9 and azobenzenes 1, 2, and 4 suggests that isomerization of either olefin or azobenzene chromophore by a rotational path depends strongly on a solvent and resonance assisted lowering of the bond orders to reach transition states very close to 7b or 8,9b, respectively.

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Synthesis and Crystal Structure of the First Stannacyclopropene Derivative

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Recent interest in the chemistry of the Main Group carbene analogues, R_2M : (M = Si, Ge, Sn), has centered on the reactions of these species with carbon-carbon multiple bonds.¹ Herein, we describe the reaction of a diorganostannylene (R₂Sn:), 1 [R = bis(trimethylsilyl)methyl],² with an acetylene 2^3 to provide the first known example of a stannacyclopropene 3 (Scheme I). Full characterization of 3, including the crystal structure and ¹¹⁹Sn NMR, reveals an unique thermal equilibrium among 1, 2, and 3 which occurs in solution above -16 °C, with 1 and 2 being favored at higher temperatures (Scheme I).

Synthesis of 3 (Scheme I). Silylenes (R2Si:) and germylenes (R₂Ge:) have previously been shown to react with the cyclic acetylene 2 to form the corresponding silacyclopropenes and germacyclopropenes, respectively.^{1e,f} Analogously, titration of a deep red equilibrium mixture of 1 and the distannene 4 in methylcyclohexane with 1.2 equiv of 2 at room temperature results in complete decolorization of the solution. Removal of the solvent and excess acetylene under reduced pressure quantitatively provides 3 as a pale yellow crystalline material which is subsequently recrystallized twice from methylcyclohexane at -40 °C.

Compound 3 exhibits physical properties that are fully consistent with the stannacyclopropene structure.4 A ¹³C¹H NMR (75 MHz, -25 °C, methylcyclohexane- d_{14}) δ (ppm from solvent reference peak at 34.6 ppm) displays a resonance at 163.9 ppm $[{}^{1}J({}^{117/119}Sn{}^{-13}C) = 9.2 Hz]$ which is assigned to the stannacyclopropene carbon atoms.⁴ In addition, a ¹¹⁹Sn{¹H} NMR (112 MHz, -25 °C, methylcyclohexane- d_{14}) δ (ppm from Me₄Sn, negative for upfield) shows a single resonance at -536.8 ppm which is more than 100 ppm upfield from the chemical shifts of the highly strained cyclotristannanes.5 IR (Nujol) and Raman (solid, -60 °C) data show $\nu_{C=C}$ at 1587 cm⁻¹ which first decreases in the IR and then disappears within 5 min after exposure to air.

Crystallographic Analysis of 3.4 As shown in Figure 1, the stannacyclopropene ring system of 3 forms an isosceles triangle with Sn-C_{sp²} bond lengths of 2.136 (5) and 2.134 (4) Å, respectively, which are comparable in length to Sn-C_{sp2} bond distances found in acyclic systems.⁶ The C₁-C₂ bond length of 1.340

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(4) Detailed information is supplied in the Supplementary Material. (5) Cf. (a) δ -416.5 for hexakis(2,6-diethylphenyl)cyclotristannane [Masamune, S.; Sita, L. R.; Williams, D. J. J. Am. Chem. Soc. 1983, 105, 630] and (b) δ -378.9 for hexakis(2,4,6-triisopropylphenyl)cyclotristannane [Masamune, S.; Sita, L. R. J. Am. Chem. Soc. 1985, 107, 6390].



Figure 1. Crystal structure of 3: bond lengths (Å) Sn-C₁ 2.136 (5), Sn-C₂ 2.134 (4), Sn-C_{1a} 2.172 (4), Sn-C_{1b} 2.181 (3), C₁-C₂ 1.340 (6), C₄-S 1.849 (8), C₅-S 1.776 (7); bond angles (deg) C₁SnC₂ 36.6 (2), SnC_1C_2 71.6 (3), SnC_2C_1 71.8 (3), C_1SnC_{1a} 124.0 (1), C_1SnC_{1b} 121.8 (2), C_2SnC_{1a} 121.6 (1), C_2SnC_{1b} 124.6 (1), $C_{1a}SnC_{1b}$ 110.1 (2).

Scheme I



(6) Å is in agreement with the value found for the C_{sp} - C_{sp} bond length in the analogous germacyclopropene derivative, ^{le} while the exocyclic Sn-C bond lengths of 2.172 (4) Å and 2.181 (3) Å, respectively, are shorter than those found in tetrakis[bis(trimethylsilyl)methyl]distannene, 4 [2.207 (5) - 2.225 (6) Å].² Due to the absence of any close intermolecular distances between tin and sulfur, the difference in bond lengths between S-C₄ (1.849 (8) Å) and S-C₅ (1.776 (7) Å) may arise from crystal packing interactions.

