high; however, the high selectivity of the enzymatic reaction may be due to the cooperative function of the substrate binding pocket in the active site of tyrosinase.

Chemical Reduction of a Pentastanna[1.1.1]propellane Derivative and the Synthesis and Molecular Structure of a Bicyclo[1.1.1]pentastannane

Lawrence R. Sita*,† and Isamu Kinoshita

Contribution from the Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213. Received March 21, 1990

Abstract: Cyclic voltammetry of 2,2,4,4,5,5-hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane (**3**) in THF shows two quasireversible one-electron reduction waves at $E_{1/2}$ = -1.41 and -1.93 V (V vs NHE) which correspond to the [**3**]/[**3**]⁻ and the [**3**]⁻/[**3**]²⁻ redox couples, respectively. Chemical reduction of **3** with 0.5% potassium amalgam can be achieved in the presence of 4,7,13.16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (abbreviated as crypt) to produce the radical anion complex [**3**]⁻[K,crypt]⁺. This radical anion has been characterized by ESR which shows g_{iso} = 1.92, $a(^{119/117}Sn_{1,3})$ = 15 G, and $a(^{119/117}Sn_{2,4,5})$ = 57 G for the isotropic spectrum at 410 K and $g_{\parallel}$ = 1.99 and $g_{\perp}$ = 1.89 for the anisotropic frozen spectrum at 130 K. Compound **3** quantitatively reacts with methyl iodide to produce 2,2,4,4,5,5-hexakis(2,6-diethylphenyl)-1-iodo-3-methylbicyclo[1.1.1]pentastannane (**4**), which can be isolated as deep-red crystals. Single crystals of **4** are, at 20 °C, monoclinic, space group $P2_1/c$-C_{2h}^5 (No. 14) with a = 14.785 (2) Å, b = 20.319 (3) Å, c = 22.951 (3) Å, β = 97.63 (1)°, V = 6834 (2) Å³, and Z = 4. The tin–tin bond lengths between the bridging and bridgehead tin atoms of **4** are in the range of 2.825 (1) to 2.842 (1) Å, and the distance between the two bridgehead tin atoms is 3.361 (1) Å. The results of these investigations support the view that the central bridgehead–bridgehead bonding interaction of **3** contributes very little to the stability of this system.

Introduction

Investigations of "nonclassical" structures of the group IVA elements are of special interest since conclusive results can either support or challenge prevailing views concerning the nature of bonding in these molecules.[1] [1.1.1]Propellanes are a class of nonclassical structures since they possess bridgehead atoms having inverted tetrahedral geometries that force the four bonds from each of the bridgehead atoms to all lie within the same hemisphere as shown by **1** in Chart 1. Given this configuration, theoretical investigations have long sought to determine the stability and reactivity of these molecular frameworks prior to the availability of representative synthetic derivatives.[2,3] Indeed, these investigations had previously led to the prediction that the simplest carbon [1.1.1]propellane derivative **1a** (M = C, R = H in **1**) should be a viable synthetic target, and this was later confirmed by its preparation.[2] Furthermore, Wiberg, Bader, and Lau[4] point out that by using total electronic charge density (ρ) as determined by all of the occupied orbitals in **1a**, there can be seen an appreciable accumulation of charge between the bridgehead nuclei which corresponds to a calculated bond order of four-fifths of a normal C–C bond. Thus, while generally accepted models of hybridized orbitals cannot adequately describe the bonding situation in [1.1.1]propellanes, as noted by these authors, an indepth theoretical analysis of nonclassical structures has led to the understanding "that the charge distribution of a carbon atom can be so arranged as to yield bond paths that correspond to an inverted structure for the atom".

In contrast to the situation with carbon, recent theoretical investigations of the simple silicon and germanium [1.1.1]propellane analogues, **1b** and **1c** (M = Si, R = H and M = Ge, R

Chart I

1a	M = C and R = H	**2a**
1b	M = Si and R = H	**2b**
1c	M = Ge and R = H	**2c**
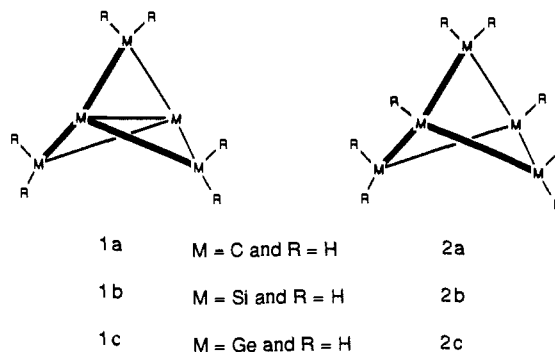
= H, respectively), all agree that these structures should possess very small bond orders between the two bridgehead atoms with the effect being that the calculated bridgehead–bridgehead bond lengths are unusually long and quite similar to the corresponding calculated nonbonding distances between the bridgehead nuclei in the silicon and germanium bicyclo[1.1.1]pentane analogues, **2b** and **2c** (M = Si, R = H and M = Ge, R = H, respectively, in **2**, Chart I).[3] Interestingly, an outcome of the reduced central

(1) Minkin, V. I.; Minyaev, R. M.; Zhdanov, Yu. A. *Nonclassical Structures of Organic Compounds*; MIR Publishers: Moscow, 1987.

