1,5,9-Tristannacyclododecanes as Lewis Acids. Novel Structure of a Chloride Complex

Klaus Jurkschat,[†] Henry G. Kuivila,^{*,‡} Shuncheng Liu,[‡] and Jon A. Zubieta[‡]

Departments of Chemistry, Martin-Luther University Halle-Wittenberg, Postfach, DDR-4010 Halle/S., German Democratic Republic, and State University of New York at Albany, Albany, New York 12222

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A simple procedure for the preparation of substituted 1,5,9-tristannacyclododecanes RRSn-(CH₂)₃SnRR'(CH₂)₃SnRR(CH₂)₃ {R = R' = CH₃ (3); R = CH₃, R' = Cl (4); R = R' = Cl (5)} is described. Their complexing behavior toward chloride was investigated by means of ¹¹⁹Sn NMR spectroscopy. Both 4 and 5 yielded evidence for complex formation but behaved differently from each other. A complex {(5Cl)(Ph₃P=N=PPh₃)⁺} (6) was isolated; its structure as determined by single-crystal X-ray diffraction shows that 5 acts as a bidentate Lewis acid via unsymmetrical transannular bridging by a chloride ion. 6 crystallizes in the monoclinic space group $P_{2_1/c}$ with the unit-cell dimensions a = 11.691 (2) Å, b = 24.652(4) Å, c = 17.353 (4) Å, $\beta = 92.70$ (1)°, V = 5110.6 Å³, and D(calcd) = 1.65 g/cm^{-3} for Z = 4. The structure was refined to a final R value of 0.039 for 4003 independent reflections.

Introduction

The complexation chemistry of multidentate acyclic ligands with cations has developed steadily over the last century; during the past 2 decades it has expanded rapidly to macrocyclic ligands that are a familiar part of the chemists inventory. In contrast, reports on studies of the chemistry of the complementary multidentate acids have only recently begun to appear. These include cationic species such as polyammonium compounds that interact with donors via hydrogen bonds.^{2,3} Apparently the earliest report that is relevant to this study involving a neutral Lewis acids is that of Shriver on ethane-1,2-bis(difluoroborane) describing evidence for a chelate effect.⁴ More recently Katz has observed powerful bidentate effects with 1,8-naphthalenebis(dichloroborane) chloride^{5a,b} and a silylborane.^{5c} Bidentate complexes of 1,2-phenylenedimercury with halide ions,^{6a,b} dimethylformamide,^{6c} and tetrahydrofuran^{6d} have been isolated and characterized. Halogen-bridged and oxygen-bridged complexes of bis-(halostannyl)methanes have also been isolated and characterized.^{7,8} NMR evidence has been adduced for cooperative binding of halide ions with macrocyclic and bicyclic ditins.⁹ Transfer of halide ions in liquid membrane experiments with 1,5,9-trisiladodecane has been reported, although other evidence for complexation was not obtained.¹⁰ In this paper we report the first preparative scale synthesis of 1,5,9-tristannacyclododecane derivatives along with complexation studies with chloride of two chloro derivatives and the isolation and structure determination of the first chloride complex of a monocyclic multitin.

Results and Discussion

As shown in Scheme I the reaction of disodium 1,3bis(trimethylstannyl)propane (1) with bis(3-chloropropyl)dimethyltin (2) yields 1,1,5,5,9,9-hexamethyl-1,5,9-tristannacyclododecane $(3)^{11}$ in about 35% yield. Compound 3 is a colorless, volatile liquid that can be easily transformed into the trichloro derivative 4 and into the heaxachloro derivative 5 upon reaction with the appropriate number of equivalents of mercuric chloride. Compounds 4 and 5 are colorless, very fine needles that display limited solubility in noncoordinating solvents. This sug-



gests that these compounds form polymeric networks in the solid state by intermolecular chlorine bridges. The ¹H NMR spectrum of 4 shows only a one signal for methyl protons, suggesting that it may be the all-cis isomer. The cis-cis-trans isomer would show two signals with an in-

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Figure 1. Plots of chloride/tin ratios vs 119 Sn chemical shifts for 4 and 5 in chloroform at 298 K: (a) compound 5; (b) compound 4.

tensity ratio of 2:1. However, it is possible that both isomers are present in solution and undergo interconversion by way of a chloride exchange with inversion.

