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Reactions of Stannylenes with Alkynes: Synthesis and Chemical Reactivity of a Stable 1,2-Distannacyclobut-3-ene Derivative

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Bis[bis(trimethylsilyl)methyl]tin (**1a**) reacts with cyclooctyne (**5**) to provide $\Delta^{1,8}$-9,10-distanna-9,9,10,10-tetrakis[bis(trimethylsilyl)methyl]bicyclo[6.2.0]decene (**6**) in 71% yield. This 1,2-distannacyclobut-3-ene derivative, which is air- and moisture-stable, does not dissociate in solution and thereby allows for the first time an investigation of the chemical reactivity of this small cyclic system. Compound **6** reacts with *m*-chloroperbenzoic acid (MCPBA) in toluene to provide $[Sn_2(CH(Si(CH_3)_3)_2)_4(C_8H_{12})(O)]$ (**7**) in 79% yield and with iodine (1 equiv) to cleave the tin–tin bond and provide the air-sensitive adduct $[Sn_2(CH(Si(CH_3)_3)_2)_4(C_8H_{12})(I)_2]$ (**8**) in 79% yield. Treatment of **6** with 2 equiv of iodine in the presence of moisture produces a dark yellow-brown solution from which bronze-colored crystals of the triiodide anion complex of the hydroxy-bridged ditin cation $[Sn_2(CH(Si(CH_3)_3)_2)_4(C_8H_{12})(OH)][I_3]$ (**9**) can be isolated in 76% yield. The new compounds have been fully characterized by spectroscopic methods, and the structures of **6** and **9** have been determined by crystallographic analysis. Single crystals of **6** are (at 23 °C) orthorhombic, space group $P2_12_12_1$, with a = 18.694 (1) Å, b = 19.053 (1) Å, c = 14.895 (1) Å, V = 5305 (1) Å^3, and Z = 4. Single crystals of **9** are (at 20 °C) monoclinic, space group $P2_1/n$, with a = 19.928 (4) Å, b = 12.198 (2) Å, c = 26.345 (5) Å, β = 111.09 (1)°, V = 5975 (2) Å^3, and Z = 4.

Introduction

The [2 + 4] chelatropic addition of stannylenes, R_2Sn (**1**), to 1,3-dienes is a well-known reaction that has been shown to occur in a synchronous fashion.[1] However, the factors that govern the reactivity of these singlet carbene analogues with *isolated* carbon–carbon multiple bonds still remain poorly understood. Recently, the first examples of stannacyclopropenes (**2a** and **2b**)[2] and a 1,2-distannacyclobut-3-ene derivative (**3**)[3] were obtained from the reaction of the corresponding stannylenes (**1a–c**) with the ring-strained cycloheptyne **4** (Scheme I). While the structures of both **2** and **3** have been determined by crystallographic analysis, it is important to note that, in solution, each three- and four-membered ring compound, **2** and **3**, respectively, was found to be in rapid equilibrium with the stannylene and cycloalkyne starting materials.[2,3] Herein, we report that the reaction of the stannylene **1a**[4] with cyclooctyne (**5**)[5] provides the first example of an *air- and moisture-stable* 1,2-distannacyclobut-3-ene (**6**) that *does not* dissociate in solution and thereby provides further valuable insights concerning the steric and electronic factors which govern the formation and stability of small rings containing tin from unsaturated organic precursors (Scheme I). Given the stability of **6** in solution, a preliminary investigation of the chemical reactivity of this rare heterocyclic system is also reported.

Results

In contrast to the instantaneous reaction of **1a** with the cycloheptyne **4** to quantitatively produce **2a**,[2] reaction of **1a** with cyclooctyne (**5**) proceeds only slowly under identical conditions and requires 2 days to quantitatively provide **6** as the sole product as monitored by ^1H NMR spectroscopy. Since **6** was found to be stable toward both air and moisture, it was convienently purified by flash chromatography[6] on silica gel with hexane as the eluant to provide analytically pure **6** as a white crystalline material in 71% isolated yield.

Compound **6** exhibits physical properties that are fully consistent with the 1,2-distannacyclobut-3-ene structure. A ^{13}C NMR (75 MHz, benzene-d_6) spectrum displays a resonance at 173.2 ppm that is assigned to the 1,2-distannacyclobut-3-ene ring carbons, and a $^{119}Sn\{^1H\}$ NMR (112 MHz, benzene-d_6) spectrum shows a single resonance at +56.5 ppm ($^1J(^{119}Sn-^{117}Sn)$ = 2436 Hz). This latter value is similar to the ^{119}Sn chemical shift of +155 ppm ($^1J(^{119}Sn-^{117}Sn)$ = 3723 Hz) reported for **3**.[3] Resembling distannanes,[7] compound **6** exhibits ultraviolet absorption maxima in *n*-hexane at λ 226 nm (ϵ_{max} 49 300) and at λ 284 nm (ϵ_{max} 14 300), which indicates that the 1,2-distannacyclobut-3-ene system can serve as a unique optical chromophore.

In order to elucidate the structural features associated with the unique stability of **6**, an X-ray structure determination was carried out. Fractional coordinates of non-hydrogen atoms are given in Table I; bond lengths and bond angles are given in Tables II and III, respectively.[8] As can be seen in Figure 1, the four-membered ring of **6** is essentially planar with the sum of the angles about Sn_1 ($C_{1a}Sn_1C_1$, $C_{1a}Sn_1C_{1b}$, and $C_{1b}Sn_1C_1$) and Sn_2 ($C_{1c}Sn_2C_2$, $C_{1c}Sn_2C_{1d}$, and $C_{1d}Sn_2C_2$) being 340.8 and 342.6°, respectively. A direct comparison of the bond lengths of the 1,2-distannacyclobut-3-ene moiety in **6** with the corresponding bond lengths found for the solution-unstable derivative **3**[3] is informative and shows that both the Sn_1-Sn_2 bond length of 2.817 (1) Å and the C_1-C_2 bond length of 1.337 (10) Å in **6** are *longer* than their counterparts in **3** (2.803 (1) and 1.31 (2) Å, respectively), whereas the Sn–C bond lengths of **6** (2.220 (7) and 2.263 (7) Å) are