(2) Wiberg, K. B. *Chem. Rev.* **1989,** *89,* 975 and references cited therein.

(3) For theoretical investigations of nonclassical structures of silicon see: (a) Schleyer, P. v. R.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 1267. (b) Nagase, S.; Kudo, T. *Organometallics* **1987,** *6,* 2456. (c) Schoeller, W. W.; Dabisch, T.; Busch, T. *Inorg. Chem.* **1987,** *26,* 4383. (d) Nagase, S.; Kudo, T.; Kurakake, T. *J. Chem. Soc., Chem. Commun.* **1988,** 1063. (e) Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990,** *112,* 3408. For germanium see: (f) Nagase, S.; Kudo, T. *Organometallics* **1988,** *7,* 2534.

(4) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987,** *109,* 985.

†Present address: Division of Chemistry and Chemical Engineering, Beckman Institute Materials Resource Center, California Institute of Technology, Pasadena, CA 91125.
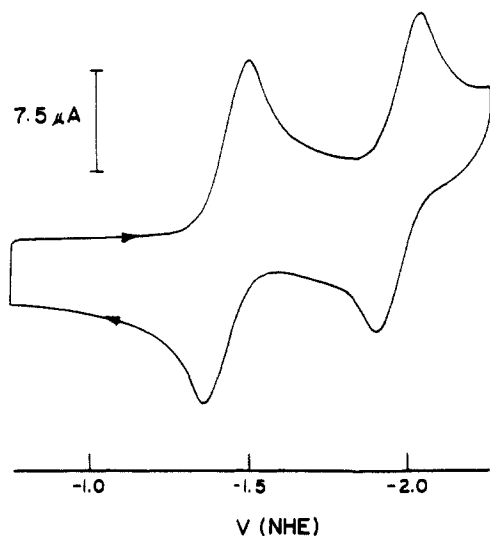
bonding interactions for **1b** and **1c** is that these [1.1.1]propellane derivatives are now predicted to have lower degrees of strain energy than **1a**, and therefore, they also should represent viable synthetic targets. At the present time, however, no synthetic derivatives of **1b** or **1c** have been reported.

With regard to new [1.1.1]propellane analogues, we recently documented the isolation and characterization of the first pentastanna[1.1.1]propellane derivative, Sn$_5$(DEP)$_6$ (DEP = 2,6-diethylphenyl) (3) (M = Sn, R = DEP in 1).[5] Since 3 is readily available, this compound offers the first opportunity to experimentally probe the stability and reactivity of nonclassical frameworks of the heavier group IVA elements. Herein, we report results of investigations aimed at establishing what role the central bridgehead–bridgehead bonding interaction in 3 might play in stabilizing the pentastanna[1.1.1]propellane system.

Results and Discussion

The bridgehead–bridgehead bond length of 3.367 (1) Å found for the pentastanna[1.1.1]propellane **3** falls well outside the range typically observed for normal tin–tin bonds (2.77–2.90 Å). Although bond lengths do not always correlate with bond orders in a simple way, this long bond of **3** does imply that there is a significant reduction in bond order between the two bridgehead nuclei in **3** which is in agreement with the trend predicted by recent theoretical investigations.[3] An important question then becomes, to what extent does this interbridgehead interaction contribute to the overall stability of the pentastanna[1.1.1]propellane framework of **3**? Qualitatively, one can approach an answer to this question by considering the structure and stability of frameworks in which this central bridgehead–bridgehead interaction has been either partially or completely removed.

Chemical Reduction. Ab initio calculations reveal for the [1.1.1]propellane series, **1a–c**, that the highest occupied molecular orbital (HOMO) corresponds to the molecular orbital that represents the bonding interaction between the bridgehead nuclei, and the lowest unoccupied molecular orbital (LUMO) is its corresponding antibonding molecular orbital counterpart.[2,3] For **3**, we felt that if the HOMO contributes little, if anything, to the stability of the [1.1.1]propellane framework, then it should be possible to generate stable reduced species that would formally have the LUMO of **3** occupied by one or two electrons, respectively.