Qualitative Anion Complexation Studies. The complexation of 3, 4, and 5 with chloride added as $[Ph_3P=N=Ph_3]^+Cl^-$ was studied by ¹¹⁹Sn NMR. Only one tin signal was observed in each experiment indicating rapid chloride exchange on the NMR time scale. When 1 equiv of chloride/tin was added to a chloroform solution of 3, a change in the chemical shift from -10.4 to -10.9 ppm occurred, indicating that no significant complexation occurred.

Substantial effects were observed with 4 and 5 as can be seen from Figure 1. Although 4 is essentially insoluble in chloroform, addition of a 0.5 mol of chloride/mol of tin did cause 4 to dissolve and provide a solution showing a chemical shift of 83.1 ppm. Nonetheless it was deemed to be desirable to estimate the chemical shift of 4 itself. This could be approximated in two ways. Cyclic analogues with two methylchlorotins in rings of seven, eight, nine, and ten members show chemical shifts in the range 150-163 ppm.^{12a} Also linear extrapolation of the plot in Figure 1 leads to a value around 150 ppm. With these values in hand one can estimate that the addition of the first 0.5 mol of chloride/mol of tin in 4 moves the signal upfield by about 70 ppm to 83.1 ppm, and the second 0.5 mol brings about an additional shift of 40-43.3 ppm. The total shift of 110 ppm suggests formation of a very stable 1:1 complex. Further addition of the second and third moles of chloride caused changes in the chemical shift to 28.8 and 22.1 ppm, respectively. The values of 43.3 and 22.1 ppm fall within the range for pentacoordinate tins.¹³ The small increment of only 21 ppm implies little change in the average coordination number of the tins upon addition of more than 1 mol of chloride/mol of 4! This may be rationalized in at least three ways. In one of these the chloride is bonded to 4 symmetrically in the complex (eq 1, S = 4). This suggests the formation of a rather stable

$$S + Cl^- \rightleftharpoons SCl^-$$
 (1)

$$\mathrm{SCl}^- + \mathrm{Cl}^- \rightleftharpoons \mathrm{SCl}_2^-$$
 (2)

1:1 complex. Addition of only 1 mol of chloride converts most of 4 to 4Cl⁻, a symmetrically bridged species. Further



increments simply shift the equilibrium of eq 1 to the right causing the modest upfield shift observed. In a second formulation the equilibria of eq 1 and 2 are established. The product of eq 1 is $4Cl^{-}$ and that of eq 2 is $4Cl_{2}^{-}$. In each of these all three tins are pentacoordinate so the chemical shifts of the two species should be similar but not identical.

The third alternative for $4Cl^-$ would involve monodentate coordination with rapid exchange of the chloride ion among the three tin sites. In this case the chemical shift should move upfield from that for 4 by one-third of the difference between tetracoordinate and pentacoordinate tins. The total change upon addition of three chlorides/mol of 4 is about 130 ppm. A shift of one-third of this value, or 43 ppm, from the initial value near 150 ppm would lead to a value of 97 ppm that is well below that of 43.3 ppm observed when 1 mol of chloride/mol of tin is present.

As 5 is also insoluble in chloroform its chemical shift must be estimated, but data for the cyclic tetrachlorodistannacycloalkanes are of limited use. Observed values are as follows: for 1,1,5,5-tetrachloro-1,5-distannacyclooctane, +15 ppm (in the solid state both tins are pentacoordinate due to intra- and intermolecular chloride bridging in a linear polymeric structure^{12b}); for 1,1,5,5tetrachloro-1,5-distannacyclononane, +119 ppm; for 1,1,6,6-tetrachloro-1,6-distannacyclodecane, +36 ppm.^{12a} Extrapolation of the data presented in Figure 1 leads to a value of about 120 ppm for 5. With use of this value the first mole of chloride causes an upfield shift of about 90 ppm to -32 ppm in the chemical shift. The second mole causes an additional shift of 91 ppm to -123 ppm, whence further additions cause a change of only about 10 ppm. The striking observation here is the large chemical shift changes caused by the additions of each of the first 2 mol of chloride; this represents a distinct difference in the the behavior of 5 as compared to that of 4. It leads to the conclusion that 5 forms very stable complexes with one and with two chlorides, respectively; i.e., the equilibria of eq 1 and 2 (S = 5) lie very far to the right. The average coordination number is lower in 5Cl⁻ than in 5Cl₂⁻ whose maximum value must be near five because a coordination number of six would require a chemical shift higher by at least 100 ppm.¹³ The structure shown for $5Cl_2^{-1}$ is an em-



inently reasonable one for it accommodates the stoichiometry with two chlorides/mol and the pentacoordinate structure of all of the three tins. Three structures can be considered for $5Cl^-$ in relation to chemical shifts on the assumption that the total chemical shift change from 5 to $5Cl^-$ is 250 ppm. If $5Cl^-$ is a stable, rapidly exchanging