An essential feature of the structure of 3 is the 355.9° and 356.3° sums for two sets of angles (C_{1b} -Sn- C_{1a} , C_1 -Sn- C_{1b} , C_1 -Sn- C_{1a} and C_{1b} -Sn- C_{1a} , C_2 -Sn- C_{1b} , C_2 -Sn- C_{1a} , respectively) at tin. Compared to the 328.5° value expected for an idealized tetrahedral configuration, the arrangement of C1a, C1b, and the midpoint of C1-C2 can best be considered nearly trigonal coplanar about the tin atom (the Sn atom and these other three atoms or points are coplanar to within 0.005 Å) which undoubtedly helps to minimize steric interactions between the bulky substituents. In addition, C₃ and C₆ are not coplanar with the plane of the stannacyclopropene ring but rather lie 0.024 Å below and 0.058 Å above it, respectively.

Properties of 3. Besides being air- and moisture-sensitive in the solid state, 3, in solution, is in rapid equilibrium above -16°C with 1 (and presumably, to some extent, with 4) and the free acetylene 2.7 Both the ¹¹⁹Sn{¹H} NMR and ¹³C{¹H} NMR of 3 show temperature dependency, with no resonance for the Csp2 atoms being observed at 20 °C in the latter. Upon the addition of 1.3 equiv of 2 to a solution of 3 (c = 0.069 M, methylcyclohexane), a dynamic exchange between free and complexed acetylene is observed by ¹H NMR at 20 °C (the coalescence

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⁽⁷⁾ This behavior is reminiscent of the thermal equilibrium reported between a cyclotristannane and a distannene, see ref 5b

temperature) by a broad resonance at 2.65 ppm, which separates into two resonances (2.69 ppm and 2.55 ppm) at -16 °C and sharpens to a single resonance (2.64 ppm) at 40 °C. Photolysis of 3 in methylcyclohexane at -196 °C (glass matrix) and -78 °C to 25 °C (solution) using a Hanovia high-pressure lamp (quartz) produced no apparent change as monitored by ¹H NMR at the corresponding temperatures (-78 °C and 25 °C, respectively).

We believe the model that best describes bonding interactions in 3 is, at least at -25 °C, that of a π -complex, a formulation which has been developed for three-membered ring Main Group heterocycles.^{8,9} Further experimental and theoretical investigations are currently underway to probe this model for stannacyclopropenes.

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Supplementary Material Available: Detailed information concerning the spectral data and crystallographic analysis of 3, including listings of atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and an ORTEP representation of 3 (11 pages). Ordering information is given on any current masthead page.

A New Strategy for 1,4- and 1,4,7-Polycarbonyl Compounds

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1,4-Dicarbonyl compounds constitute key intermediates in various natural product syntheses, and a number of methodologies for their syntheses have appeared.¹ Now we report a conceptually new strategy based on the successive C_1 and C_2 homologation of

Fable I.	Synthesis	of α -F	henylthioa	ldehydes	3
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entry	2	MeSO ₂ Cl (equiv)	Et ₃ N (equiv)	reactn time, h	3 yield, ^b %
1	0H 0Me	1.5	1.5	12	83
2	OH OMe SPh	1.3	1.3	12	79
3		1.8	1.8	12	88
4	Ph OMe SPh	1.3	1.3	0.25 ^c	77
5	OH OMe SPh	1.3	1.3	10	71
6	OH SPh	3.3	3.3	24	88

^aReaction conditions: in benzene at 20 °C unless otherwise noted. ^bIsolated yields after column chromatography. All compounds gave satisfactory NMR, IR, and HRMS spectral data. ^cIn benzene-hexane (4:1) at 0 °C.



^a(i) DIBAH (1.0 equiv), toluene, -78 °C, 15 min; (ii) MeO(PhS)-CHLi (3 equiv), THF, -78 to -40 °C, 1 h, 51% through i and ii; (iii) MeSO₂Cl (1.5 equiv)–Et₃N (1.5 equiv), benzene, 0 °C, 1 h, 68%; (iv) 6a (2.0 equiv), THF, 50 °C, 12 h; (v) *t*-BuOK (1.6 equiv), THF, -78°C, 30 min, 75% through iv and v; (vi) CF₃COOH–H₂O (4:1), 20 °C, 10 h, 100%.

an aldehyde which can be extended to the synthesis of 1,4,7-tricarbonyl compounds.

In the course of the studies on synthetic applications of methoxy(phenylthio)methane (1),² we have found that exposure of the carbonyl adducts 2^3 to methanesulfonyl chloride-triethylamine provides α -sulfenyl aldehydes 3 in good yields (eq 1, Table I).⁴ Previously de Groot et al. reported analogous phe-



nylthio migration reaction with thionyl chloride-pyridine which,

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