As shown in Figure 1, cyclic voltammetry of **3** in freshly distilled dry tetrahydrofuran (THF) displays two quasireversible one-electron reduction waves at $E_{1/2}$ = -1.41 and -1.93 V (V vs NHE) which correspond to the [Sn$_5$(DEP)$_6$]/[Sn$_5$(DEP)$_6$]$^-$ and the
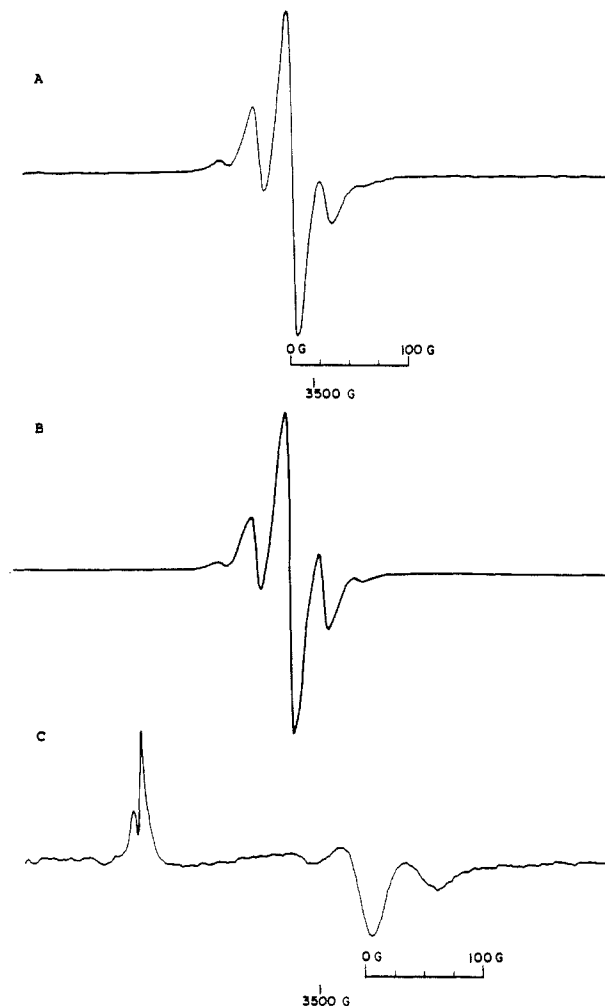

Figure 2. ESR spectra of [Sn$_5$(DEP)$_6$]$^-$[K,crypt]$^+$ in 2-methoxyethyl ether. Spectrum A was recorded at 410 K (g = 1.92). Spectrum B is a simulation of spectrum A with $a(^{119/117}$Sn$_{1,3}$) = 15 G, $a(^{119/117}$Sn$_{2,4,5}$) = 57 G, and line width = 8 G. Spectrum C was recorded at 130 K (frozen) ($g_{\parallel}$ = 1.99 and $g_{\perp}$ = 1.89).

[Sn$_5$(DEP)$_6$]$^-$/[Sn$_5$(DEP)$_6$]$^{2-}$ redox couples, respectively. As hoped for, these data suggested that the radical anion [Sn$_5$(DEP)$_6$]$^-$ should be a stable species, and indeed, we found that in the presence of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane (abbreviated as crypt), the pentastanna-[1.1.1]propellane **3** could be chemically reduced with 0.5% potassium amalgam in toluene at 25 °C to precipitate the complex [Sn$_5$(DEP)$_6$]$^-$[K,crypt]$^+$ as an oil. After exploring a variety of different conditions, we also found that this complex could be obtained in crystalline form; however, none of the crystals proved to be suitable for X-ray analysis.

Of particular interest is whether or not the pentastanna-[1.1.1]propellane framework remains intact upon reduction since any stabilizing role of the central bridgehead–bridgehead bond should now be greatly reduced. With regard to this question, we find that the radical anion [Sn$_5$(DEP)$_6$]$^-$[K,crypt]$^+$ is extremely robust in solution at elevated temperatures and ESR spectroscopy provides compelling evidence to support the view that the five tin atoms in the reduced [1.1.1]propellane maintain the same relative configuration they have in **3**. As shown in Figure 2, the isotropic ESR spectrum of pure [Sn$_5$(DEP)$_6$]$^-$[K,crypt]$^+$ in 2-methoxyethyl ether (diglyme) taken at 410 K (spectrum A) can best be simulated by assuming that spin density is unequally located on two sets of nonequivalent tin atoms, represented by the two bridgehead tin atoms (Sn$_1$ and Sn$_3$) and the three bridging tin atoms (Sn$_2$, Sn$_4$, and Sn$_5$), with the following parameters: g_{iso} = 1.92, $a(^{119/117}$Sn$_{1,3}$) = 15 G, $a(^{119/117}$Sn$_{2,4,5}$) = 57 G, line width = 8 G (spectrum B in Figure 2). Furthermore, the ESR spectrum of this species recorded at 130 K is also consistent with an axially

(5) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454.
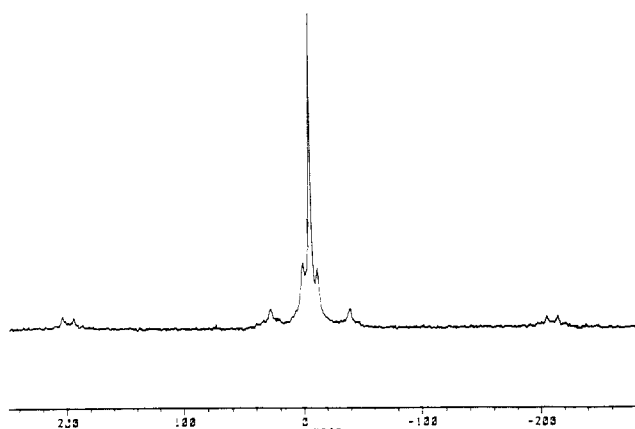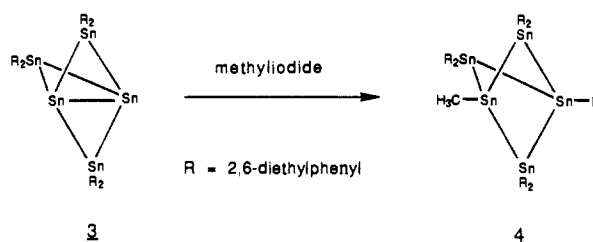
Synthesis of Bicyclo[1.1.1]pentastannane

J. Am. Chem. Soc., Vol. 112, No. 24, 1990 8841

Figure 3. Partial ^{13}C NMR (75 MHz, toluene-d_8, −40 °C) spectrum of isotopically enriched (^{13}CH$_3$)-4 showing the resonance at −8.29 ppm for the methyl group attached to one of the bridgehead tin atoms.

