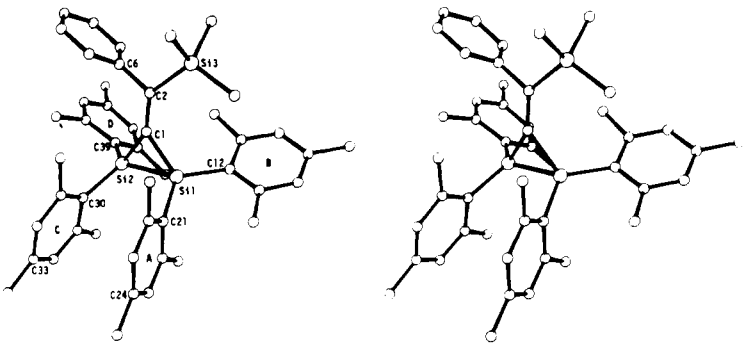

Figure 1. Stereoscopic view of 1,1,2,2-tetramesityl-3-[phenyl(trimethylsilyl)methylene]-1,2-disilacyclopropane (7).

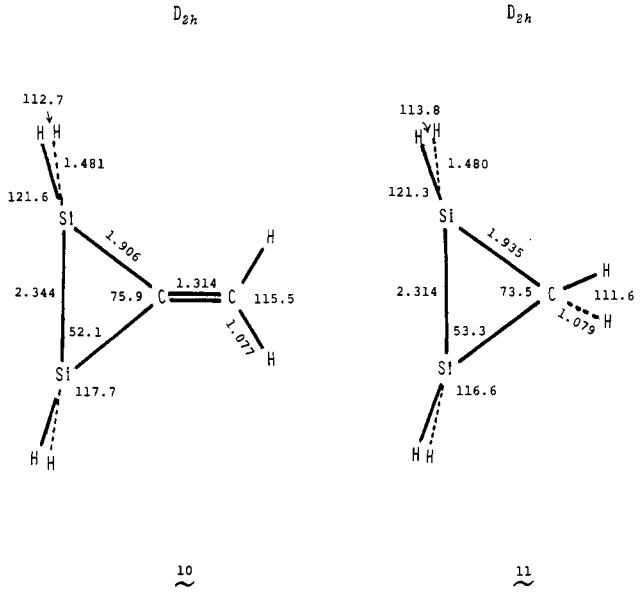

Figure 2. Geometries of 3-methylene-1,2-disilacyclopropane (**10**) and disilacyclopropane (**11**).

In contrast to the photolysis of **1**, when **6** was photolyzed in the absence of **2**, compound **7** was obtained in 8% yield,[11] together with 1-silacyclopropene **8** (65% yield). Both disilacyclopropanes **3** and **7** are stable toward atmospheric oxygen and moisture. They do not react with alcohols at room temperature.

The structure of **7** was determined by X-ray diffraction study. We also carried out ab initio MO calculations for 3-(methylene)-1,2-disilacyclopropane (**10**) and disilacyclopropane (**11**).[12,13] The crystals of **7** are triclinic of space group $P\bar{1}$ with cell dimensions a = 16.710 (3) Å, b = 13.150 (2) Å, c = 11.268 (3) Å, α = 70.96 (2)°, β = 66.94 (2)°, γ = 69.87 (2)°; V = 2085.6 (7) Å^3, and D_x = 1.171 Kg M^{-3} (Z = 2). The structure was solved by direct method.[15] Only the 3491 reflections with $I > 2\sigma(I)$ were used in the least-squares refinement (R = 0.053). Figure 1 shows a stereoscopic view of a single molecule. The disilacyclopropane ring and a plane consisting of Si(3), C(2), and C(6) atoms are almost coplanar with the dihedral angle of 7.6°. The sum of the bond angles of C(21)–Si(1)–Si(2), C(12)–Si(1)–Si(2), and C(12)–Si(1)–C(21) is 355.1° which is consistent with the corresponding values obtained from MO calculations for **10** (355.9°) and for **11** (356.4°), while the sum of the bond angles of C(39)–Si(2)–Si(1), C(30)–Si(2)–Si(1), and C(30)–Si(2)–C(39) is 343.4°. These results suggest that Si(1), C(12), C(21), Si(2), C(30), and C(39) atoms lie in almost the same plane. Two mesityl groups on Si(1) and Si(2) atoms, A and C rings, are fairly parallel to each other. The inter-ring distances C(21)–C(30) and C(24)–C(33) are 3.38 and 4.25 Å, respectively. The bond lengths of Si–Si (2.327 (2) Å) and two Si–C bonds (1.907 (4) Å (average)) in the disilacyclopropane ring are consistent with those of the respective normal bond. The bond angles of Si–C–Si and C–Si–Si in the ring are 75.2 (2) and 52.4 (1)° (average), respectively. Interestingly, these values are in good agreement with those obtained from MO calculations for **10** but not for **11** as shown in Figure 2.