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Table I. Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(Å^2 \times 10^3)$ for the Anionic Mojety of 7

	A.	momic molet,	y 01 7		
	x	у	z	U(eq)	
Sn(1)	2783 (1)	-1223 (1)	10793 (1)	42 (1)	
Sn(2)	3957 (1)	877 (1)	11701 (1)	47 (1)	
Sn (3)	1634 (1)	-50(1)	9299 (1)	36 (1)	
Cl(1)	4447 (2)	-1763(1)	10719 (2)	74 (1)	
Cl(2)	2007 (3)	-1758(1)	11810 (2)	67 (1)	
C1(3)	2234 (3)	910 (2)	12342 (2)	95 (1)	
Cl(4)	5055 (3)	1522 (1)	12393 (2)	107 (2)	
Cl(5)	2331 (2)	267 (1)	8135 (1)	46 (1)	
Cl(6)	-312(2)	406 (1)	9058 (1)	53 (1)	
Cl(7)	3644 (2)	-566 (1)	9584 (1)	46 (1)	
C(1)	3253 (8)	-554 (4)	11502 (5)	48 (4)	
C(2)	4477 (8)	-360(4)	11481 (6)	52 (4)	
C(3)	4729 (8)	123 (4)	12015 (5)	49 (4)	
C(4)	3597 (8)	1231 (4)	10634 (5)	46 (4)	
C(5)	3299 (7)	820 (4)	9991 (5)	49 (4)	
C(6)	2150 (7)	560 (3)	10103 (5)	40 (3)	
C(7)	862 (8)	-811(4)	9034 (5)	46 (4)	
C(8)	1487 (9)	-1330 (4)	9155 (5)	57 (4)	
C(9)	1585 (8)	-1550 (4)	9968 (5)	51 (4)	

Table II. Bond Lengths (Å)

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	Sn(1)-Cl(1)	2.365 (3)	Sn(1)-Cl(2)	2.445 (2)
	Sn(1)-Cl(7)	2.906(2)	Sn(1) - C(1)	2.132 (9)
	Sn(1)-C(9)	2.135 (9)	Sn(2) - Cl(3)	2.361 (3)
	Sn(2)-Cl(4)	2.353 (3)	Sn(2) - C(3)	2.130 (9)
	Sn(2)-C(4)	2.111 (9)	Sn(3)-Cl(5)	2.387 (2)
	Sn(3)-Cl(6)	2.556(2)	Sn(3)-Cl(7)	2.700 (2)
	Sn(3)-C(6)	2.140 (8)	Sn(3) - C(7)	2.127 (8)
	C(1) - C(2)	1.510 (12)	C(2) - C(3)	1.542 (12)
	C(4) - C(5)	1.554 (12)	C(5) - C(6)	1.509 (11)
	C(7) - C(8)	1.483 (12)	C(8)-C(9)	1.540 (12)

monodentate structure, then the chemical shift change would be upfield by 83 ppm to +37 ppm, well below that observed. If it is a bidentate structure analogous to that shown for $4Cl^-$ the chemical shift change would be 166 ppm to -46 ppm. And if it were a tridentate species, all three tins being pentacoordinate, the shift would be to the maximum value observed, around -130 ppm. The value for the bidentate structure is clearly the only one near that observed, making it the preferred structure.

It would be desirable to obtain evidence to test these conclusions. To this end we have sought to isolate and to determine the structures of complexes and have succeeded in one case. When an attempt was made to obtain a crystalline complex of $4Cl^{-}$, an oil that turned to a glass 6 resulted, but no crystals could be obtained. Reaction of 5 with $Ph_3P=N=PPh_3^+Cl^-$ provided crystals of a compound (7) with the composition $5Cl^-$.