Scheme 1

R = 2,6-diethylphenyl

symmetric structure, such as that of **3**, with $g_{\parallel}$ = 1.99 and $g_{\perp}$ = 1.89 (spectrum C in Figure 2). It is interesting to point out that the spin delocalization observed for [Sn$_5$(DEP)$_6$]$^-$ is similar to that observed previously in the ESR spectra of radical anions of permethylated cyclopolysilanes, [(Me$_2$Si)$_n$]$^-$ (n = 5 and 6).[6] The g values for [Sn$_5$(DEP)$_6$]$^-$, however, are unusual in that they are substantially lower than those previously reported for tin-centered radicals. For example, g_{iso} = 2.03 and g_{aniso} = 1.97, 2.07 for [Sn$_9$]$^{-3}$ and g_{iso} = 2.007 for R$_3$Sn• [R = 2,4,6-R$_3$C$_6$H$_2$ (R = Me, Et, i-Pr)].[7,8]

In addition to the ESR work, we determined that the radical anion [Sn$_5$(DEP)$_6$]$^-$ can be oxidized back to **3** in near quantitative yield with tin dichloride, and this once again implies that the reduced [1.1.1]propellane system is inherently stable. Preliminary data show that this stability of reduced species also extends to dianion [Sn$_5$(DEP)$_6$]$^{2-}$, and this is in agreement with similar studies of the stability and chemical reactivity of dianion [C$_5$H$_6$]$^{2-}$, which is prepared by chemical reduction of **1a**.[9a] On the basis of these results of the chemical reduction of **3**, it is our conclusion that the central interaction between the bridgehead tin atoms in **3** contributes very little to the stability of this system.

Comparison to Bicyclo[1.1.1]pentastannanes. One practice commonly used to qualitatively measure the bond order of the central bond between the bridgehead nuclei in experimental and calculated structures of [1.1.1]propellanes is to compare the bridgehead–bridgehead separations in these molecules with the analogous separations in the corresponding bicyclo[1.1.1]pentane derivatives (i.e. **1a** vs **2a** and **1b** vs **2b** in Chart I). For a similar comparison to be made of the pentastanna[1.1.1]propellane framework of **3**, however, we first required a bicyclo[1.1.1]pentastannane.

In a reaction similar to the photochemical addition of methyl iodide to **1a**,[9b] compound **3** reacted quantitatively at room temperature with methyl iodide in toluene to produce the bicyclo-[1.1.1]pentastannane derivative **4** as determined by NMR spec-

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**[a,b]

	Bond Lengths		
Sn$_1$–Sn$_2$	2.837 (1)	Sn$_2$–Sn$_3$	2.825 (1)
Sn$_1$–Sn$_4$	2.828 (1)	Sn$_3$–Sn$_4$	2.838 (1)
Sn$_1$–Sn$_5$	2.830 (1)	Sn$_3$–Sn$_5$	2.842 (1)
Sn$_1$···Sn$_3$[d]	3.361 (1)	Sn$_1$–I$_1$[c]	2.619 (2)
		Sn$_3$–I$_2$[c]	2.631 (2)