The chemical behavior of the disilacyclopropanes is currently being examined and will be reported elsewhere.

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Registry No. 1, 75529-54-3; 2, 79184-72-8; 3, 83846-02-0; 4, 75529-57-6; 6, 75529-55-4; 7, 83846-03-1; 8, 75535-87-4; 10, 83846-04-2; 11, 51130-21-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and tables of positional and anisotropic thermal parameters and bond lengths and angles (17 pages). Ordering information is given on any current masthead page.

(11) All spectral data for the previous compound were identical with those of **7**.

(12) The ab initio MO calculations for **10** and **11** were carried out by using a 3-21G basis set.[14] The geometries were optimized with the energy gradient technique.

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Macrocycles Containing Tin. Two Syntheses of 1,1,6,6,11,11,16,16-Octaphenyl-1,6,11,16-tetrastannacycloeicosane and a Synthesis of 1,1,6,6-Tetraphenyl-1,6-distannacyclodecane

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Summary: The title syntheses are described. The synthetic and purification and analytical methods employed are of general utility for the preparation and functionalization of members of this class of compounds.

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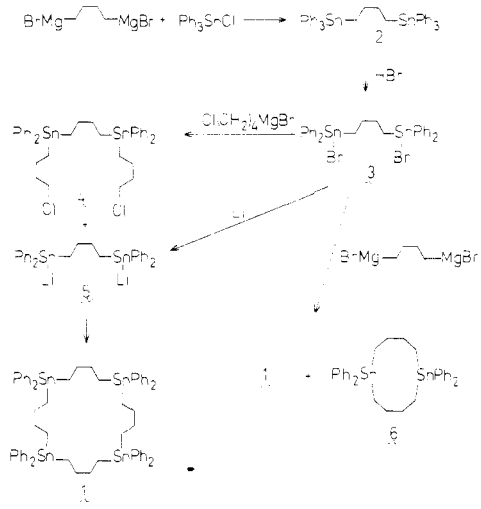
Scheme I



Macrocyclic, polydentate cation-complexing ligands (crown ethers, cryptands, etc.) have enjoyed a broad and useful chemistry during the past decade and a half, but their counterparts, anion-complexing macrocycles, have received relatively little attention. Recent advances in anion complexation, including structural selectivity, by macrocyclic polyammonium ligands suggest that this will be a fertile area of study.[2] Reasoning that polystanna macrocycles may be appropriately substituted to give *Lewis acid* complexing ligands that are direct analogues of crown ethers or cryptands, we have developed synthetic procedures for this class of compounds represented by the title compound **1**. Two approaches (Scheme I) have yielded the target 20-membered ring compound. The synthetic methods and purification techniques described herein are generally applicable for this class of compounds and also furnish tin functionalized macrocycles. We are unaware of other neutral macrocycles with the potential for anion complexation.

All reactions were run in argon or nitrogen atmospheres. Treatment of the diGrignard reagent from 1,4-dibromobutane with triphenylstannyl chloride in tetrahydrofuran (THF) gave 1,4-bis(triphenylstannyl)butane[3a,b] (**2**, mp 148.5–149 °C) in 77% isolated yield after recrystallization from hexane–dichloromethane (2:1, v:v). Unacceptably low selectivity was observed in several attempted conversions of **2** to 1,4-bis(bromodiphenylstannyl)butane (**3**) with various reagents and conditions; a second phenyl group was readily replaced, giving the dibromophenylstannyl moiety. However, treatment of **2** with 2.1 molar equiv of hydrogen bromide in dry dichloromethane at −78 °C followed by slow warming to room temperature gave, after recrystallization (dry ether), **3**[3a] in 75% yield (mp 88–90 °C). The dibromide **3** was treated with excess (4-chlorobutyl)magnesium bromide in THF at −10 °C for 1.5 h followed by warming to room temperature (7 h) to give 1,14-dichloro-5,5,10,10-tetraphenyl-5,10-distannatetradecane (**4**)[3a] that was purified by reverse-phase chromatography (C-18, methanol elution) in 62% yield (oil).