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Table I. Fractional Coordinates of the Non-Hydrogen Atoms (×10⁴) and Equivalent Isotropic Thermal Parameters (×10⁴) for 6[a]

atom[b]	x	y	z	B_{eq}, Å^2
Sn_1	-679 (0)	843 (0)	511 (0)	3084 (9)
Sn_2	74 (0)	-67 (0)	-642 (0)	3027 (9)
Si_{1a}	-1035 (2)	2649 (1)	552 (2)	4919 (77)
Si_{2a}	-2119 (1)	1707 (2)	-563 (2)	5188 (81)
Si_{1b}	689 (1)	1075 (1)	2067 (2)	4524 (72)
Si_{2b}	-867 (1)	703 (1)	2797 (2)	4452 (77)
Si_{1c}	-260 (2)	-405 (2)	-2893 (2)	4889 (80)
Si_{2c}	268 (2)	1128 (1)	-2372 (2)	5023 (82)
Si_{1d}	1930 (1)	-419 (2)	-750 (2)	5262 (85)
Si_{2d}	942 (1)	-1483 (1)	332 (2)	4238 (72)
C_1	-1303 (4)	-139 (4)	330 (5)	327 (20)
C_2	-977 (4)	-570 (4)	-249 (5)	324 (21)
C_3	-1270 (5)	-1234 (4)	-649 (7)	528 (28)
C_4	-1402 (5)	-1856 (5)	-15 (7)	625 (32)
C_5	-1816 (5)	-1710 (6)	934 (9)	1031 (49)
C_6	-2507 (6)	-1421 (6)	844 (9)	959 (48)
C_7	-2590 (6)	-662 (5)	392 (8)	746 (38)
C_8	-2060 (4)	-192 (5)	719 (6)	497 (27)
C_{1a}	-1161 (4)	1809 (4)	-63 (5)	358 (22)
C_{2a}	-1497 (6)	2688 (5)	1692 (6)	595 (32)
C_{3a}	-1408 (6)	3420 (5)	-80 (7)	703 (37)
C_{4a}	-43 (5)	2831 (5)	693 (7)	637 (31)
C_{5a}	-2825 (5)	1828 (6)	320 (7)	709 (37)
C_{6a}	-2266 (6)	2370 (5)	-1454 (7)	723 (38)
C_{7a}	-2287 (5)	836 (5)	-1140 (7)	632 (33)
C_{1b}	-313 (4)	1121 (4)	1871 (5)	411 (24)
C_{2b}	965 (5)	1764 (5)	2882 (7)	637 (33)
C_{3b}	1220 (5)	1299 (5)	986 (7)	594 (31)
C_{4b}	1005 (5)	186 (5)	2549 (7)	604 (32)
C_{5b}	-791 (5)	-286 (5)	2840 (7)	590 (31)
C_{6b}	-1843 (5)	950 (5)	2654 (6)	555 (30)
C_{7b}	-581 (6)	1095 (6)	3943 (6)	669 (36)
C_{1c}	276 (4)	172 (4)	-2080 (5)	373 (22)
C_{2c}	-63 (7)	-158 (6)	-4103 (6)	812 (39)
C_{3c}	16 (6)	-1359 (5)	-2761 (6)	600 (31)
C_{4c}	-1269 (5)	-334 (6)	-2754 (7)	747 (38)
C_{5c}	-680 (5)	1435 (5)	-2747 (7)	680 (35)
C_{6c}	596 (5)	1731 (4)	-1451 (6)	515 (29)
C_{7c}	915 (6)	1303 (6)	-3384 (7)	729 (39)
C_{1d}	1060 (4)	-565 (4)	-99 (6)	451 (26)
C_{2d}	2719 (5)	-465 (7)	43 (8)	916 (46)
C_{3d}	2042 (5)	517 (5)	-1266 (7)	591 (32)
C_{4d}	2032 (6)	-1099 (6)	-1675 (8)	797 (42)
C_{5d}	1794 (5)	-1864 (5)	815 (7)	615 (32)
C_{6d}	617 (6)	-2104 (4)	-566 (7)	632 (31)
C_{7d}	260 (5)	-1467 (5)	1270 (5)	467 (26)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

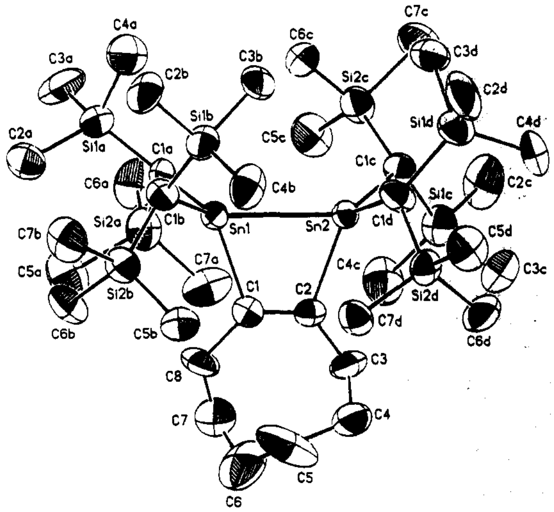


Figure 1. ORTEP drawing of $[Sn_2(CH(Si(CH_3)_3)_2)_4(C_8H_{12})]$ (6). The hydrogen atoms have been omitted for clarity.

Table II. Bond Lengths (Å) for 6[a,b]