	Bond Angles		
Sn$_2$Sn$_1$Sn$_3$	53.4 (1)	Sn$_2$Sn$_1$Sn$_4$	88.3 (1)
Sn$_3$Sn$_1$Sn$_4$	53.8 (1)	Sn$_2$Sn$_1$Sn$_5$	88.3 (1)
Sn$_3$Sn$_1$Sn$_5$	53.8 (1)	Sn$_4$Sn$_1$Sn$_5$	88.8 (1)
Sn$_1$Sn$_3$Sn$_2$	53.7 (1)	Sn$_2$Sn$_3$Sn$_4$	88.3 (1)
Sn$_1$Sn$_3$Sn$_4$	53.5 (1)	Sn$_2$Sn$_3$Sn$_5$	88.3 (1)
Sn$_1$Sn$_3$Sn$_5$	53.5 (1)	Sn$_4$Sn$_3$Sn$_5$	88.4 (1)
Sn$_2$Sn$_1$I$_1$[c]	126.5 (1)	Sn$_2$Sn$_3$I$_2$[c]	124.4 (1)
Sn$_4$Sn$_1$I$_1$[c]	130.0 (1)	Sn$_4$Sn$_3$I$_2$[c]	125.3 (1)
Sn$_5$Sn$_1$I$_1$[c]	122.4 (1)	Sn$_5$Sn$_3$I$_2$[c]	129.4 (1)
Sn$_3$Sn$_1$I$_1$[c]	175.7 (1)	Sn$_1$Sn$_3$I$_2$[c]	177.0 (1)
Sn$_1$Sn$_2$Sn$_3$	72.8 (1)	C$_{1a}$Sn$_2$C$_{2a}$	106.7 (4)
Sn$_1$Sn$_4$Sn$_3$	72.8 (1)	C$_{3a}$Sn$_4$C$_{4a}$	108.7 (5)
Sn$_1$Sn$_5$Sn$_3$	72.7 (1)	C$_{5a}$Sn$_5$C$_{6a}$	108.8 (5)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 4. [c] The methyl and I atoms bonded to the "apical" Sn atoms (Sn$_1$ and Sn$_3$) appear to be nearly statistically disordered in the solid state. The occupancy factors of an iodine atom at the positions for I$_1$ and I$_2$ refined to 0.540 (3) and 0.573 (3), respectively. A statistically disordered methyl and iodine atom would correspond to an occupancy factor of approximately 0.557. [d] Nonbonded distance.
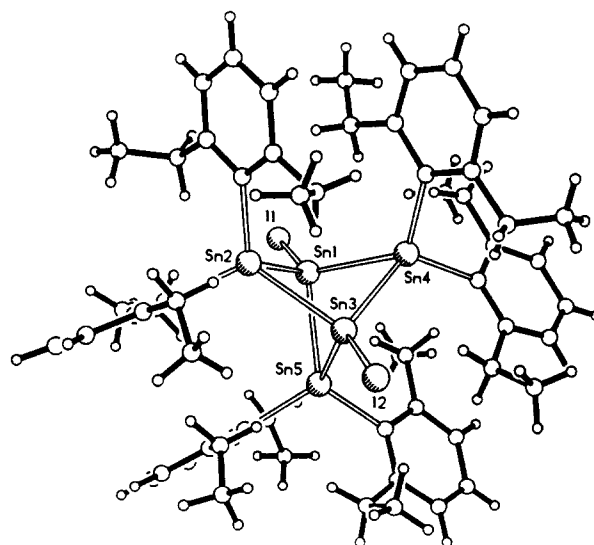

Figure 4. Molecular structure of **4** with all atoms represented by spheres of varying size for purposes of clarity. The methyl group and the iodine atom (collectively labeled I$_1$ and I$_2$) bonded to the bridgehead tin atoms (Sn$_1$ and Sn$_3$) appear to be nearly stastistically disordered in the solid state.

troscopy (Scheme I). Conclusive proof for the presence of the methyl substituent at the bridgehead position, however, could only be obtained from a ^{13}C NMR spectrum, taken at −40 °C, of a pure sample of **4** that was prepared by treating **3** with isotopically enriched ^{13}CH$_3$I (99%). As shown in Figure 3, this spectrum revealed a resonance at −8.29 ppm for the methyl substituent that exhibited coupling to three sets of nonequivalent tin atoms with coupling constants assigned as follows: $^1J(^{119}$Sn$_1$–^{13}C) = 418 Hz, $^1J(^{117}$Sn$_1$–^{13}C) = 399 Hz, $^2J(^{119/117}$Sn$_{2,4,5}$–^{13}C) = 12 Hz, ^3J-($^{119/117}$Sn$_3$–^{13}C) = 67 Hz.[10]

Bicyclo[1.1.1]pentastannane derivative **4** displays unique optical properties with an absorption maximum in hexane at λ_{max} 500 nm (ϵ_{max} 1700) and it is unstable in solution at room temperature

(6) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.
(7) Critchlow, S. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 5715.
(8) Lehnig, M.; Buschhaus, H.-U.; Neumann, W. P.; Apoussidis, Th. *Bull. Soc. Chim. Belg.* **1980**, *89*, 907.
(9) (a) Bunz, U.; Szeimies, G. *Tetrahedron Lett.* **1990**, *31*, 651. (b) Benz, U.; Szeimies, G. *Ibid.* **1989**, *30*, 2087.

(10) Assignment of $^nJ(^{119/117}$Sn–^{13}C) values is based on the relative intensity of each satellite pair to the parent resonance.

8842 *J. Am. Chem. Soc., Vol. 112, No. 24, 1990*

Sita and Kinoshita

$(t_{1/2} = 1 \text{ h})$.[11] However, this compound could be isolated as deep-red crystals by simply cooling the reaction mixture to -40 °C, and crystals obtained in this fashion, using a 5:1 toluene–pentane solvent mixture, were found to be suitable for crystallographic analysis. Selected bond lengths and bond angles are given in Table I.[12]

As can be seen in Figure 4, the crystallographic data reveal that, in the solid state, the methyl group and the iodine atom bonded to the bridgehead tin atoms (Sn_1 and Sn_3, respectively) are nearly statistically disordered with the occupancy factor of an iodine atom at the positions labeled I_1 and I_2 refining to 0.540 (3) and 0.573 (3), respectively.[13] While this disorder prevents an accurate determination of the Sn–I and Sn–CH$_3$ bond lengths, all other non-hydrogen atoms in the structure can be accurately positioned, and this allows one to make the desired comparison of the tin-bonded framework comprised of the five tin atoms of 4 with that previously determined for pentastanna[1.1.1]propellane 3.

