187-188 °C. The spectral parameters were found to be identical with that reported above.

X-ray Diffraction Study of $Sn_2(C_{10}H_6)_2(CH_3)_2Cl_4{\cdot}(CH_3)_2SO{\cdot}CCl_4$. Single crystals of this compound were grown by slow cooling of warm CCl_4 solution. One rectangular crystal, of approximate dimensions 0.23 × 0.35 × 0.24 mm, was mounted on a glass fiber for data collection on a Nicolet P3m diffractometer. The unit cell parameters were determined from 25 centered reflections. The details of the crystal data, data collection methods, and refinement procedures are given in Table V. Full details of the crystallographic methodologies may be found in ref 28. Atomic positional parameters, selected bond lengths, and bond angles are given in Tables III and IV, respectively. The intensities of three standard reflections were periodically measured and indicated 20% decay in intensity at the end of data collection. No empirical absorption correlation was applied. In addition to the decay problem, the sulfur and C(23) atom of DMSO as well as the solvent of crystallization (CCl_4) were disordered. In the initial stages, refinement of all atoms excluding biphenyl rings and hydrogens gave an R value of 0.108. At this point, it was evident that sulfur, C(23) of DMSO, as well as CCl_4 are disordered. After changing the population density of sulfur, C(23) and C(15), C(16) and C(18), and C(17) to 70%; 60%, and 50% and including all hydrogen atoms at their fixed positions, the R factor converged to 0.0811 with R_w to 0.858. Although this refinement produced a perfectly satisfactory molecular geometry, C–C bond distances of the biphenyl rings displayed considerable spread. Also, around the sulfur and C(23) of DMSO and C(16), C(17) of CCl_4, peaks and troughs of considerable electron density were located due to disorder that could not be adequately modeled (1.3 e/Å^3).

As a final recourse, the population density of C(23) was fixed at 70% and for C′ at 30%; the CCl_4 molecule was fixed at 50% and Cl′ and Cl″ as 20%. The R factor converged to 0.0735 and R_w to 0.0752. This model resulted in some exaggerated thermal parameters but appeared to be adequate. The disorder problems associated with this structure containing the solvent of crystallization posed some considerable difficulty. However, since the Sn complex was well-behaved, no further attempts were made to resolve the disorder.

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Supplementary Material Available: Tables containing bond lengths, bond angles, anisotropic temperature factors, and hydrogen atom coordinates (5 pages); tables of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

AM1 Parameters for Tin

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The AM1 semiempirical method has been successfully extended to tin. AM1 heats of formation are slightly better than those obtained by using MNDO, but ionization potential and geometric results have been significantly improved. The AM1 results for organometallic species are especially promising. The correct prediction of the bent sandwich structure for stannocene is indicative of this.

Introduction

The MNDO[1] semiempirical method has been successfully applied to a wide range of tin chemistry. MNDO has been used to study multiple bonding in tin,[2] reactions of stannylene,[3] tin radical cations,[4] and S_N2 reaction of tetramethyltin with Br_2,[5] as well as the cation and radical of trithiatristannaadamantane.[6] Despite these successes, some deficiencies have become apparent. The failure of MNDO to predict the bent C_{2v} structure of stannocene as a minimum on the potential energy surface probably results from its well-documented tendency to overestimate core–core repulsions for extended nonbonded distances. In addition, there is a systematic underestimation of bond lengths.

To correct these failures and to continue our extension of the very successful[7] AM1[8] procedure, we now report AM1 parameters for Sn and calculations for a number of compounds containing tin.

Procedure

Determination of parameters was accomplished by minimizing the sum of the squares (SSQ) of the weighted errors in the heat of formation (ΔH_f), the ionization potential (IP), the dipole moment (μ), and the geometries of a parameterization set of molecules representing the important chemistry of tin. The

Table I. AM1 and MNDO Parameters for Tin

parameter	AM1	MNDO[a]
	Optimized	
U_{ss}/eV	-35.496741	-40.851802
U_{pp}/eV	-28.097636	-28.560249
ζ_s/au	2.599376	2.080380
ζ_p/au	1.695962	1.937106
β_s/eV	-3.235000	-3.235147
β_p/eV	-2.577890	-4.290416
α/Å^{-1}	1.836936	1.800814
g_{ss}/eV	9.80	9.80
g_{pp}/eV	8.30	8.30
g_{sp}/eV	7.30	7.30
g_{p2}/eV	6.50	6.50
h_{sp}/eV	1.30	1.30
	Derived	
E_{ht}/kcal mol^{-1}	72.20	72.20
E_{el}/eV	-80.688754	-92.324102
D_1/au	1.152823	1.569777
D_2/au	1.514802	1.326230
AM/au	0.360162	0.360162
AD/au	0.382378	0.321999
AQ/au	0.340076	0.371383

[a] See ref 8.