Sn_1–Sn_2	2.817 (1)	Si_{1c}–C_{1c}	1.918 (8)
Sn_1–C_1	2.220 (7)	Si_{1c}–C_{2c}	1.899 (11)
Sn_1–C_{1a}	2.220 (8)	Si_{1c}–C_{3c}	1.898 (10)
Sn_1–C_{1b}	2.203 (8)	Si_{1c}–C_{4c}	1.904 (11)
Sn_2–C_2	2.263 (7)	Si_{2c}–C_{1c}	1.873 (8)
Sn_2–C_{1c}	2.223 (8)	Si_{2c}–C_{5c}	1.947 (10)
Sn_2–C_{1d}	2.226 (8)	Si_{2c}–C_{6c}	1.892 (9)
Si_{1a}–C_{1a}	1.858 (8)	Si_{2c}–C_{7c}	1.960 (11)
Si_{1a}–C_{2a}	1.907 (10)	Si_{1d}–C_{1d}	1.914 (9)
Si_{1a}–C_{3a}	1.878 (11)	Si_{1d}–C_{2d}	1.890 (12)
Si_{1a}–C_{4a}	1.899 (10)	Si_{1d}–C_{3d}	1.953 (10)
Si_{2a}–C_{1a}	1.951 (8)	Si_{1d}–C_{4d}	1.900 (12)
Si_{2a}–C_{5a}	1.876 (11)	Si_{2d}–C_{1d}	1.876 (9)
Si_{2a}–C_{6a}	1.853 (11)	Si_{2d}–C_{5d}	1.892 (10)
Si_{2a}–C_{7a}	1.894 (10)	Si_{2d}–C_{6d}	1.887 (10)
Si_{1b}–C_{1b}	1.898 (8)	Si_{2d}–C_{7d}	1.892 (9)
Si_{1b}–C_{2b}	1.861 (10)	C_1–C_2	1.337 (10)
Si_{1b}–C_{3b}	1.939 (10)	C_1–C_8	1.533 (11)
Si_{1b}–C_{4b}	1.933 (10)	C_2–C_3	1.503 (12)
Si_{2b}–C_{1b}	1.900 (8)	C_3–C_4	1.536 (13)
Si_{2b}–C_{5b}	1.891 (10)	C_4–C_5	1.635 (15)
Si_{2b}–C_{6b}	1.896 (10)	C_5–C_6	1.410 (17)
Si_{2b}–C_{7b}	1.939 (10)	C_6–C_7	1.603 (16)
		C_7–C_8	1.422 (14)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

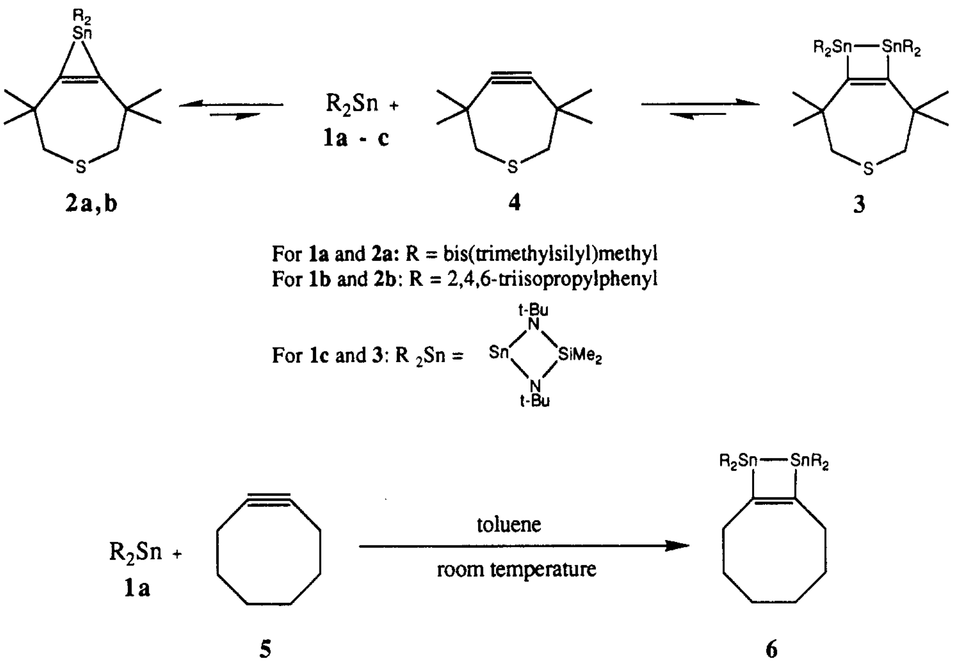
Table III. Bond Angles for 6[a,b]