Table I. Spectroscopic Data for Isolated Products[a,b]

compd	^{1}H NMR, δ	^{1}H-decoupled ^{13}C NMR, δ	mol wt calcd	mol wt found[c]
2	7.10-7.53 (30 H, m)	138.9, 137.0, 128.7	755	734
	1.65-1.90 (4 H, m)	128.4, 31.3, 10.6		
	1.30-1.60 (4 H, m)			
3	7.17-7.67 (20 H, m)			
	1.71-1.93 (8 H, m)			
4	7.20-7.57 (20 H, m)			
	3.47 (4 H, t, J = 6 Hz)			
	1.57-1.87 (12 H, m)			
	1.03-1.40 (8 H, m)			
1	7.17-7.50 (40 H, m)	140.3, 136.7, 128.4	1315	1341
	1.53-1.87 (16 H, m)	128.2, 31.6, 10.4		
	1.17-1.47 (16 H, m)			
6	7.23-7.60 (20 H, m)	140.6, 136.5, 128.4	657	654
	1.57-2.03 (8 H, m)	128.2, 29.3, 10.1		
	1.37-1.50 (8 H, m)			

[a] NMR spectra of $CDCl_3$ solutions; chemical shifts are reported relative to Me_4Si. [b] Relatively featureless IR spectra (Nujol) were recorded for each compound; a characteristic Sn–Ph band at 1070 cm^{-1} was present in each spectrum. [c] Determined with chloroform solutions using a Hewlett-Packard Model 302B vapor pressure osmometer.

The two component macrocyclization was accomplished at high dilution. The dibromide **3** was added to excess lithium metal in THF to give the dilithium reagent **5** (total base = 63% of theory). A THF solution of **5** (diluted to 0.037 M) was added slowly (2 h) to a THF solution of **4** (1.0 molar equiv, 0.02 M) at 0 °C followed by warming to room temperature (12 h). After a conventional workup,[4] the crude product was purified by reverse-phase chromatography (C-18) with THF–acetonitrile elution (1:3, v:v) to give the desired macrocycle **1**[3] in 43% isolated yield (mp 107.5–108 °C from hexane–ether, 3:1).

Alternatively, macrocycle **1** was also obtained in lower yield from a high dilution, four-component macrocyclization reaction. Thus, the diGrignard reagent from 1,4-dibromobutane in THF (0.07 M) was added over 2 h to 1 molar equiv of dibromide **3** in THF (0.034 M) at 0 °C. After 12 h at room temperature, the reaction was quenched and worked up. The crude products were purified by preparative reverse-phase chromatography as above to give, after recrystallization, the desired macrocycle **1** in 16% yield and 1,1,6,6-tetraphenyl-1,6-distannacyclodecane[3a,b] (**6**, mp 114–114.5 °C, lit.[5] mp 96–98 °C) in 10%

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(3) (a) The compound was characterized by ^{1}H NMR spectroscopy. (b) The compound was characterized by ^{1}H-decoupled ^{13}C NMR spectroscopy and by osmometric molecular weight determination. (c) A satisfactory elemental analysis (±0.4% for C and H) was obtained; see Table I for details of the spectroscopic characterization.[4]

(4) The workup of each reaction involving an organomagnesium or organolithium reagent was the same. At the completion of the reaction period the reaction mixture (a THF solution of 30–150 mL) was treated with 50 mL of saturated aqueous NH_4Cl solution. Phases were separated, and the aqueous phase was extracted with ether (2 × 50 mL). The combined organic phases were washed with 50 mL of saturated aqueous NaCl solution and dried with $MgSO_4$, and the solvent was removed in vacuo. The crude products were recrystallized or purified by chromatography as indicated in the text. Yields of isolated products 1–4 and 6 are given in the text.

yield. Compound 6 has been prepared by a different route.[5]

The macrocycles 1 and 6 may be analyzed readily by analytical HPLC (reverse phase, C-18) with methanol elution; the 10-membered ring compound 6 elutes before 1. However, for preparative chromatography, the solubilities of 1 and 6 in methanol are inconveniently low. Thus, chromatography with the mixed-solvent system THF–acetonitrile was developed. We found that analytical HPLC on 10 μm Spherisorb ODS columns correlated well with preparative chromatography on 40 μm ODS supplied by J. T. Baker Co.; the analytical phase retained material about 1.5 times as long as the preparative phase in terms of column volumes.