Molecular Structure of 6. Single-crystal X-ray diffraction showed the anionic moiety of 6 to have the structure shown in Figure 2. Atomic coordinates and equivalent isotropic displacement parameters for all atoms of the anion are presented in Table I. Bond lengths and angles are presented in Tables II and III, respectively. The structure shows that 5 acts as a bidentate Lewis acid toward the chloride ion in 6: Sn(1) and Sn(3) are pentacoordinate whereas Sn(2) is tetracoordinate. The chloride bridge is unsymmetrical, and the trigonal-bipyramidal geometries around Sn(1) and Sn(3) are distorted, but to different degrees. At Sn(3) the equatorial groups fall in the same plane with a maximum deviation of ca 0.1 Å from the best least-squares plane through the atoms although the angles are different from 120°. For example, the intraannular angle C(7)-Sn(3)-C(6) is expanded to 150.5 (3)°, and the other two angles are smaller: 104.9 (3)° and 104.5 (2)°. The axial tin-chlorine bond lengths at Sn(3)are 2.700 (2) and 2.556 (1) Å. At Sn(1) these lengths are



Figure 2. ORTEP view of the structure of 7. The cationic part is omitted for clarity.

Table III. Dond Angles (deg	Table	III.	Bond	Angles	(deg
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Cl(2)-Sn(1)-Cl(1)	94.2 (1)	Cl(7)-Sn(1)-Cl(1)	87.6 (1)
Cl(7)-Sn(1)-Cl(2)	178.3 (1)	C(1)-Sn(1)-Cl(1)	106.1 (3)
C(1)-Sn(1)-Cl(2)	94.3 (3)	C(1)-Sn(1)-Cl(7)	85.2 (3)
C(9)-Sn(1)-Cl(1)	105.4 (3)	C(9)-Sn(1)-Cl(2)	92.8 (2)
C(9)-Sn(1)-Cl(7)	86.7 (2)	C(9)-Sn(1)-C(1)	147.1 (4)
Cl(4)-Sn(2)-Cl(3)	100.5 (1)	C(3)-Sn(2)-Cl(3)	105.3 (3)
C(3)-Sn(2)-Cl(4)	103.9 (3)	C(4)-Sn(2)-Cl(3)	106.3 (3)
C(4)-Sn(2)-Cl(4)	105.6 (3)	C(4)-Sn(2)-C(3)	131.3 (4)
Cl(6)-Sn(3)-Cl(5)	92.8 (1)	Cl(7)-Sn(3)-Cl(5)	89.3 (1)
Cl(7)-Sn(3)-Cl(6)	177.5 (1)	C(6)-Sn(3)-Cl(5)	104.5 (2)
C(6)-Sn(3)-Cl(6)	91.3 (2)	C(6)-Sn(3)-Cl(7)	89.5 (2)
C(7)-Sn(3)-Cl(5)	104.9 (3)	C(7)-Sn(3)-Cl(6)	89.2 (3)
C(7)-Sn(3)-Cl(7)	88.9 (3)	C(7)-Sn(3)-C(6)	150.5 (3)
Sn(3)-Cl(7)-Sn(1)	94.2 (1)	C(2)-C(1)-Sn(1)	116.7 (6)
C(3)-C(2)-C(1)	112.5 (7)	C(2)-C(3)-Sn(2)	116.5 (6)
C(5)-C(4)-Sn(2)	114.7 (6)	C(6) - C(5) - C(4)	110.5 (7)
C(5)-C(6)-Sn(3)	115.8 (6)	C(8)-C(7)-Sn(3)	121.9 (6)
C(9)-C(8)-C(7)	117.0 (8)	C(8)-C(9)-Sn(1)	121.8 (6)

more divergent at 2.906 (2) and 2.445 (2) Å; the trigonal-bipyramidal geometry is more distorted at this site. The largest of these bond lengths are comparable to those observed in the 1,2-bis(stannylethane), [(Ph₂ClSnCH₂)₂Cl]⁻[Ph₃P=N=PPh₃]^{+.14} These values may also be compared with the shorter equatorial Sn-Cl lengths of 2.387 Å at Sn(3) and 2.445 Å at Sn(1), which are similar to those in other pentacoordinate diorganotin dichlorides,14 and the more nearly normal values of around 2.36 Å at Sn(2). The intraannular C(9)-Sn(1)-C(1) bond angle is opened up to 147.1 (4)°. Additional angle strain in the ring is found in the value of 117° for the C(7)-C-(8)-C(9) bond and values near 122° for the C(8)-C(7)-Sn(3) and C(8)-C(9)-Sn(1) bonds. Further strain is observed in the C(4)-Sn(2)-C(3) bond angle of 131.3 (4)°. Thus formation of the Sn-Cl-Sn bridge occurs at the cost of significant strain in the ring angles in the six-membered ring; this implies substantial driving force for formation of the bidentate structural unit provided that 5 itself is relatively unstrained, as inspection of Dreiding models suggests. It is rather striking that that all three tins are not involved in coordination in 5Cl- as appears to be the case in 4Cl⁻. Clarification of this point and others must await further study.