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required derivatives were determined analytically with the exception of those for the dipole moment and geometry, which were determined by finite difference. A knowledge of these derivatives allowed the calculation of the derivative of the SSQ with respect to the various parameters. A line search along the search direction yielded the optimum step size, and this information was used to update the Hessian matrix. By repeating this procedure, an optimum set of parameters was obtained. The algorithm used was a modification of the Davidon–Fletcher–Powell procedure.[9]

Results and Discussion

The AM1 parameters are given in Table I along with those from MNDO.[10] One notable feature of the AM1 parameters is the absence of gaussian terms, indicating that a successful parameterization was possible without modification of the core–core repulsion term for tin, as has been required for several other elements.[11]

Table II shows the heats of formation (ΔH_f), first ionization potentials (IPs, as computed from Koopmans' theorem[12]), and dipole moments (μ) for a number of tin-containing molecules, radicals, and cations. Where available, experimental values are included. The mean absolute MNDO error for the heats of formation is 15.8 kcal/mol for this set of molecules. This has been reduced slightly to 15.5 kcal/mol in AM1. The largest error has been reduced as well from 45 to 33 kcal/mol. While this is not a marked improvement, the AM1 parameters perform much better for the organometallic species. Much of the AM1 error is also concentrated in the halides, a problem that was encountered in previous AM1 parameterizations.[13] This condition is especially exacerbated by the significant amount of experimental data available for halogen species.

The mean error in IP for AM1, 0.86 eV, is *significantly* lower than that in MNDO, 1.37 eV, indicating a more accurate prediction of molecular orbital energies. A large component of the error for the AM1 IPs results from the IP error for SnH_4 (−2.81). This is much improved over the value for MNDO (−3.53) but still strongly skews the average error in AM1. Without SnH_4, the AM1 IPs are even more significantly improved over those in MNDO. The AM1 errors in μ are the same as in MNDO, at 0.35 D.

Table III shows various geometric parameters from optimized AM1 geometries along with experimental values. AM1 improves on the MNDO values in nearly every case, and the average error in bond lengths has been reduced from 0.08 to 0.06 Å. As was the case with MNDO, AM1 invariably predicts the bond lengths to be too short, but the systematic error has been substantially reduced. The most notable improvement is to be seen in the Sn–C and Sn–H bonds.

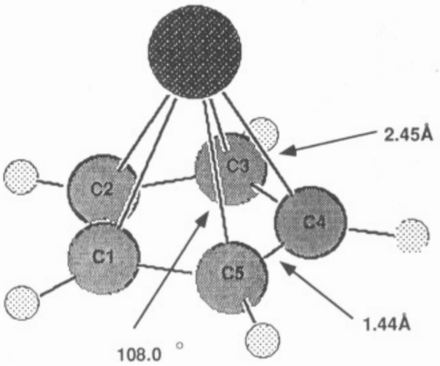

Figure 1. Nido isomer of the tin cyclopentadienyl cation complex (1).

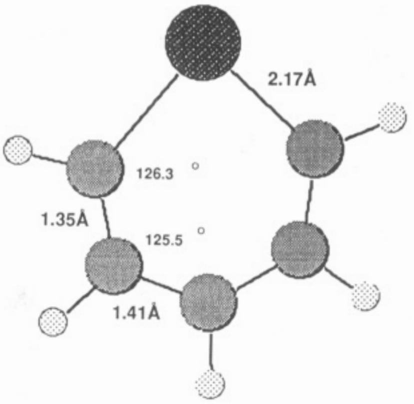

Figure 2. Monocyclic isomer of the tin cyclopentadienyl cation complex (2).

