Macrocycles containing Tin. Synthesis and Structure of 1,10-Diphenyl-1,10-distannabicyclo[8.8.8]hexacosane

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The title macrobicycle was prepared and studied by *X*-ray crystallography.

We have reported the syntheses of macrocycles containing two or four diphenylstanna moieties in the ring with various length polymethylene chains between the tin atoms.[1] Since acyclic, Lewis acidic distanna compounds have been shown to exhibit co-operative binding of donors,[2] we predicted that macrocycles containing Lewis acidic tin atoms would display co-operative and size-selective binding properties. In confirmation of this expectation, we have found that replacement of one or both phenyl groups on each tin atom in a macrocycle with chlorine or bromine atoms gives Lewis acidic macrocycles which form complexes with donor compounds containing basic nitrogen and oxygen atoms; complexes with donor atom to tin atom ratios of both 2 : 1 and 1 : 1 have been isolated and are under investigation.[3] In this communication we report the preparation and structure of a representative of a new class of organotin compounds, a macrobicycle containing two tin atoms in which the tin atoms serve as bridgeheads in a manner analogous to the nitrogen atoms of a cryptand. It may be expected that Lewis acidic macrobicyclic organotin compounds will be highly selective complexing agents.

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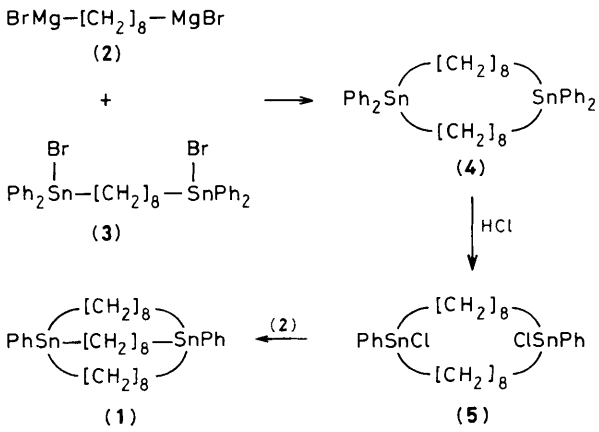

Scheme 1

The preparation of 1,10-diphenyl-1,10-distannabicyclo-[8.8.8]hexacosane (**1**) follows the sequence shown in Scheme 1. The preparation of the macrocycle (**4**) has been reported,[1] but we modified the procedure by using a double dilution

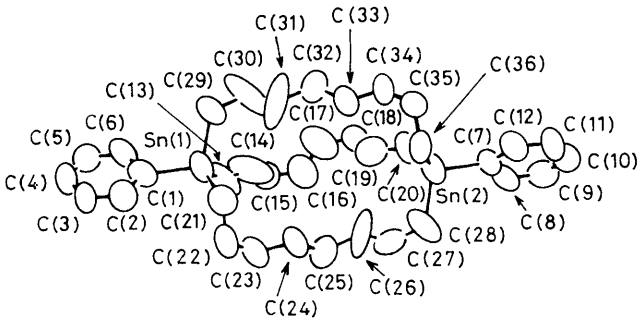

Figure 1. ORTEP representation of (**1**). The hydrogen atoms have been omitted for clarity.

method wherein dilute (*ca.* 0.03 M) solutions of the reagents (**2**) and (**3**)[1] were added simultaneously to tetrahydrofuran (THF) over 2 h at 25 °C to give (**4**) in 62% yield after purification by reverse phase chromatography[1] and recrystallization. Treatment of the macrocycle (**4**) with HCl (2.1 mol. equiv.) in CH_2Cl_2 at −78 °C followed by slow warming to 25 °C and distillation of the solvent at reduced pressure gave the dichlorinated product (**5**) which appeared to be pure by ^1H n.m.r. spectroscopy. The crude sample of (**5**) was then allowed to react with the Grignard reagent (**2**) in THF at 25 °C, again using the double dilution method (0.03 M solutions, 2 h addition). After a standard work-up,[1] the bicycle (**1**) was purified by preparative reverse phase chromatography [Baker bonded-phase ODS, 40 μ; MeOH–THF (60 : 40) elution; *ca.* 5 column volume retention] followed by recrystallization from MeOH–THF to give pure (**1**) in 15% yield from the macrocycle (**4**). The macrobicycle (**1**) (m.p. 92—94 °C) was characterized by ^1H and ^{13}C n.m.r. spectroscopy, osmometric molecular weight measurement (calc.: 728; found: 734), and elemental analysis (C, H).

A crystal of (**1**) was suitable for *X*-ray crystallographic analysis.‡ An ORTEP drawing of (**1**) is shown in Figure 1. The compound crystallized in a cylindrical form with a tin–tin distance of 8.45 Å. The interior of the cavity in (**1**) is filled with the hydrogen atoms of the polymethylene chains. The tin atoms of (**1**) are essentially tetrahedral in the crystal, and from the $^1J(^{119}Sn–^{13}C)$ of 332 Hz appear to be tetrahedral in solution.[4]

Crystal data: $Sn_2C_{36}H_{58}$, M = 728.24, triclinic, space group $P\bar{1}$, a = 13.508(8), b = 16.154(9), c = 9.094(3) Å, α = 106.35(4), β = 109.67(4), γ = 92.49(5)°, U = 1772(1) Å^3, Z = 2, D_c = 1.365 g cm^{-3}. Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer with Mo-K_α radiation. Data were corrected for Lorentz, polarization, and absorption effects (μ = 14.38 cm^{-1}) to yield 2193 observed structure factors with $I > 3\sigma(I)$ which were used for the structure solution and refinement. The positions of the two tin atoms were determined by direct methods. Successive least squares refinement and difference-Fourier methods were used to locate the remaining carbon atoms. While exhibiting rather high thermal motion, all non-hydrogen atoms were successfully refined anisotropically. The hydrogen atoms were included in calculated positions with fixed temperature factors and were not refined. Least squares refinement converged at R = 0.061 and R_w = 0.084.

Distanna macrobicycles of other sizes should be available by the procedure used to prepare (**1**), and, indeed, the corresponding 32 atom bicycle has already been prepared in our laboratory. In addition, functionalization of the macrobicycle (**1**) to give a Lewis acidic species (replacement of phenyl groups with chloro groups) was achieved by treatment of (**1**) with HCl in a reaction similar to that used for the conversion of (**4**) into (**5**), and complexation properties of this derivative are under investigation.[3]

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‡ All crystallographic computing and plotting was performed using the Enraf–Nonius Structure Determination Package (1982), Enraf–Nonius, Delft, Holland. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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