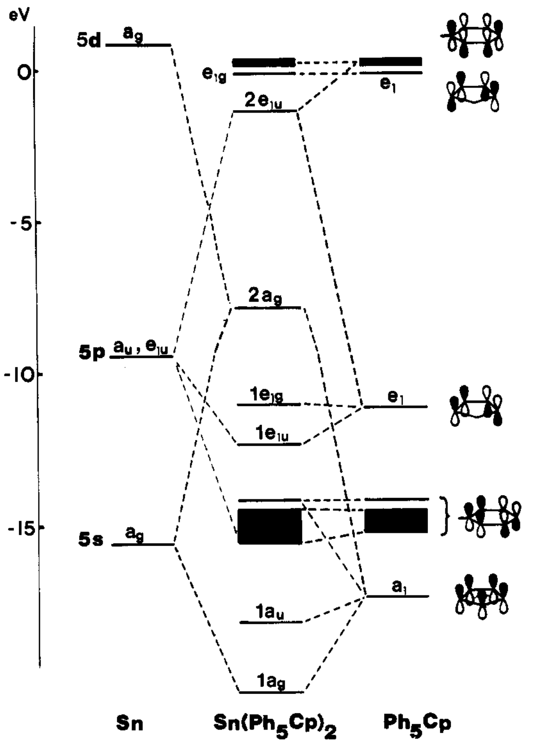

Figure 1. Molecular diagram for decaphenylstannocene as calculated by the Fenske–Hall MO method.

the Mulliken populations of the Fenske–Hall MO calculation gave a value of 3.56 mm s^{-1} (3.60 mm s^{-1} without 5d functions), in good agreement with the experimental value. The calculated Mulliken populations of decaphenylstannocene predict an isomer shift value of 4.09 mm s^{-1} (4.48 mm s^{-1} without 5d functions) and zero quadrupole splitting as compared to an experimental isomer shift values of 3.74 mm s^{-1} and a quadrupole splitting value of 0.58 mm s^{-1} with a line width of 0.77 mm s^{-1}.[19] The calculations showed substantial interactions of the 5d$_{z^2}$ orbital with the 2a$_g$ HOMO of decaphenylstannocene but little interaction with the corresponding orbital of stannocene. The high value for the calculated and experimental isomer shift would be consistent with the tin lone pair localized in the 5s-like orbital with some 5d$_{z^2}$ character and not delocalized into the π system of the rings.

Geometry and Phenyl Ring Packing. The geometry of decaphenylstannocene positions the phenyl rings in an unexpected orientation. One might expect the phenyl rings of one Cp ring to be parallel to the phenyl rings of the other Cp ring; however, the phenyl rings of one Cp ring are all tilted an average angle of 39° from the plane of the Cp ring and the phenyl rings of the other Cp ring are titled −39°, which aligns the two sets of phenyl rings nearly perpendicular to each other. The crystal structure of solid benzene shows the same perpendicular packings of the benzene rings.[21]

Decaphenylstannocene was examined on a LUNDY 5688 graphics terminal using the CHEMGRAF molecular modeling program to study the steric interactions between the phenyl rings. The eight configurations of decaphenylstannocene studied are shown in Figure 2. The two long horizontal lines in each figure represent the parallel planes of the two Cp ring. The short lines are the planes of the phenyl rings. The Cp rings for a, c, e, and g are eclipsed and the Cp rings for b, d, f, and h are staggered. Calculated repulsive energies using van der Waals radii showed the crystal structure configuration d to have the lowest repulsion energy; see Table I. A slight increase of 10° in the tilt at the phenyl rings increased the repulsion energy by about 8 kcal. These energies, though poor quantitatively, are very useful in comparing various configurations. The closest H–H distance in the d configuration of decaphenylstanocene is 2.45 Å which is 0.2 Å shorter than the closest H–H distance in crystalline benzene[20] but longer than analogous H–H distances for the other configurations of decaphenylstanocene.

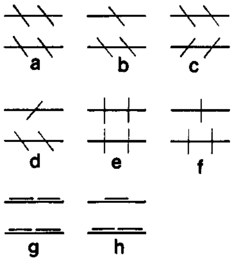

Figure 2. Side view of decaphenylstannocene. Long horizontal lines are the planes of the Cp rings. Short lines are the planes of the closest phenyl rings.

Table I. Results of Molecular Modeling

config	repulsion energy, kcal	closest H–H dist, Å
a	992.46	1.88
b	1077.00	1.64
c	1137.74	1.47
d	988.23	2.45
e	very large	0.51
f	1019.19	1.84
g	very large	0.11
h	very large	0.11
crystalline benzene		2.64

The nearly perpendicular orientation of the phenyl rings is sterically the most favorable one for two pentaphenylcyclopentadienyl rings sandwiching a metal atom. One might imagine the evolution of this geometry by beginning with two pentaphenylcyclopentadienyl ligands at a long distance from Sn and with phenyl rings perpendicular to the plane of the Cp (configuration f). As the Cp rings get closer to each other, the phenyl rings do a disrotatory twist to maximize the H–H nonbonded distance of the inner ortho hydrogens. Simultaneously, as the phenyl rings are twisted, the distances between the inner ortho hydrogens and the inner ortho carbons decrease. Before the tilt of the rings reaches 45°, strong repulsive interaction of the ortho hydrogen with the ortho carbon stops the rotation at about 39°.[21]

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