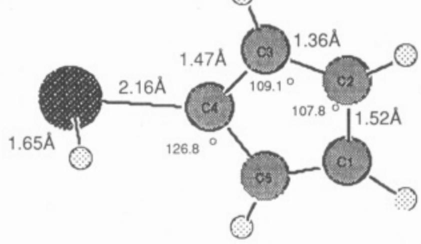

Figure 3. Fulvenyl isomer of the tin cyclopentadienyl cation complex (3).

Considering that cyclopentadienyltin compounds are among the most interesting tin molecules and since they illustrate both a success and a failure of the MNDO tin parameterization, it was decided to study these in more depth.

C_5H_5Sn Cation. Similar to its isoelectronic analogues, CpIn and CpTh[14] (Cp = cyclopentadienyl), $SnCP^+$ (**1–3**) has been found to have a nido structure[15] (**1**). Estimation of the atomization energy of **1–3** also supports this arrangement as the most stable of the three considered.[16] The two other structures, the monocycle **2** and its fulvene analogue **3**, appear likely to be minima on the potential surface but have not been observed experimentally. As was the case with MNDO, **1–3** proved to be minima on the

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Table II. Comparison of Predicted (AM1) and Experimental Heats of Formation,[a] Ionization Potentials,[b] and Dipole Moments[c]

species	exptl ΔH_f	AM1 ΔH_f	error	exptl μ	AM1 μ	error	exptl IP	AM1 IP	error
Sn_2	99.90[d]	126.63	26.73		0.00			6.26	
Sn_3	118.50[d]	128.06	9.56		0.00			6.96	
$SnF^{\bullet}$	-9.00[e]	-4.39	4.61		2.73		7.04[e]	6.65	-0.3
$SnCl^{\bullet}$	16.00[e]	-2.10	-18.10		3.17		7.04[e]	6.91	-0.13
$SnBr^{\bullet}$	24.00[e]	9.22	-14.78		2.97			6.99	
$SnI^{\bullet}$	36.00[e]	40.25	4.25		3.35			7.18	
SnF_2	-116.00[e]	-83.32	32.68		4.43			9.86	
$SnCl_2$	-56.40[e]	-76.08	-19.68		4.43		10.31[f]	10.21	-0.10
$SnBr_2$	-29.00[e]	-49.57	-20.57		3.85		9.83[f]	9.72	-0.11
SnI_2	2.00[e]	12.25	10.25		3.81		9.05[f]	9.36	0.31
$SnIBr$	-16.80[g]	-18.54	-1.74		3.86		10.00[g]	9.47	-0.53
$SnCl_4$	-112.70[i]	-132.86	-20.16		0.00		11.88[j]	12.80	0.92
$SnBr_4$	-75.20[i]	-84.97	-9.77		0.00		11.00[k]	11.74	0.74
SnH	49.00[e]	62.68	13.68		0.72			6.67	
SnH_4	38.90[l]	42.07	3.17		0.00		9.20[m]	12.01	2.81
$SnMe_2H_2$	21.00[n]	19.81	-1.19	0.78[p]	0.19	-0.59		10.68	
$SnMe_2Cl_2$	-71.00[q]	-73.32	-2.32	4.14[p]	3.85	-0.29	10.43[r]	10.93	0.50
$SnMe_2Br_2$		-48.62		3.86[s]	3.37	-0.49		10.58	
$SnMe_2I_2$	-19.70[e]	4.60	24.30	3.37[s]	2.82	-0.55		10.27	
$SnEt_2H_2$	10.20[n]	7.75	-2.45		0.21			9.92	
$SnMe_3H$	5.20[n]	8.65	3.45	0.67[p]	0.17	-0.50		10.50	
$SnMe_3Cl$	-46.40[t]	-39.11	7.29	3.46[p]	3.23	-0.23	9.88[u]	10.60	0.72
$SnMe_3Br$	-33.60[v]	-26.71	6.89	3.45[s]	3.01	-0.44	9.60[u]	10.31	0.71
$SnMe_3I$	-19.70[t]	0.52	20.22	3.37[s]	2.76	-0.61		9.95	
$SnMe_3^{\bullet}$	27.22[w]	14.55	-12.67		0.54		7.10[x]	8.33	1.23
$SnMe_3^{+}$	184.25[w]	183.72	-0.53					15.77	
$SnMe_3Et$	-7.10[e]	-8.45	-1.35	0.04		-0.04		9.82	
$SnMe_3C{=}C$	21.70[y]	21.47	-0.23	0.45[z]	0.22	-0.23		10.03	
$SnMe_3iPr$	-11.20[y]	-12.53	-1.33		0.04			9.52	
$SnMe_3tBu$	-16.00[y]	-14.58	1.42		0.07		8.34[w]	9.34	1.00
$SnMe_3Ph$	25.00[v]	36.42	11.42	0.51[p]	0.51	-0.00		8.28	
$SnMe_3Bz$	21.70[y]	22.55	0.85	0.45[y]	0.60	0.15		8.79	
$SnMe_3N(Me)_2$	-4.30[t]	12.14	16.44		1.14			8.35	
$SnMe_3OH$	-75.80[t]	-42.36	33.44		2.51			10.41	
$SnMe_3OEt$	-63.10[t]	-44.91	18.19		2.29			9.92	
$SnMe_4$	-4.60[y]	-2.38	2.22		0.00		8.76[w]	10.35	1.59
$SnEt_4$	-10.70[y]	-26.32	-15.62		0.01			9.69	
$SnPr_4$	-34.60[v]	-52.33	-17.73		0.00			9.80	
$SnBu_4$	-52.90[v]	-79.80	-26.90		0.00			9.76	
$SnPh_4$	100.60[aa]	129.39	28.79		0.05			9.56	
Sn_2Me_6	-6.40[y]	9.80	16.20		0.00		8.21[bb]	9.11	0.90
Sn_2Et_6		-27.01			0.02		7.82[bb]	9.04	1.22
$SnMeCl_3$		-104.25		3.62[p]	3.13	-0.49		11.55	
$SnMeBr_3$		-68.12		3.24[s]	2.89	-0.35		11.04	
$SnMeI_3$		11.10		2.52[s]	2.27	-0.25		10.51	
$PhMe_2GeSnMe_3$		16.46			0.82		8.20[cc]	9.08	0.88
$PhMe_2SiSnMe_3$		3.83			0.64		8.15[cc]	8.68	0.53
$Me_3SiSnMe_3$		-27.08			0.47		8.39[bb]	9.00	0.61
$Me_3GeSnMe_3$		-15.57			0.98		8.36[bb]	9.50	1.14
$Et_3SiSnEt_3$		-41.89			0.21		8.10[bb]	9.34	1.24
$Et_3GeSnEt_3$		-50.91			0.63		8.05[bb]	9.50	1.45
$Ph_2Sn(CH_2)_4$	72.10[dd]	58.40	-13.70		0.12			9.30	
$Ph_2Sn(CH_2)_5$	69.00[dd]	50.44	-18.56		0.21			9.23	
number of examples			42			15			23
average			-1.83			0.33			-0.75
unsigned average			12.27			0.35			0.86