Sn_2–Sn_1–C_1	70.7 (2)	C_{1a}–Si_{2a}–C_{5a}	111.4 (4)
Sn_2–Sn_1–C_{1a}	118.6 (2)	C_{1a}–Si_{2a}–C_{6a}	109.9 (4)
Sn_2–Sn_1–C_{1b}	123.6 (2)	C_{1a}–Si_{2a}–C_{7a}	114.4 (4)
C_1–Sn_1–C_{1a}	116.1 (3)	C_{5a}–Si_{2a}–C_{6a}	108.3 (5)
C_1–Sn_1–C_{1b}	118.5 (3)	C_{5a}–Si_{2a}–C_{7a}	108.0 (5)
C_{1a}–Sn_1–C_{1b}	106.2 (3)	C_{6a}–Si_{2a}–C_{7a}	104.3 (5)
Sn_1–Sn_2–C_2	70.7 (2)	C_{1b}–Si_{1b}–C_{2b}	110.0 (4)
Sn_1–Sn_2–C_{1c}	123.1 (2)	C_{1b}–Si_{1b}–C_{3b}	111.5 (4)
Sn_1–Sn_2–C_{1d}	117.1 (2)	C_{1b}–Si_{1b}–C_{4b}	113.5 (4)
C_2–Sn_2–C_{1c}	118.9 (3)	C_{2b}–Si_{1b}–C_{3b}	104.1 (4)
C_2–Sn_2–C_{1d}	116.4 (3)	C_{2b}–Si_{1b}–C_{4b}	106.9 (4)
C_{1c}–Sn_2–C_{1d}	107.3 (3)	C_{3b}–Si_{1b}–C_{4b}	110.2 (4)
Sn_1–C_1–C_2	110.9 (5)	C_{1b}–Si_{2b}–C_{5b}	113.7 (4)
Sn_1–C_1–C_8	119.7 (5)	C_{1b}–Si_{2b}–C_{6b}	109.8 (4)
C_2–C_1–C_8	128.5 (7)	C_{1b}–Si_{2b}–C_{7b}	109.1 (4)
Sn_2–C_2–C_1	107.6 (5)	C_{5b}–Si_{2b}–C_{6b}	108.9 (4)
Sn_2–C_2–C_3	124.8 (5)	C_{5b}–Si_{2b}–C_{7b}	109.5 (4)
C_1–C_2–C_3	127.4 (7)	C_{6b}–Si_{2b}–C_{7b}	105.6 (4)
C_2–C_3–C_4	117.7 (1)	C_{1c}–Si_{1c}–C_{2c}	110.9 (4)
C_3–C_4–C_5	118.4 (8)	C_{1c}–Si_{1c}–C_{3c}	110.0 (4)
C_4–C_5–C_6	114.7 (9)	C_{1c}–Si_{1c}–C_{4c}	114.1 (4)
C_5–C_6–C_7	118.7 (9)	C_{2c}–Si_{1c}–C_{3c}	106.5 (5)
C_6–C_7–C_8	110.9 (9)	C_{2c}–Si_{1c}–C_{4c}	106.1 (5)
C_1–C_8–C_7	123.8 (8)	C_{2c}–Si_{1c}–C_{4c}	109.0 (5)
Sn_1–C_{1a}–Si_{1a}	118.3 (4)	C_{1c}–Si_{2c}–C_{5c}	111.5 (4)
Sn_1–C_{1a}–Si_{2a}	115.8 (4)	C_{1c}–Si_{2c}–C_{6c}	114.8 (4)
Si_{1a}–C_{1a}–Si_{2a}	113.0 (4)	C_{1c}–Si_{2c}–C_{7c}	109.8 (4)
Sn_1–C_{1b}–Si_{1b}	115.9 (4)	C_{5c}–Si_{2c}–C_{6c}	108.7 (4)
Sn_1–C_{1b}–Si_{2b}	113.4 (4)	C_{5c}–Si_{2c}–C_{7c}	106.9 (5)
Si_{1b}–C_{1b}–Si_{2b}	114.0 (4)	C_{6c}–Si_{2c}–C_{7c}	104.7 (4)
Sn_2–C_{1c}–Si_{1c}	113.7 (4)	C_{1d}–Si_{1d}–C_{2d}	109.8 (5)
Sn_2–C_{1c}–Si_{2c}	115.0 (4)	C_{1d}–Si_{1d}–C_{3d}	115.0 (4)
Si_{1c}–C_{1c}–Si_{2c}	114.0 (4)	C_{1d}–Si_{1d}–C_{4d}	110.7 (4)
Sn_2–C_{1d}–Si_{1d}	117.3 (4)	C_{2d}–Si_{1d}–C_{3d}	101.8 (5)
Sn_2–C_{1d}–Si_{2d}	115.1 (4)	C_{2d}–Si_{1d}–C_{4d}	110.1 (5)
Si_{1d}–C_{1d}–Si_{2d}	114.1 (4)	C_{3d}–Si_{1d}–C_{4d}	109.0 (5)
C_{1a}–Si_{1a}–C_{2a}	114.5 (4)	C_{1d}–Si_{2d}–C_{5d}	112.9 (4)
C_{1a}–Si_{1a}–C_{3a}	112.3 (4)	C_{1d}–Si_{2d}–C_{6d}	112.4 (4)
C_{1a}–Si_{1a}–C_{4a}	109.6 (4)	C_{1d}–Si_{2d}–C_{7d}	108.5 (4)
C_{2a}–Si_{1a}–C_{3a}	104.4 (5)	C_{5d}–Si_{2d}–C_{6d}	107.5 (4)
C_{2a}–Si_{1a}–C_{4a}	109.6 (4)	C_{5d}–Si_{2d}–C_{7d}	107.0 (4)
C_{3a}–Si_{1a}–C_{4a}	106.0 (5)	C_{6d}–Si_{2d}–C_{7d}	108.4 (4)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

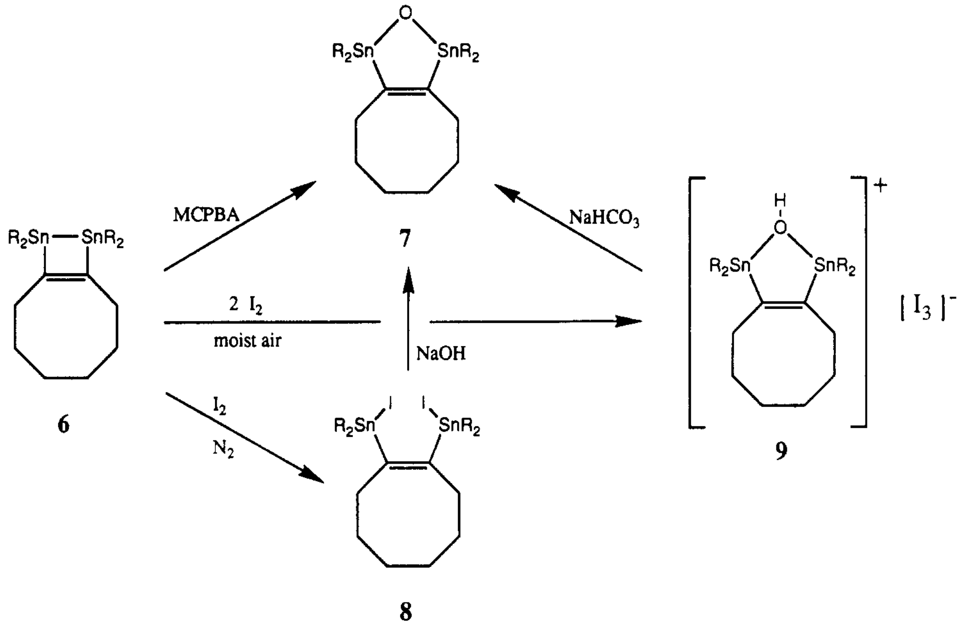
shorter than those found for **3** (2.27 (1) Å). Thus, the solid-state structure of **3** can best be viewed as being

Scheme I



For **1a** and **2a**: R = bis(trimethylsilyl)methyl
For **1b** and **2b**: R = 2,4,6-triisopropylphenyl
For **1c** and **3**: R $_2$Sn =

Scheme II



R = bis(trimethylsilyl)methyl
MCPBA = m-chloroperbenzoic acid

further along the trajectory leading to dissociation, and this is in keeping with its solution behavior. The endocyclic bond angles of the four-membered ring of **6** follow from the geometry of this structure and the bond lengths mentioned above (Table III).