Experimental Section

General Data. All solvents were dried according to standard procedures and freshly distilled before use. ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were recorded on a Varian XL 300 spectrometer

⁽¹⁴⁾ Jurkschat, K.; Hesselbarth, S.; Tzschach, A.; Piret-Meunier, J., in press.

 Table IV. Summary of Crystal Data and Experimental Details for the Structural Study of 7

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	(a) Crystal F	Parameters at 23	۰Ca		
a, Å	11.691 (2)	V, Å ³	5110.3 (12)		
b, Å	24.652 (4)	space group	$P2_1/c$		
c, Å	17.353 (4)	Ż	4		
β , deg	92.70 (1)	$D_{ m calcd}$, g cm ⁻³	1.65		
	(b) Measurem	ent of Intensity	Data		
cryst dimen, mr	n 0.24	\times 26 \times 0.21			
instrument	Nic	olet $R3m/V$	let R3m/V		
radiatn Mo K α	λ =	0.71073 Å).71073 Å		
scan mode	cou	pled $\theta(crystal) - \theta(e)$	counter)		
scan rate	3-2	0° min ⁻¹			
scan length	[20($\mathbf{K}\alpha_1 - 1.0$]-[2 θ (K	$\alpha_2 + 1.0$]°		
background	stat	ionary crystal, st	ationary counter.		
-	n	easurement at th	e beginning and		
	e	nd of each 2θ scal	n, each for the time		
	ta	aken for the scan	,		
stds	3 cc	llected every 197			
no, of reflectns collected $6545 (\pm h, \pm k, \pm l)$					
no, of reflectns used 4003		$3[F_{2} > 6(F_{2})]$			
no, of paramete	rs 391	- (- 0) (- 0)]			
-					
(c) Reductio	n of Intensity Solution a	⁷ Data and Summ and Refinement ^b	ary of Structure		
absorptn correc	tn	based on ψ scal	ns for 5 reflections		
		with y near 9	90° or 270°		
$T_{\rm max}/T_{\rm min}$		1.090			
structure soln		Patterson man	vielded the Sn		
		positions: all	remaining		
		non-hydroge	n atoms were		
		located via s	tandard Fourier		
		techniques			
anomalous scatt	ering factors	neutral atomic	scattering factors		
anomatous scattering factors		were used throughout			
enomelous disperson		applied for all non-hydrogen			
anomatous disp		atoma	non nyurogon		
final discrepance	v factorse	R = 0.039			
inal discrepane	y lactors	R = 0.000			
goodness of fit		1.006			
goodness of HP		1.090			

^a From a least-squares fitting of the setting angles of 25 reflections. ^bAll calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using local versions of the programs as described in: Sheldrick, G. M. Nicolet SHELXTL Operations Manual: Nicolet XRD Corp.: Cupertino, CA, 1979. ^c Cromer, D. T.; Mann, J. B. Acta Crystallography: Kynoch Press: Birmingham, U.K., 1974; Vol. III. ^eR = $\sum ||F_0| - |F_c|/\sum |F_0||$ and $R_w = [\sum w(|F_0| - |F_c|)^2/\sum_w |F_0|^2]^{1/2}$, where $w = 1/\sigma^2(F_0) + g(F_0)$ and g = 0.005. ^f GOF = $[\sum w(|F_0| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables. ^g Data corrected for background, attenuation, Lorentz, and polarization effects.

operating at 111.86 MHz with tetramethylsilane and tetramethyltin as external references. Typical operating parameters were as follows: 50-KHz spectral width, 5-s pulse width, 0.3-s acquisition time, and 30-K data points.