[a] In kcal/mol. [b] In eV. [c] In debyes. [d] K. A. Gingerich, E. A. Ramakrishnan, J. E. Kingcade, Jr. *High Temp. Sci.*, *21* (1986), 1. [e] *Gmelin's Handbuch anorganischen Chemie*; Zinn, Teil, Ed.; Verlag Chemie, GMBH: Weinheim, 1972. [f] I. Novak, A. W. Potts. *J. Electron Spectrosc. Relat. Phenom.*, (1984) 1. [g] C. Hirayama, R. D. Straw. *Thermochim. Acta*, *80* (1984), 297. [i] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, R. Schemm. *NBS Tech. Note* (*U.S.*) *270-3* (1968), 182. [j] P. J. Basset, D. R. Lloyd. *J. Chem. Soc.*, *A*, (1971) 641. [k] J. C. Green, M. L. H. Green, J. J. Joachim, A. Orchard, D. W. Turner. *Philos. Trans. R. Soc. London, Ser. A*, 268 (1970), 111. [l] P. Gunn, L. G. Green. *J. Phys. Chem.*, *65* (1961), 779. [m] F. E. Saalfe, H. J. Svec. *Inorg. Chem.*, *2* (1963), 46. [n] W. F. Lautsch, A. Trober, W. Zimmer, L. Mehner, W. Linck, H. M. Lehman, H. Brandenberger, H. Kerner, P. Metzchker, K. Wagner, R. Kaden. *Z. Chem.*, *3* (1963), 415. [p] R. Gupta, B. Majee. *J. Organomet. Chem.*, *33* (1971), 169. [q] G. A. Nash, H. A. Skinr, W. F. Stack. *Trans. Faraday Soc.*, *61* (1965), 640. [r] I. Fragala, E. Ciliberto, R. G. Edgell, G. Granozzi. *J. Chem. Soc., Dalton Trans.*, (1980), 145. [s] E. van den Berghe, G. B. van der Kelen. *J. Organomet. Chem.*, *6* (1966), 515. [t] J. C. Baldwin, M. F. Lappert, J. B. Pedley, J. S. Poland. *J. Chem. Soc., Dalton Trans.*, (1972), 1943. [u] A. Flamini, E. Simprini, F. Stefani, S. Serriso, G. Cardaci. *J. Chem. Soc., Dalton Trans.*, (1976), 731. [v] H. A. Skinner. *J. Organomet. Chem.*, *2* (1964), 49. [w] M. F. Lappert, J. B. Pedley, B. Simpson, T. R. Spaulding. *J. Organomet. Chem.*, *29* (1971), 195. [x] F. W. Lampe, A. J. Niehaus. *J. Chem. Phys.*, *49* (1968), 2949. [y] J. D. Cox, G. Pilcher. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970. [z] J. Nagy, T. Reffy. *J. Organomet. Chem.*, *22* (1970), 565. [aa] L. Thakur, A. K. Thakur, M. F. Ahmad. *Indian J. Chem.*, *19A* (1980), 793. [bb] J. Fernandez, G. Lespes, T. Dargelos. *Chem. Phys.*, *111* (1986), 97. [cc] H. Sakurai, M. Ichinose, M. Kira, T. G. Traylor. *Chem. Lett.*, (1984), 1383. [dd] A. S. Carson, E. H. Jam, P. G. Laye, J. A. Spencer. *J. Chem. Thermodyn.* *20* (1988), 923.