The chemical reactivity of **6** is dominated by that of the tin–tin bond. Thus, while **6** is inert to oxygen in solution, it reacts with *m*-chloroperbenzoic acid (MCPBA) in toluene to give the distannoxane **7** in 79% yield and 1 equiv of iodine readily cleaves the tin–tin bond to give the air-sensitive diiodide **8** (79% yield), which can be further converted to **7** upon base hydrolysis (50% yield) (Scheme II). Surprisingly, addition of 2 equiv or more of iodine to a solution of **6** in toluene under an atmosphere of air, followed by concentration of the resulting dark yellow-brown solution through slow evaporation of the solvent, provides bronze-colored crystals of the triiodide anion (I_3^-) complex of the cationic species **9** in 76% yield (Scheme II). The cation **9** is air- and moisture-stable, soluble in polar solvents (e.g. methanol), and can be deprotonated with sodium bicarbonate to provide the distannoxane **7**. Further proof of a bridging hydroxy group in **9** is provided by an IR (Nujol) spectrum, which exhibits a sharp absorption frequency at 3603 cm^{-1} (ν_{O-H}). A ^{13}C NMR (75 MHz, chloroform-*d*) spectrum of **9** displays a resonance at 163.4 ppm for the alkene carbon atoms and a ^{119}Sn{^{1}H} NMR (112 MHz, chloroform-*d*) spectrum shows a single resonance at +136.5 ppm. Solutions of **9** are highly colored and show absorption maxima in ethanol at λ 225 nm (ϵ_{max} 47 600), 291 nm (ϵ_{max} 29 000), and an absorption at 361 nm (ϵ_{max} 16 800) that might be attributable to a charge-transfer transition.

Table IV. Fractional Coordinates of the Non-Hydrogen Atoms (×10^4) and Equivalent Isotropic Thermal Parameters (×10) for 9^a

atom^b	x	y	z	B_{eq}, Å^2
		Anion		
I_1	5222 (1)	6635 (1)	1365 (1)	82 (1)
I_2	4958 (1)	6049 (1)	2350 (1)	63 (1)
I_3	4763 (1)	5503 (1)	3367 (1)	90 (1)
		Cation		
Sn_1	2627 (1)	2643 (1)	705 (1)	27 (1)
Sn_2	2254 (1)	3629 (1)	−676 (1)	25 (1)
Si_{1a}	2387 (1)	5260 (2)	1082 (1)	39 (1)
Si_{2a}	2266 (1)	3235 (2)	1826 (1)	40 (1)
Si_{1b}	4362 (1)	2103 (2)	1395 (1)	44 (1)
Si_{2b}	3389 (2)	−61 (2)	1081 (1)	55 (1)
Si_{1c}	1559 (1)	6366 (2)	−993 (1)	45 (1)
Si_{2c}	3211 (1)	5823 (2)	−778 (1)	38 (1)
Si_{1d}	3113 (1)	1383 (2)	−962 (1)	45 (1)
Si_{2d}	2009 (1)	2760 (2)	−1943 (1)	45 (1)
O	2965 (3)	3450 (4)	135 (2)	29 (2)
C_1	1627 (4)	2268 (6)	43 (3)	36 (2)
C_2	1490 (4)	2655 (6)	−463 (3)	33 (2)
C_3	855 (4)	2215 (8)	−953 (3)	51 (3)
C_4	122 (5)	2737 (10)	−1055 (4)	76 (4)
C_5	−235 (6)	2446 (19)	−666 (5)	182 (10)
C_6	−4 (8)	2602 (17)	−182 (8)	177 (11)
C_7	501 (6)	1939 (12)	265 (5)	99 (6)
C_8	1132 (5)	1460 (8)	168 (4)	60 (3)
C_{1a}	2666 (4)	3813 (5)	1328 (3)	32 (2)
C_{2a}	3087 (5)	5925 (7)	872 (4)	48 (3)
C_{3a}	2324 (7)	6150 (8)	1641 (4)	70 (4)
C_{4a}	1502 (4)	5217 (7)	509 (4)	51 (3)
C_{5a}	2281 (5)	1703 (7)	1814 (4)	56 (3)
C_{6a}	1309 (5)	3654 (10)	1677 (4)	67 (4)
C_{7a}	2827 (6)	3718 (8)	2524 (3)	61 (4)
C_{1b}	3488 (4)	1459 (6)	943 (3)	34 (2)
C_{2b}	4507 (4)	3463 (7)	1122 (4)	53 (3)
C_{3b}	5137 (5)	1234 (10)	1382 (4)	72 (4)
C_{4b}	4386 (5)	2308 (9)	2104 (3)	59 (3)
C_{5b}	3813 (7)	−448 (10)	1817 (5)	86 (5)
C_{6b}	3858 (7)	−842 (8)	692 (5)	81 (5)
C_{7b}	2460 (6)	−584 (8)	841 (5)	79 (5)
C_{1c}	2347 (4)	5399 (5)	−685 (3)	30 (2)
C_{2c}	1654 (6)	7522 (7)	−507 (4)	64 (4)
C_{3c}	678 (5)	5681 (9)	−1101 (5)	67 (4)
C_{4c}	1519 (6)	6972 (10)	−1668 (4)	78 (5)
C_{5c}	3172 (5)	5633 (8)	−1494 (3)	49 (3)
C_{6c}	3987 (4)	5023 (7)	−313 (3)	46 (3)
C_{7c}	3416 (7)	7297 (7)	−585 (5)	75 (5)
C_{1d}	2662 (4)	2735 (6)	−1213 (3)	33 (2)
C_{2d}	3988 (5)	1605 (8)	−387 (4)	56 (3)
C_{3d}	3335 (6)	679 (9)	−1515 (4)	71 (4)
C_{4d}	2532 (5)	461 (7)	−733 (5)	63 (4)
C_{5d}	2516 (6)	2995 (10)	−2408 (4)	66 (4)
C_{6d}	1374 (5)	3941 (8)	−2047 (4)	62 (3)
C_{7d}	1460 (5)	1463 (8)	−2149 (4)	65 (4)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2.