The most striking feature of a comprison of the structures of 3 and 4 is that the two systems are essentially isostructural with regard to tin–tin bond lengths and angles, and this includes the nonbonded distance of 3.361 (1) Å between the bridgehead tin atoms of 4, which can be compared with the corresponding distance of 3.367 (1) Å between the bridgehead tin atoms found for 3. Qualitatively, these data suggest that the bond order between the bridgehead tin atoms is very low in 3 and that the separations between the bridgehead atoms in both of the frameworks of 3 and 4 are governed largely by geometrical constraints.

In conclusion, the stability of the reduced pentastanna-[1.1.1]propellane species, and the very small bond order suggested for 3 on the basis of structural data, supports the view that the central bonding interaction between the bridgehead tin atoms in pentastanna[1.1.1]propellanes contributes very little to stability. Furthermore, the reaction of 3 with methyl iodide indicates that the chemical reactivity of this compound may best be viewed as that of a diradical, and in this regard, pentastanna[1.1.1]propellane 3 should be a valuable synthetic starting material for a variety of bicyclo[1.1.1]pentastannanes. Currently, this idea is being explored.

Experimental Section

Manipulations were performed under an inert atmosphere of nitrogen or argon by using standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. For electrochemistry, THF was distilled from Na–benzophenone under nitrogen and used immediately thereafter. Methyl iodide and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane were used as obtained from Aldrich. Methyl iodide (99% ^{13}C) was used as obtained from Cambridge Isotope Laboratories. 2,2,4,4,5,5-Hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane, $Sn_5(DEP)_6$ (3), was prepared according to procedures described elsewhere.[5]

Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories or Oneida Research Services, Inc. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on an IBM NR 300 spectrometer, infrared spectra were recorded on a Nicolet FT-IR spectrometer, and absorption spectra were recorded on a Perkin-Elmer 3840 Lamda Array spectrometer. ESR spectra were recorded with an IBM ESP 300 spectrometer operating at X-band frequencies and isotropic ESR spectra were simulated on a MacIntosh II computer with use of the ESR II software of Calleo Co. without compensation for anisotropic line widths. Electrochemical measurements were made with standard PAR instrumentation. In cyclic voltammetric experiments, the supporting electrolyte 0.1 M Bu_4NPF_6 in THF was used and potentials were measured at 298 K in a simple one-compartment cell. The reference electrode was a Ag wire immersed in a solution of 0.1 M $AgNO_3$ in acetonitrile which was connected to the supporting electrolyte with a

---

(11) The instability of 4 in solution is attributed to facile heterolytic dissociation of the tin–iodine bond since 1,3-dimethyl-2,2,4,4,5,5-hexakis(2,6-diethylphenyl)bicyclo[1.1.1]pentastannane, which can be prepared from 4 and methyllithium, is indefinitely stable: Sita, L. R.; Kinoshita, I. Results to be published.

(12) Detailed information is supplied in the supplementary material.

(13) The occupancy factor of an iodine atom at a site that is iodine half of the time and carbon the other half of the time would refine to a value of $(53 + 6)/(2 \times 53) = 0.557$, and two such sites would sum to 1.113.

Table II. Crystal, Data Collection, and Refinement Parameters for **4**

formula	$C_{61}H_{81}ISn_5$
system	monoclinic
cryst size, mm	$0.30 \times 0.35 \times 0.88$
a, Å	14.785 (2)
b, Å	20.319 (3)
c, Å	22.951 (3)
β, deg	97.63 (1)
V, Å^3	6834 (1)
D(calcd), g cm^{-3}	1.492
space group	$P2_1/c$–C_{2h}^5 (No. 14)
Z	4
temp, °C	20
radiation	Mo Kα (graphite monochromated)
scan technique	ω
μ, mm^{-1}	2.29
$2\theta_{max}$, deg	45.8
no. of data	9395
no. of data in refinement	4924
R	0.043
criteria	$I > 3\sigma(I)$

Vycor tip filled with 0.1 M Bu_4NPF_6 in THF. A Pt wire was used as the counter electrode, and glassy carbon was used as the working electrode. Under the conditions employed, the potential (V) of the ferrocinium–ferrocene couple was 0.125 in THF and a reference value of 0.4 for this redox couple was used to correct measured potentials to those reported vs NHE.

Preparation of [$Sn_5(DEP)_6$]$^-$[K,crypt]$^+$. To a deep-purple solution of 64 mg (0.046 mmol) of $Sn_5(DEP)_6$ (3) in 3 mL of toluene, 17 mg (0.046 mmol) of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (abbreviated as crypt) and 410 mg of potassium amalgam (0.1313 mmol/g) were added. The mixture was stirred for 30 min whereupon an oily product was formed and the toluene supernatant was nearly colorless. The mixture was left to stand for 30 min and then the toluene layer was removed by decanting. The oily product was dissolved in 3 mL of 1,2-dimethoxyethane to produce a deep blue–purple solution. At this time, 15 mL of toluene was added and the solution was stored at -40 °C. After 7 days, fine black needles appeared which reverted easily to an oil at room temperature in the presence of the mother liquor. However, by washing the crystals with cold hexane at -40 °C, and quickly drying them in vacuo, 20 mg (24% yield) of the product was obtained as a stable black microcrystalline powder. Absorption spectrum (THF) λ_{max} 400 nm (ϵ_{max} 8710), 458 nm (sh) (4190), 558 nm (6610), 633 nm (5320) and 720 nm (1910).