Table III. Comparison of AM1 and Experimental Geometrical Results[a,b]

molecule	parameter(s)		ref
$SnBr_2$	Sn–Br	2.37 (2.51)	*c*
	Br–Sn–Br	100 (105.6)	
SnI_2	Sn–I	2.58 (2.70)	*c*
	I–Sn–I	103 (105.9)	
SnH_4	Sn–H	1.70 (1.62)	*d*
$SnCl_4$	Sn–Cl	2.28 (2.26)	*e*
$SnBr_4$	Sn–Br	2.44 (2.38)	*f*
$SnMe_2H_2$	Sn–C	2.15 (2.10)	*g*
	Sn–H	1.68 (1.62)	*g*
	C–Sn–H	108 (109.1)	
	C–Sn–C	104.8 (110.4)	
$SnMe_2Cl_2$	Sn–C	2.11 (2.09)	*g*
	Sn–Cl	2.33 (2.30)	
$SnMe_2Br_2$	Sn–C	2.17 (2.11)	*g*
	Sn–Br	2.48 (2.39)	
$SnMe_2I_2$	Sn–C	2.18 (2.11)	*h*
	Sn–I	2.69 (2.59)	
$SnMe_3Cl$	Sn–C	2.11 (2.10)	*g, h*
	Sn–Cl	2.35 (2.32)	
	C–Sn–Cl	108 (106.6)	
$SnMe_3Br$	Sn–C	2.17 (2.10)	*h*
	Sn–Br	2.49 (2.40)	
$SnMe_3I$	Sn–C	2.17 (2.11)	*h*
	Sn–I	2.72 (2.60)	
$SnMeCl_3$	Sn–C	2.10 (2.10)	*g*
	Sn–Cl	2.30 (2.28)	
$SnMeBr_3$	Sn–C	2.17 (2.11)	*h*
	Sn–Br	2.45 (2.38)	
$SnMe_4$	Sn–C	2.13 (2.11)	*i*

[a] Bond lengths in angstroms (Å), bond angles in degrees. [b] Experimental values in parentheses. [c] A. V. Demidov, *J. Struct. Chem., 24* (1983), 7. [d] G. R. Wilkinson, M. K. Wilson. *J. Chem. Phys., 25* (1965), 784. [e] H. Fujii, M. Kimura. *Bull. Chem. Soc. Jpn., 43* (1970), 1933. [f] E. Coop, L. E. Sutton. *J. Chem. Soc.,* (1938), 1269. [g] B. Beagley, K. McAloon, J. M. Freeman. *Acta Crystallogr. B30* (1974), 444. [h] H. A. Skinner, L. E. Sutton. *Trans. Faraday Soc., 40* (1944), 164. [i] H. Fujii, M. Kimura. *Bull. Chem. Soc. Jpn., 44* (1970), 2643.