Table V. Bond Lengths (Å) for 9^{a,b}

		Anion	
I_1–I_2	2.915 (1)	I_2–I_3	2.919 (1)
		Cation	
Sn_1–O	2.100 (6)	Si_{1c}–C_{1c}	1.898 (7)
Sn_1–C_1	2.172 (6)	Si_{1c}–C_{2c}	1.868 (11)
Sn_1–C_{1a}	2.155 (7)	Si_{1c}–C_{3c}	1.871 (10)
Sn_1–C_{1b}	2.157 (7)	Si_{1c}–C_{4c}	1.901 (12)
Sn_2–O	2.108 (4)	Si_{2c}–C_{1c}	1.896 (8)
Sn_2–C_2	2.159 (8)	Si_{2c}–C_{5c}	1.873 (10)
Sn_2–C_{1c}	2.168 (7)	Si_{2c}–C_{6c}	1.866 (8)
Sn_2–C_{1d}	2.162 (8)	Si_{2c}–C_{7c}	1.873 (10)
O–H_0	0.66 (5)	Si_{1d}–C_{1d}	1.882 (7)
Si_{1a}–C_{1a}	1.893 (7)	Si_{1d}–C_{2d}	1.872 (8)
Si_{1a}–C_{2a}	1.862 (11)	Si_{1d}–C_{3d}	1.876 (13)
Si_{1a}–C_{3a}	1.870 (12)	Si_{1d}–C_{4d}	1.863 (12)
Si_{1a}–C_{4a}	1.865 (8)	Si_{2d}–C_{1d}	1.895 (6)
Si_{2a}–C_{1a}	1.901 (9)	Si_{2d}–C_{5d}	1.870 (13)
Si_{2a}–C_{5a}	1.869 (9)	Si_{2d}–C_{6d}	1.871 (10)
Si_{2a}–C_{6a}	1.873 (10)	Si_{2d}–C_{7d}	1.888 (10)
Si_{2a}–C_{7a}	1.870 (8)	C_1–C_2	1.347 (11)
Si_{1b}–C_{1b}	1.891 (7)	C_1–C_8	1.512 (13)
Si_{1b}–C_{2b}	1.871 (10)	C_2–C_3	1.543 (9)
Si_{1b}–C_{3b}	1.884 (12)	C_3–C_4	1.526 (13)
Si_{1b}–C_{4b}	1.868 (10)	C_4–C_5	1.486 (20)
Si_{2b}–C_{1b}	1.913 (8)	C_5–C_6	1.204 (23)^c
Si_{2b}–C_{5b}	1.877 (11)	C_6–C_7	1.483 (21)
Si_{2b}–C_{6b}	1.877 (15)	C_7–C_8	1.490 (18)
Si_{2b}–C_{7b}	1.843 (12)		

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2. [c] Methylene carbon atoms C_5 and C_6 appear to be slightly disordered in the solid state about the average positions given for these atoms in Table IV. This disorder manifests itself in relatively high (18 vs 10 Å^2 for the next highest non-hydrogen atom (C_7) in the structure) equivalent isotropic thermal parameters (see Table IV) and a foreshortened C_5–C_6 bond.

Other tin-centered cations that are stabilized by either intramolecular[9] or intermolecular[10] coordination of a donor ligand have been previously reported; however, structural data for these species have remained scarce. Thus, unequivocal proof of the ionic character of 9 was pursued by crystallographic analysis (see Figure 2 and Tables IV–VI).[8] As shown in Figure 2, the five-membered-ring fragment of 9 is essentially planar with the endocyclic Sn–C bond lengths of 2.159 (8) and 2.172 (6) Å and the C_{sp^2}–C_{sp^2} bond length of 1.347 (11) Å being within the expected ranges. The tin–oxygen bond lengths of 2.100 (6) and 2.108 (4) Å, however, are quite long,[11] a feature that is undoubtedly due to strong steric interactions between the exocyclic ligands on each tin atom. The iodine–iodine bond lengths are 2.915 (1) and 2.919 (1) Å, respectively, and a distance of 5.34 Å separates I_1 from the the hydrogen atom, H_o. Of particular interest are the sums of the three sets of angles about Sn_1 ($C_{1a}Sn_1C_1$, $C_{1a}Sn_1C_{1b}$, and $C_{1b}Sn_1C_1$), Sn_2

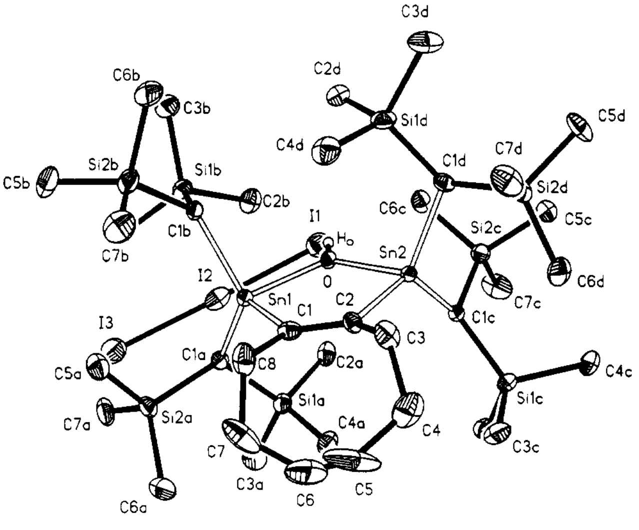


Figure 2. ORTEP drawing of $[Sn_2(CH(Si(CH_3)_3)_2)_4(C_8H_{12})(OH)][I_3]$ (9). The hydrogen atoms (except for H_o) have been omitted for clarity.

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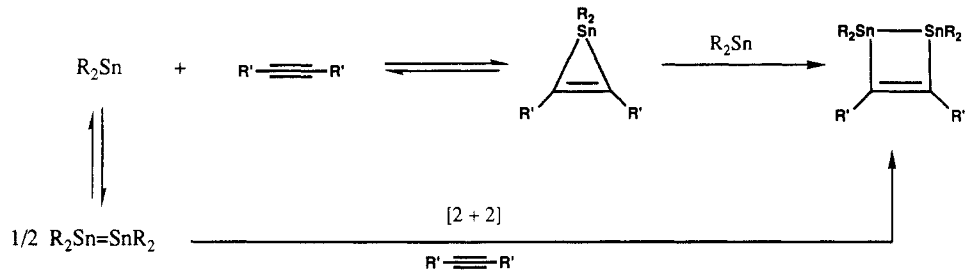
(10) Kumar, Das, V. G. *J. Inorg. Nucl. Chem.* **1976**, 1241.

(11) The Sn-O bond lengths are 1.955 Å in $(Ph_3Sn)_2O$ (Glidewell, C.; Likes, D. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1693) and 1.957–1.988 Å in hexakis(2,4,6-trimethylphenyl)cyclotristannoxane (Weber, U.; Pauls, N.; Winter, W.; Stegmann, H. B. *Z. Naturforsch., B* **1982**, *37*, 1316).