As a proof of structure, 2.5 mL of a solution of [$Sn_5(DEP)_6$]$^-$[K,-crypt]$^+$ in THF ($c = 8.7 \times 10^{-4}$ M) was oxidized with 1 mL of a solution of $SnCl_2$ in THF ($c = 2.2 \times 10^{-3}$ M) to produce 3 in a 98% yield as determined by a photometric assay based on the absorption maxima of 3.[5]

Preparation of 2,2,4,4,5,5-Hexakis(2,6-diethylphenyl)-1-iodo-3-methylbicyclo[1.1.1]pentastannane (4). To a solution of 52 mg (0.037 mmol) of 3 in 7 mL of n-pentane, 4.6 μL (0.073 mmol) of methyl iodide (or methyl iodide, 99% ^{13}C) was added at room temperature. The reaction mixture was stirred at room temperature for 5 min and then cooled to -40 °C whereupon 4 deposited as dark-red crystals. After 3 days, 33 mg (58% yield) of the product was collected. Anal. Calcd for 4: C, 47.76; H, 5.32; I, 8.27. Found: C, 48.05; H, 5.30; I, 8.01. Absorption spectrum (hexane) λ_{max} 500 nm (ϵ_{max} 1700). For variable-temperature ^{1}H NMR (toluene-d_8) spectra of 4 and a ^{13}C NMR (toluene-d_8, -40 °C) spectrum of isotopically enriched 4 (99% ^{13}CH$_3$), see the supplementary material. A portion of this latter spectrum showing the resonance at -8.29 ppm [$^1J(^{119}Sn_1–^{13}C) = 418$ Hz, $^1J(^{117}Sn_1–^{13}C) = 399$ Hz, ^2J-($^{119/117}Sn_{2,4,5}–^{13}C) = 12$ Hz, $^3J(^{119/117}Sn_3–^{13}C) = 67$ Hz] for the methyl group attached to one of the bridgehead tin atoms is shown in Figure 3.

Crystal Data for Compound 4.[12] Crystals suitable for X-ray analysis were obtained from a 5:1 toluene–pentane solvent mixture at -40 °C. Crystallographic data are summarized in Table II. Single crystals of 4 are (at 20 °C) monoclinic, space group $P2_1/c$–C_{2h}^5 (No. 14) with $a = 14.785$ (2) Å, $b = 20.319$ (3) Å, $c = 22.951$ (3) Å, $\beta = 97.63$ (1)°, $V = 6834$ (2) Å,^{3} and $Z = 4$ ($D_{calcd} = 1.492$ g cm^{-3}; μ_a(Mo K$\bar{\alpha}$) = 2.29 mm^{-1}. A total of 9395 independent reflections having 2θ(Mo Kα) < 45.8° (the equivalent of 0.6 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer with full (0.90° wide) ω scans and graphite-monochromated Mo Kα radiation. The structure was solved by using "direct methods" techniques with the Nicolet SHELTX software package as modified at the Crystalytics Company. The resulting structural parameters have been refined to convergence {R_1(unweighted, based on F) = 0.043 for 4924 independent absorption-corrected reflec-

tions having 2θ(Mo Kᾱ < 45.8° and *I* > 3σ(*I*)| with counter-weighted cascade block diagonal least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all non-hydrogen atoms except C_{6s} and $C_{6s'}$, which were refined isotropically, and isotropic thermal parameters for all hydrogen atoms. The methyl groups were included in the refinement as idealized sp³-hybridized rigid rotors and gave final values for the C–C–H angles that ranged from 92° to 130°. The remaining hydrogen atoms were fixed at idealized sp²- or sp³-hybridized positions with a C–H bond length of 0.96 Å. The methyl and I atoms bonded to the "apical" Sn atoms (Sn_1 and Sn_2) appear to be nearly statistically disordered in the solid state. The occupancy factor of an iodine atom at the positions for I_1 and I_2 refined to 0.540 (3) and 0.573 (3), respectively. A statistically disordered methyl and iodine would correspond to an occupancy factor of approximately 0.56. There also appears to be a disordered pentane molecule of crystallization in the lattice that can be specified by various combinations of atoms C_{1a}, C_{2s},

C_{3s}, C_{4s}, $C_{4s'}$, C_{5s}, C_{6s}, and $C_{6s'}$. Occupancy factors of 1.00 were used for carbon atoms at C_{2s}, C_{3s}, and C_{5s}, while occupancy factors of 0.50 were used for C_{1s}, C_{4s}, and $C_{4s'}$, and 0.25 for C_{6s} and $C_{6s'}$.