The procedures described above are generally useful for the preparation and functionalization of other tin-containing macrocycles. For example, the reactions of the 6-, 8-, and 10-carbon analogues of 3 with the corresponding chain-length α,ω-diGrignard reagents gave the 14-, 18-, and 22-membered ring analogues of the distanna compound 6, respectively, as well as low yields of the 28-, 36-, and 44-membered ring analogues of tetrastanna compound 1, respectively. All separations were accomplished by reverse-phase chromatography. Further, when the selective bromination procedure was applied to macrocycle 6, we obtained 1,6-dibromo-1,6-diphenyl-1,6-distannacyclodecane;[3a] this reaction exemplifies a critically important functionalization of the macrocycles. Finally, preparative reverse-phase chromatography of the intermediate tin bromides is also possible on a C-18 column with THF–acetonitrile elution if *dry* solvents are used.

As in any macrocyclization reaction, the high dilution methods we used required careful technique. However, in our minds, the key steps to obtaining macrocycle 1 were the selective bromination of 2 and our development of a preparative chromatography method. The two-component macrocyclization route and reverse-phase preparative chromatography permit the synthesis of 1 in gram batches. With the methods at hand we plan to prepare and functionalize several members of this class of compounds and explore their application in anion coordination chemistry.

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Registry No. 1, 83802-01-1; 2, 5274-40-8; 3, 83815-91-2; 4, 83815-92-3; 5, 83802-02-2; 6, 68970-21-8; $Br(CH_2)_4Br$, 110-52-1; Ph_3SnCl, 639-58-7; $Cl(CH_2)_4Br$, 6940-78-9.

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Investigations of Polymer-Supported Complexes of Platinum(II) by High-Resolution Solid-State ^{31}P NMR Spectroscopy Employing Magic-Angle Spinning and Cross-Polarization Techniques

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Summary: Solid-state ^{31}P NMR spectroscopy employing high-power proton decoupling, cross-polarization, and magic-angle spinning has been used to characterize various polymer-supported phosphines and their platinum complexes. The reduction of polymer (polystyrene cross-linked with divinylbenzene) bound phosphine oxide, to the tertiary phosphine, and the immobilization of a platinum complex via the bound phosphine were monitored by these NMR techniques. The polymer-supported complex was synthesized by an alternate route, and the success of this process was confirmed by this NMR method. Platinum complexes were coordinated to poly(4-vinyl)pyridine, through the pyridine nitrogen, and the outcome of this process was elucidated from the solid-state ^{31}P NMR spectra of triphenylphosphine ligands which were coordinated to the platinum but which were not part of the polymer support.

In recent years there has been considerable research on polymer-bound transition-metal catalysts[2-7] but as yet little success has been achieved in determining either their general structure or the structure at the active site.

Theoretically, ^{31}P NMR spectroscopy is an attractive technique with which to investigate metal complexes which are bound to polymers via phosphine ligands. Research has been done on these systems employing high-resolution solution ^{31}P NMR[8,9] to study solvent-swollen polymers, but no resonances were observed for the immobilized catalyst. Solid-state ^{31}P NMR spectroscopy employing cross-polarization[10] with magic-angle spinning[11] (CP/MAS) has been used to study transition-metal phosphine complexes.[12,13] We have recently reported a thorough study[14] of tertiary phosphines, transition-metal phosphine complexes, and their analogues immobilized on glass and silica surfaces.

In the present study we have examined metal complexes supported on organic polymers, functionalized with tertiary phosphine and pyridine moieties utilizing solid-state CP/MAS ^{31}P NMR and high-resolution solution ^{31}P NMR spectroscopy in solution.

In the past polymer-immobilized catalysts have been prepared by first fixing a phosphine ligand to the polymer surface and then reacting this functionalized polymer with a metal complex. Two general methods have been used to synthesize such functionalized polymers: the first involves performing a chemical reaction on the polymer[15,16]

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