X-ray Crystallography. The details of the crystal data collection methods and refinement procedures are given in Table IV. (Supplementary Tables I-VI provide atomic positional and thermal parameters, bond lengths and angles, anisotropic thermal parameters, calculated hydrogen atom positions, and calculated and observed structure factors.) Full details of the crystallographic methodologies have been described.¹⁶ Extinction correction was not deemed necessary. Idealized hydrogen atom positions were used throughout the analysis, with the C-H distance set at 0.96 Å. All non-hydrogen atoms of the anion and the N and P atoms of the cation were refined anisotropically. Isotropic temperature factors were employed for the ring carbons of the cation.

1,3-Bis(trimethylstannyl)propane. This compound was prepared from (trimethylstannyl)sodium and 1,3-dichloropropane

in liquid ammonia in a procedure similar to that for the preparation of 2,2-bis(trimethylstannyl)propane:^{7b} bp 110 °C (10 Torr); ¹H NMR (CDCl₃) δ 0.04 (s, 18 H, ²J(¹¹⁹Sn-C-H) = 52.2 Hz, SnMe₃), 0.85 (t, 4, ²J(¹¹⁹Sn-C-H) = 51.5 Hz, SnCH₂), 1.72 (q, 2 H, CH₂).

1,3-Bis(chlorodimethylstannyl)propane (1). 1,3-Bis(trimethlylstannyl)propane (11.1 g, 0.03 mol) and dimethyldichlorostannane (13.2 g, 0.06 mol) were heated for 12 h at 60 °C. The trimethylchlorostannane formed was removed in vacuo and the residue recrystallized from diethyl ether to yield 10.5 g (85.3%) of the desired product: mp 81 °C; ¹H NMR (CDCl₃) δ 0.64 (s, 12 H, ²J(¹¹⁹Sn-C-H) = 55 Hz, SnCH₃), 1.37 (t, 4 H, ²J(¹¹⁹Sn-C-H) = 50.6 Hz), 2.06 (q, 2 H, ³J(¹¹⁹Sn-C-C-H) = 68.9 Hz, CH₂).

1,1,5,5,9,9-Hexamethyl-1,5,9-tristannacyclododecane. Bis(2-(methoxycarbonyl)ethyl)dimethylstannane (217 g, 0.67 mol) was added dropwise to a suspension of LiAlH₄ (28 g, 0.738 mol) in 1 L of diethyl ether. The mixture was refluxed for 1 h. Under ice cooling, 200 mL of water was added and the mixture was filtered. The ether layer was dried over MgSO₄, and, after the solvent was evaporated off, the product was distilled to give 115 g (43%) of bis(3-hydroxypropyl)dimethylstannane as a colorless oil: bp 120–125 °C 0.05 Torr); ¹H NMR (CDCl₃) δ –0.01 (s, 6 H, ${}^{2}J({}^{119}Sn-C-H) = 51.1 Hz), 0.76 (t, 4 H, SnCH_{2}), 1.70 (q, 4 H, CH_{2}), 3.52 (t, 4 H, CH_{2}), 2.25 (s, 2 H, OH); {}^{119}Sn NMR (CDCl_{3}) \delta 3.04.$ To a magnetically stirred solution of the bis(3-hydroxypropyl)dimethylstannane (47 g, 0.176 mol) in 200 mL of methylene chloride and 55 g of tetrachloromethane was added triphenylphosphine (92.2 g, 0.352 mol) in small portions. The mixture was stirred for 24 h, and the solvent was evaporated in vacuo to yield an oil. Diethyl ether was added, and the resulting mixture was stored at -10 °C in order to cause precipitation of triphenylphosphine and triphenylphosphine oxide. After filtration, evaporation of the solvent and repeated fractionation 10 g (18.7%)of bis(3-chloropropyl)dimethylstannane (2) was obtained: bp 88 °C (0.01 Torr); ¹H NMR (CDCl₃) δ 0.07 (s, 6 H, ²J(¹¹⁹Sn-C-H) = 52.3 Hz, Sn(CH₃)₂), 0.90 (t, 4 H, SnCH₂), 1.91 (q, 4 H, CH₂), 3.47 (t, 4 H, CH₂Cl); ¹¹⁹Sn NMR (CDCl₃) δ 5.5.