Scheme III



($C_{1c}Sn_2C_2$, $C_{1c}Sn_2C_{1d}$, and $C_{1d}Sn_2C_2$), and the oxygen atom (Sn_1OSn_2, Sn_1OH_o, and Sn_2OH_o), which are 355.8, 355.6, and 359.9°, respectively. When these angles are compared to the 328.5° value expected for an idealized tetrahedral configuration, the geometry about each of these atoms (Sn_1, Sn_2, and O) can best be described as being trigonal coplanar. Finally, the I_3^- anion is nearly collinear with the angle of $I_1I_2I_3$ being 177.2 (1)°.

Discussion

From the data that have been collected so far concerning the reactivity of stannylenes with alkynes, it is becoming clear that the course of the reaction leading to either stannacyclopropene or 1,2-distannacyclobut-3-ene product formation, as well as the stability of these three- and four-membered ring systems, respectively, is highly dependent upon a fine balance between steric and electronic factors. Concerning 1,2-distannacyclobut-3-ene formation, two mechanisms are possible as shown in Scheme III. In the first mechanism, a reversible equilibrium between the starting materials and a stannacyclopropene intermediate is initially established with the relative stabilities of the stannylene, alkyne, and stannacyclopropene adduct determining the side to which this equilibrium lies (Scheme III). In this regard, it is important to note that stannylenes are inherently more stable than their carbon analogues due to the "inert s pair" effect, which stabilizes a divalent state for the heavier elements within a main-group family,[12] and recent ab initio calculations show that the reaction of H_2Sn with HC≡CH to form the parent stannacyclopropene c-$(CH_2)_2SnH_2$, is virutally thermoneutral with very small energy barriers for the forward and reverse reactions.[13] Thus, one can expect that a greater instability of the alkyne starting material will greatly favor stannacyclopropene formation in the order cycloheptyne > cyclooctyne > acyclic alkyne (not observed).

We believe that stannacyclopropenes are kinetic products, and under the equilibrium conditions stated above, rapid ring expansion occurs via stannylene insertion into a Sn–C bond to provide the more thermodynamically stable 1,2-distannacyclobut-3-ene adduct (Scheme III). Support for this presumed thermodynamic preference for 1,2-distannacyclobut-3-ene formation is provided by ab initio calcultions, which show that, unlike cyclopropane and cyclobutane, which possess essentially the same amount of ring strain, four-membered rings containing the heavier elements (Si, Ge, Sn, and Pb) have *less* ring strain than three-membered rings containing these same elements.[14] If the steric bulk of the stannylene and alkyne fragments is sufficient, then stannylene insertion is prevented and one isolates only the kinetically stabilized stannacyclopropene adduct as in the case of **2a**. If, however, the extent of these steric interactions is decreased or removed altogether, then stannylene insertion is rapid and the stannacyclopropene adduct can be assumed to be present as only a steady-state concentration. This latter situation may explain the failure to observe a stannacyclopropene adduct (via variable-temperature ^1H NMR spectroscopy) in the reaction of **1a** with cyclooctyne at any point in the conversion of these materials to the 1,2-dis-

Table VI. Bond Angles for 9[a,b]

I_1–I_2–I_3	177.2 (1)	C_{2a}–Si_{1a}–C_{4a}	111.3 (4)
O–Sn_1–C_1	87.9 (3)	C_{3a}–Si_{1a}–C_{4a}	110.0 (5)
O–Sn_1–C_{1a}	107.5 (3)	C_{1a}–Si_{2a}–C_{5a}	110.2 (5)
O–Sn_1–C_{1b}	95.4 (3)	C_{1a}–Si_{2a}–C_{6a}	113.7 (4)
C_1–Sn_1–C_{1a}	121.5 (3)	C_{1a}–Si_{2a}–C_{7a}	108.1 (4)
C_1–Sn_1–C_{1b}	119.8 (3)	C_{5a}–Si_{2a}–C_{6a}	106.9 (5)
C_{1a}–Sn_1–C_{1b}	114.5 (2)	C_{5a}–Si_{2a}–C_{7a}	108.9 (4)
O–Sn_2–C_2	87.7 (2)	C_{6a}–Si_{2a}–C_{7a}	109.0 (5)
O–Sn_2–C_{1c}	94.9 (2)	C_{1b}–Si_{1b}–C_{2b}	111.2 (3)
O–Sn_2–C_{1d}	109.7 (2)	C_{1b}–Si_{1b}–C_{3b}	109.3 (4)
C_2–Sn_2–C_{1c}	128.4 (3)	C_{1b}–Si_{1b}–C_{4b}	111.9 (4)
C_2–Sn_2–C_{1d}	111.0 (3)	C_{2b}–Si_{1b}–C_{3b}	104.5 (5)
C_{1c}–Sn_2–C_{1d}	116.2 (3)	C_{2b}–Si_{1b}–C_{4b}	108.3 (5)
Sn_1–O–Sn_2	120.1 (2)	C_{3b}–Si_{1b}–C_{4b}	111.5 (5)
Sn_1–O–H_o	118.2 (49)	C_{1b}–Si_{2b}–C_{5b}	113.7 (4)
Sn_2–O–H_o	121.6 (50)	C_{1b}–Si_{2b}–C_{6b}	106.4 (5)
Sn_1–C_1–C_2	121.4 (6)	C_{1b}–Si_{2b}–C_{7b}	115.5 (4)
Sn_1–C_1–C_8	116.4 (5)	C_{5b}–Si_{2b}–C_{6b}	108.0 (6)
C_2–C_1–C_8	121.9 (6)	C_{5b}–Si_{2b}–C_{7b}	106.9 (6)
Sn_2–C_2–C_1	122.7 (5)	C_{6b}–Si_{2b}–C_{7b}	105.9 (6)
Sn_2–C_2–C_3	114.6 (6)	C_{1c}–Si_{1c}–C_{2c}	108.2 (4)
C_1–C_2–C_3	121.3 (7)	C_{1c}–Si_{1c}–C_{3c}	111.9 (4)
C_2–C_3–C_4	116.5 (8)	C_{1c}–Si_{1c}–C_{4c}	113.0 (5)
C_3–C_4–C_5	116.4 (10)	C_{2c}–Si_{1c}–C_{3c}	107.4 (5)
C_4–C_5–C_6[c]	126.6 (15)	C_{2c}–Si_{1c}–C_{4c}	107.9 (5)
C_5–C_6–C_7[c]	130.3 (20)	C_{3c}–Si_{1c}–C_{4c}	108.1 (5)
C_6–C_7–C_8	116.7 (14)	C_{1c}–Si_{2c}–C_{5c}	112.6 (4)
C_1–C_8–C_7	116.1 (9)	C_{1c}–Si_{2c}–C_{6c}	110.4 (4)
Sn_1–C_{1a}–Si_{1a}	115.6 (3)	C_{1c}–Si_{2c}–C_{7c}	110.3 (5)
Sn_1–C_{1a}–Si_{2a}	111.8 (3)	C_{5c}–Si_{2c}–C_{6c}	108.7 (4)
Si_{1a}–C_{1a}–Si_{2a}	115.9 (4)	C_{5c}–Si_{2c}–C_{7c}	108.5 (5)
Sn_1–C_{1b}–Si_{1b}	111.2 (3)	C_{6c}–Si_{2c}–C_{7c}	106.0 (4)
Sn_1–C_{1b}–Si_{2b}	125.3 (4)	C_{1d}–Si_{1d}–C_{2d}	110.2 (4)
Si_{1b}–C_{1b}–Si_{2b}	114.7 (3)	C_{1d}–Si_{1d}–C_{3d}	110.1 (4)
Sn_2–C_{1c}–Si_{1c}	124.3 (3)	C_{1d}–Si_{1d}–C_{4d}	111.6 (4)
Sn_2–C_{1c}–Si_{2c}	111.0 (3)	C_{2d}–Si_{1d}–C_{3d}	106.5 (5)
Si_{1c}–C_{1c}–Si_{2c}	115.2 (4)	C_{2d}–Si_{1d}–C_{4d}	109.5 (5)
Sn_2–C_{1d}–Si_{1d}	117.2 (4)	C_{3d}–Si_{1d}–C_{4d}	108.8 (5)
Sn_2–C_{1d}–Si_{2d}	111.9 (3)	C_{1d}–Si_{2d}–C_{5d}	109.4 (4)
Si_{1d}–C_{1d}–Si_{2d}	116.0 (4)	C_{1d}–Si_{2d}–C_{6d}	110.0 (4)
C_{1a}–Si_{1a}–C_{2a}	110.4 (4)	C_{1d}–Si_{2d}–C_{7d}	113.2 (4)
C_{1a}–Si_{1a}–C_{3a}	111.5 (4)	C_{5d}–Si_{2d}–C_{6d}	106.4 (5)
C_{1a}–Si_{1a}–C_{4a}	109.0 (3)	C_{5d}–Si_{2d}–C_{7d}	109.5 (5)
C_{2a}–Si_{1a}–C_{3a}	104.6 (5)	C_{6d}–Si_{2d}–C_{7d}	108.1 (4)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2. [c] Methylene carbon atoms C_5 and C_6 appear to be slightly disordered in the solid state about the average positions given for these atoms in Table IV. This disorder manifests itself in relatively high (18 vs 10 Å^2 for the next highest non-hydrogen atom (C_7) in the structure) equivalent isotropic thermal parameters (see Table IV) and a foreshortened C_5–C_6 bond.