Table IV. Heats of Formation[a] **of Three Tin Cyclopentadienyl Cation Isomers**

isomer	ΔH_f
nido (**1**)	214.58
monocycle (**2**)	246.77
fulvenyl (**3**)	285.79

[a] In kcal/mol.

AM1 surface. Table IV lists the heats of formation for the three isomers, and Figures 1–3 show their AM1 optimized geometries. AM1, like MNDO, predicts **1** to be the most stable of the three although the difference in energy between the nido structure, **1**, and the monocycle, **2**, is much smaller when using MNDO than AM1 (8 vs 32 kcal/mol). This can be attributed to the systematic destabilization of compounds like **1** using MNDO. The AM1 bond order between the tin atom and the carbons of the Cp ring is 0.32. The AM1 calculated geometry represents a signficant improvement over that of MNDO, which predicted Sn–C bonds to be too short, 2.34 Å vs an experimentally determined Sn–C bond length of 2.46 Å for the pentamethyl derivative of **1**.[15] The AM1 value for the Sn–C bond length is in excellent agreement at 2.45 Å. Both MNDO and AM1 predict the degenerate e_1 orbitals to be the highest occupied MO's with the a_1 tin lone pair MO next highest in energy. This ordering is in accord with a HONDO pseudopotential calculation[17] as well as an interpretation of the IP data for the isoelectronic In and Th nido compounds.[17]

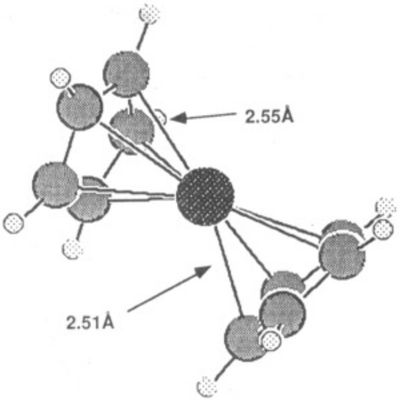

Figure 4. Bent-sandwich stannocene as predicted by AM1.

Table V. Heats of Formation[a] **of Bis(Cyclopentadienyl)tin Isomers**

isomer	ΔH_f
C_{2v} (**4**)	91.76
D_{5d} (**5**)	92.72

[a] In kcal/mol.

AM1 also correctly reproduces the out-of-plane deformation of the Cp hydrogens. The AM1 value, 6.6°, is in good agreement with the experimental result of 4.0°, from the X-ray structure of the pentamethyl derivative of **1**.[15] The out-of-plane bending has been attributed to the minimization of the antibonding s(Sn)–a_1(Cp) interaction by forcing the Cp p AOs outward, thereby reducing the overlap.

Stannocene. Stannocene (**4**) has been found to possess a bent sandwich structure by X-ray diffraction,[18] similar to that of plumbocene.[19] Methyl-substituted stannocenes have been determined to have a similar structure both in the gas phase[20] and solid state[21] (only pentaphenylstannocene has been found to have D_{5d} symmetry[22]). The lowering of symmetry, from D_{5d} to C_{2v}, in stannocene has been attributed to a strong stereochemically active lone pair on tin. Previously, MNDO calculations had been carried out on **4**, as have X_α[23] and Extended Huckel[20] calculations, with only the MNDO geometry being fully optimized. Unfortunately, MNDO found the bent sandwich structure, **4**, to not be a minimum, but a transition state on the PE surface. MNDO predicted the D_{5d} structure, **5**, to be the only minimum on the surface with a ΔH_f = 37 kcal/mol lower than that of **4**. MNDO calculations for plumbocene[24] yielded similar results. The AM1 geometry of **4** is shown in Figure 4. Frequency calculations on both isomers show that **4** is the only minimum on the PE surface, with **5** having two imaginary frequencies, corresponding to a complex point on the potential energy surface. The calculated ΔH_f of **4** is 91 kcal/mol (see Table V), very similar to that predicted by