To a solution of 1,3-bis(chlorodimethylstannyl)propane (12.3 g, 0.03 mol) in 1 L of tetrahydrofuran (THF) and 1 L of liquid ammonia was added 2.76 g (0.12 mol) of sodium in small quantities. The mixture was stirred for 30 min whence it turned yellow. To this solution was added 2 (9.2 g, 0.03 mol) in 40 mL of THF dropwise at -78 °C over a period of 1 h. Then 300 mL of diethyl ether and 100 mL of water were added, and the organic layer was separated and dried over MgSO₄. After evaporation of the solvent the residue was fractionated in vacuo to yield 6 g (35%) of 1,1,5,5,9,9-hexamethyl-1,5,9-tristannadododecane (3): bp 134-136 °C (0.02 Torr); ¹H NMR (CDCl₃) δ 0.02 (s, 18, ²J(¹¹⁹Sn-C-H) = 50.0 Hz, $Sn(CH_3)_2$, 0.90 (t, 12 H, ${}^2J({}^{119}Sn-C-H) = 49.8$ Hz, $SnCH_2$, 1.80 (q, 6 H, ${}^{3}J({}^{119}Sn-C-C-H) = 54.7$ Hz, CH_2); ${}^{13}C$ NMR $(\text{CDCl}_3) \delta - 10.6 ({}^{1}J({}^{119}\text{Sn}{}^{-13}\text{C}) = 299.7 \text{ Hz}, \text{SnCH}_3), 16.14 ({}^{1}J.$ $(^{119}\text{Sn}-^{13}\text{C}) = 339.9 \text{ Hz}, \,^{3}J(^{119}\text{Sn}-\text{C}-\text{C}-^{13}\text{C}) = 53.2 \text{ Hz}, \,\text{Sn}\text{CH}_{2}),$ 24.85 $(^{2}J(^{119}Sn-C-^{13}C) = 18.3 \text{ Hz}, CH_{2}); ^{119}Sn NMR (CDCl_{3}) \delta$ -10.4. Anal. Calcd for C₁₅H₃₆Sn₃: C, 31.46; H, 6.29. Found: C, 31.55; H, 6.54.

1,5,9-Trichloro-1,5,9-trimethyl-1,5,9-tristannacyclododecane (4). To a solution of 2.5 g (4.36 mmol) of 3 in 30 mL of acetone was added mercuric chloride (3.55 g, 13.080 mmol) under magnetic stirring at 0 °C. The mixture was stirred for 30 min at this temperature and for 1 h at room temperature. Then the solvent was evaporated, and the byproduct CH₃HgCl was removed at 0.02 Torr and 90 °C. The residue was transferred into a Soxhlet extractor and extracted with methylene chloride. The extract provided 2.1 g (76%) of 4: mp 224–226 °C; ¹H NMR (CDCl₃) δ 0.63 (s, 9 H, ²J(¹¹⁹Sn-C-H) = 52.7 Hz, SnCH₃), 1.45 (t, 12 H, SnCH₂), 2.13 (q, 6 H, ³J(¹¹⁹Sn-C-C-H) = 68.6 Hz, CH₂). Anal. Calcd for C₁₂H₂₇Cl₃Sn₃: C, 22.73; H, 4.26. Found: C, 22.62; H, 4.23.

1,1,5,5,9,9-Hexachloro-1,5,9-tristannacyclododecane (5). To a solution of 1.87 g (3.28 mmol) of 3 in 50 mL of acetone was added mercuric chloride (5.34 g, 19.7 mmol) under magnetic stirring at 0 °C. The mixture was stirred for 15 min at this temperature and then refluxed for 48 h. The solvent was evaporated, and the byproduct CH₃HgCl was removed at 0.02 Torr and 90 °C. The residue was placed in a Soxhlet extractor and extracted with methylene chloride. The extract provided 1.5 g (66%) of 5: mp

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166–168 °C; ¹H NMR (CDCl₃) δ 1.97 (t, 12 H, SnCH₂), 2.37 (q, 6 H, CH₂). Anal. Calcd for C₉H₁₈Cl₆Sn₃: C, 15.5; H, 2.59. Found: C, 15.32; H, 2.72.