Supplementary Material Available: Detailed information concerning the spectroscopic data and crystallographic analysis of **4**, including listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors (22 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Dimetallacalix[8]arene Complexes

Gretchen E. Hofmeister, Eugenio Alvarado, Julie A. Leary, Dong I. Yoon, and Steven F. Pedersen*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received March 26, 1990

Abstract: The one-pot synthesis of a variety of [4-*tert*-butylcalix[8]arene(MOR)₂]⁻[M' or R'NH₃]⁺ (M = Ti, Zr, V, Sn; M' = Li, Na, K) complexes is described. The ¹H NMR spectra of these complexes possess several interesting features, including upfield shifts (by 0.5–2.0 ppm) of α or β protons on the alkoxide ligand and a phenol hydroxyl resonance at ca. 16 ppm. The upfield shift is due to shielding of the alkoxide ligand by the aryl rings of the calixarene macrocycle. The ligands are located in cavities, made up of three aryl rings of the macrocycle. Fast atom bombardment mass spectrometry (FABMS) and tandem mass spectrometry (MS/MS and MS/MS/MS) have been used to obtain molecular ion information as well as identify fragment ions from these complexes. Two-dimensional NMR experiments have established that the solution structure is the same as in the solid state and have also allowed assignment of all of the macrocycle protons in the ¹H NMR spectrum. A difference NOE experiment has determined the location of the remaining phenol hydroxyl proton, which had not been located previously by X-ray crystallography.

Calixarenes are a class of phenol-containing macrocycles, which are easily synthesized in large quantities from commercially available starting materials (e.g. 4-*tert*-butylphenol and formaldehyde).[1] One notable property of these compounds is their ability to include small organic molecules into a cavity formed by the aryl ring framework. Furthermore, these macrocycles can be easily derivatized at the para position and/or the hydroxyl group. For example, water-soluble calixarenes have recently been synthesized by incorporating sulfate groups into the para positions of the aryl rings.[2] Further derivatization of the hydroxyl functions provided macrocyclic complexes capable of binding uranyl ions.[3]

We and others have recently reported using the hydroxyl groups in calixarenes for direct binding to metal ions.[4,5] Our interest

in this area has focused on the synthesis of metallacalixarene complexes that contain metal–ligands directed into cavities composed of aryl rings. The ultimate goal of these efforts is the application of these materials in shape-selective organic synthesis. Herein, details on the synthesis and in-depth characterization of a variety of dimetalla-4-*tert*-butylcalix[8]arene complexes (dimetallacalix[8]arenes) are provided.

Results

Synthesis. The reaction of 4-*tert*-butylcalix[8]arene (**1**) with 2 equiv of Ti(O-*i*-Pr)₄ in either toluene, dichloromethane, or tetrahydrofuran (THF) (**1** is only partially soluble in any of these solvents) produced a yellow precipitate whose ¹H NMR spectrum showed that a mixture of several compounds was present. In an effort to solubilize **1**, 2 equiv of lithium or sodium bis-(trimethylsilyl)amide were added to **1** in THF. This provided a homogeneous solution to which Ti(O-*i*-Pr)₄ was added (eq 1, *n* = 2). These reactions yielded a product with the general molecular
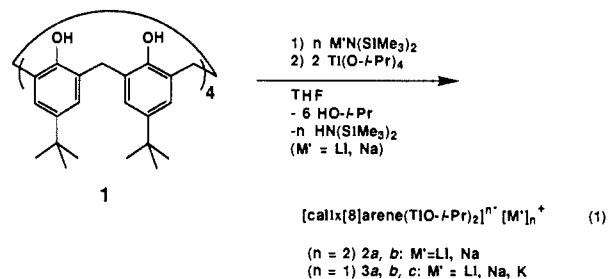
formula [4-*tert*-butylcalix[8]arene(TiO-*i*-Pr)₂]²⁻[M']₂⁺ (**2a,b**) (established by positive ion fast atom bombardment mass spec-

(1) (a) Calixarenes. Gutsche, C. D. *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1989. (b) Gutsche, C. D. In *Progress in Macrocyclic Chemistry*; Izatt, R. M., Christensen, J. J., Eds.; John Wiley and Sons, Inc.: New York, 1987; Vol. 3, Chapter 3. (c) Munch, J. H.; Gutsche, C. D. *Org. Synth.* **1989**, *68*, 243.
(2) Shinkai, S.; Mori, S.; Koreishi, H.; Tsubaki, T.; Manabe, O. *J. Am. Chem. Soc.* **1986**, *108*, 2409.
(3) (a) Shinkai, S.; Koreishi, H.; Ueda, K.; Manabe, O. *J. Chem. Soc., Chem. Commun.* **1986**, 233. (b) Shinkai, S. *Pure Appl. Chem.* **1986**, *11*, 1523.
(4) Hofmeister, G. E.; Hahn, F. E.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 2318.
(5) (a) Furphy, B. M.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H.; Wilner, F. R. *J. Chem. Soc., Dalton Trans.* **1989**, 2217. (b) Englehardt, L. M.; Furphy, B. M.; Harrowfield, J. M.; White, A. H.; Wilner, F. R. *Aust. J. Chem.* **1988**, *41*, 1465. (c) Furphy, B. M.; Harrowfield, J. M.; Kepert, D. L.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Inorg. Chem.* **1987**, *26*, 4231. (d) Andreetti, G. D.; Calestani, G.; Ugozzoli, F.; Arduini, A.; Ghidini, E.; Ungaro, R. *J. Inclusion Phenom.* **1987**, *5*, 123. (e) Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1986**, 610. (f) Olmstead, M. M.; Sigel, G.; Hope, H.; Xu, X.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 8087.