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MNDO for **5**. AM1 does appear to produce Sn–C bonds in stannocene that are somewhat too short, ranging from about 2.49 to 2.62 Å as compared to the experimental values which range from roughly 2.58 to 2.75 Å. The centroid–centroid angle for 4, 120°, is also smaller than that of the X-ray structure[18] (144° and 148°), although it is close to that derived from the GED study, 125°.[19] As the gas phase is the closest model to AM1, the discrepancy may be due to forces in the solid state not present in isolated systems, such as preferential packing arrangements.

The highest occupied orbitals of stannocene have been predicted by X_α calculations[23] to be the nearly degenerate $6a_2$ and $9b_2$[20] with the a_1 tin lone pair next highest in energy. Extended Huckel calculations reverse this ordering.[20] The X_α calculations, however, appear to be in accord with the UV PES spectrum of 4,[23] and in good agreement with the X_α calculations, AM1 predicts the nearly degenerate Cp ring MOs as the highest occupied MOs. AM1 does, unfortunately, overestimate the IP of stannocene, predicting a first ionization potential of 8.49 eV as compared to the experimentally observed value of 7.57 eV.[23] Overestimation of IPs in methods using the core approximation[25] is a common problem[26] due to the fact that repulsions between the valence and subvalence AOs are not specifically accounted for in these methods.

Conclusions

The AM1 formalism has been successfully extended to tin. In almost all cases, AM1 performs better than MNDO. The AM1 results for organometallic species are especially promising.

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Preparation and Structure of Silacycloheptatriene

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The first preparation of C-unsubstituted silacycloheptatrienes, silicon analogues of cycloheptatriene, is described along with spectroscopic properties. A 2,5-diphenyl derivative has been similarly prepared. The new and general preparative method for silacycloheptatriene is based on the reaction of the silacyclohexadienyl anion with chlorocarbene. The reaction pathway to silacycloheptatriene has been examined by the use of deuterium labeling.

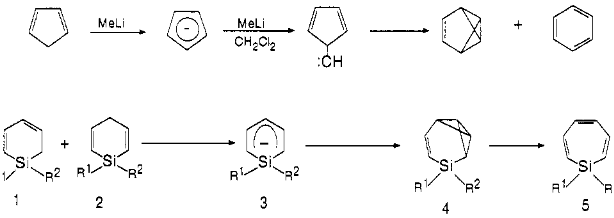
Introduction

Silacycloheptatrienes (silepins) have the possibility of delocalizing six π electrons in the ring through a vacant 3d orbital on a silicon atom, and in this respect, these may constitute neutral silicon analogues of the tropylium cation. Until our recent success in the preparation of 1,1-dimethylsilepin,[1] all silepins reported so far have been annelated derivatives such as mono-,[2] di-,[3] and tribenzosilepins[4] except for two examples,[5] which are monocyclic but C-substituted ones.

The UV spectrum of a dibenzosilepin[3a,c] does not reveal the existence of any significant cyclic delocalization of six π electrons through a silicon atom. Although in the ^1H NMR spectra of dibenzosilepin[3a] and 1,1-dimethyl-2,7-diphenylsilepin[5a] the SiMe signals appear as a singlet, these structures have been accounted for not by planar geometries but by rapidly inverting boat conformations. On the other hand, a tribenzosilepin has two distinct SiMe signals in accord with its rigid boat geometry.

These benzo- and C-substituted silepins are not always suitable for studies of subtle interaction between a triene unit and a silicon atom in a seven-membered ring. Therefore, the synthesis of C-unsubstituted silepins is an important goal. In this paper, the first successful synthesis of C-unsubstituted silepins and their structures are described in some detail.

Scheme I



Results and Discussion

Preparation of 1-Silacyclohepta-2,4,6-trienes (Silepins). One of the most important synthetic methods for the valence isomers of benzenoid hydrocarbons such as benzvalene and benzobenzvalene involves cyclization of the intermediate carbene species resulting from the reaction of a cyclohexadienyl or indenyl anion with CH_2Cl_2

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