Complex of 4 with [Ph₃P=N=PPh₃]⁺Cl⁻ (6). Into a solution of 4 (0.127 g, 0.2 mol) and [Ph₃P=N=PPh₃]⁺Cl⁻ (0.115 g, 0.2 mol) in 3 mL of methylene chloride was added 3 mL of hexane. Slow evaporation led to precipitation of an oily product that solidified to a glasslike product: ¹H NMR (CDCl₃) δ 0.70 (s, 9 H, ²J-(¹¹⁹Sn-C-H) = 59.6 Hz, SnCH₃), 1.65 (t, 12 H, ²J(¹¹⁹Sn-C-H) = 62.0 Hz, SnCH₂), 2.38 (q, 6 H, ³J(¹¹⁹Sn-C-C) = 110.7 Hz, CH₂), 7.70 (m, 12 H, o-Ph), 7.53 (m, 18 H, m- and p-Ph); ¹³C NMR (CHCl₃) δ 1.68 (¹J(¹¹⁹Sn-¹³C) = 389.3 Hz, SnCH₃), 28.36 (¹J-(¹¹⁹Sn-¹³C) = 456.6 Hz, ³J(¹¹⁹Sn-C-C-¹³C) = 49.6 Hz, SnCH₂), 22.38 (²J(¹¹⁹Sn-C-¹³C) = 27.0 Hz, CH₂).

Complex of 5 with [Ph₃P=N=PPh₃]+Cl⁻ (7). To 3 mL of methylene chloride and 2 mL of hexane were added 78.0 mg (0.136 mmol) of [Ph₃P=N=Ph₃]+Cl⁻ and 95.4 mg (0.136 mL) of 5. Slow evaporation of the solvent yielded 155 mg (90%) of colorless crystals: mp 224-225 °C; ¹H NMR δ 2.16 (t, 12 H, ²J(¹¹⁹Sn-C-H) = 71.3 Hz, SnCH₂), 2.59 (q, H, ³J(¹¹⁹Sn-C-C-H) = 187.7 Hz, CH₂), 7.46 (m, 18 H, *m*- and *p*-Ph), 7.65 (m, 12 H, *o*-Ph); ¹³C NMR (CDCl₃) δ 38.65 (¹J(¹¹⁹Sn-¹³C) = 592.6 Hz, ³J(¹¹⁹Sn-C-C-C) =

50.1 Hz SnCH₂), 21.91 (${}^{2}J({}^{119}Sn-C-C)$ = 41.6 Hz, CH₂). Anal. Calcd for C₄₅H₄₈NP₂Sn₃; C, 42.58; H, 3.78. Found: C, 42.42; H, 3.71.

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Registry No. 1, 123126-09-0; 2, 123126-05-6; 3, 85443-05-6; 4, 123126-06-7; 5, 123126-07-8; 6, 123126-11-4; 7, 123126-13-6; $[Ph_3P=N=PPh_3]^+Cl^-$, 21050-13-5; 1,3-bis(trimethylstannyl)propane, 35434-81-2; (trimethylstannyl)sodium, 16643-09-7; 1,3dichloropropane, 142-28-9; dimethyldichlorostannane, 753-73-1; bis((2-methoxycarbonyl)ethyl)dimethylstannane, 115152-95-9; bis(3-hydroxypropyl)dimethylstannane, 123126-08-9.

Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond distances, bond angles, and H-atom coordinates and isotropic displacement parameters (6 pages); a listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Electronic Absorption Spectra of Diorganogermylenes in Matrices: Formation of Diorganogermylene Complexes with Heteroatom-Containing Substrates

Wataru Ando,* Hiroyuki Itoh, and Takeshi Tsumuraya

Department of Chemistry, The University of Tsukuba, Tsukuba, Ibaraki 305, Japan

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Diorganogermylenes were generated in hydrocarbon matrices at 77 K by the photolysis of 7germanorbornadienes 1a-e or bis(trimethylsily)germanes 2a-g. The germylenes show electronic absorption bands at 420–558 nm. The germylenes react with heteroatom-containing substrates (R₂O, R₂S, R₃P, R₃N, RCl, and ROH) to form adducts, which show characteristic absorption bands at shorter wavelengths than those of germylenes.

Introduction

Divalent compounds of elements of group 14 have been the subject of considerable interest in recent years.¹⁻⁴ Although diorganogermylenes have been postulated as reactive intermediates in many reactions,⁵⁻⁹ spectroscopic

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data on diorganogermylenes remain rather limited. Dimethylgermylene and some other dialkyl- and diarylgermylenes have been observed by UV spectroscopy,^{9b,10-13}

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