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tannacyclobut-3-ene product **6**. It must be mentioned that 1,2-distannacyclobut-3-ene stability is also dependent upon steric and electronic factors, which explains the different solution behavior of the two derivatives **3** and **6**.

A second mechanism for the formation of 1,2-distannacyclobut-3-ene adducts from stannylenes and alkynes relies upon prior dimerization of the stannylene to form a distannene, $R_2Sn{=}SnR_2$, which then undergoes a formal [2 + 2] reaction to form the four-membered ring product (Scheme III). Since **1a** is known to exist to a small degree as a dimer in solution,[15] we cannot rule out at this time that formation of **6** proceeds via this alternate mechanism, as has been proposed for the formation of a phosphadistannacyclobutene derivative from **1a** and a phosphaalkyne.[16]

In conclusion, the effects of steric and electronic factors on the reactivity of stannylenes with carbon–carbon multiple bonds and on the stability of the resulting products are becoming better defined. In addition, we believe that extension of these studies to the synthesis of the presently unknown stannacyclopropane and 1,2-distannacyclobutane ring systems will be possible and that solution-stable derivatives will provide synthetic entries into other new and interesting cyclic systems containing tin such as that represented by the conversion of **6** to **9**. Work along these lines is currently in progress.

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 troughout. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded at 300, 75, and 112 MHz, respectively, on an IBM NR 300 spectrometer, and infrared spectra were recorded on a Nicolet FT-IR spectrometer. The compounds R_2Sn (R = bis(trimethylsilyl)methyl)[4] and cyclooctyne[5] were prepared according to procedures described elsewhere. *m*-Chloroperbenzoic acid (MCPBA) was used as obtained from Aldrich.

Preparation of $\Delta^{1,8}$-9,10-Distanna-9,9,10,10-tetrakis[bis(trimethylsilyl)methyl]bicyclo[6.2.0]decane (6). A solution of 740 mg (1.69 mmol) of **1a** and 264 mg (2.44 mol) of cyclooctyne in 20 mL of toluene was allowed to stand under an atmosphere of N_2 for 48 h in a sealed tube. Removal of the solvent under reduced pressure gave a crude material from which 590 mg of white crystalline **6** could be isolated through flash chromatography on silica gel (400 mesh) with *n*-hexane as the eluant (71% yield): mp 200 °C dec; ^{1}H NMR (300 MHz, benzene-d_6) δ 0.34 (s, 9 H), 0.37 (s, 9 H), 0.46 (s, 1 H), 1.59 (br s, 1 H), 1.77 (br, s, 1 H), 2.83 (m, 1 H); ^{13}C NMR (75 MHz) δ 5.07 (q), 5.31 (q), 10.24 (d), 26.66 (t), 28.42 (t), 39.68 (t), 173.17 (s); ^{119}Sn NMR (112 MHz, benzene-d_6) δ +56.5 ($^1J(^{119}Sn-^{117}Sn)$ = 2436 Hz); IR (Nujol) 1266 (s), 1247 (s), 1013 (m), 966 (m), 844 (br, s), 772 (m), 753 (w), 728 (m), 694 (w) cm^{-1}; UV (*n*-hexane) λ 226 nm (ϵ_{max} 49 300), 284 nm (ϵ_{max} 14 300). Anal. Calcd for **6**: C, 43.98; H, 9.02. Found: C, 44.03; H, 9.09.

Reaction of 6 with MCPBA. To a solution of 226 mg (0.23 mmol) of **6** in 20 mL of toluene was added a solution of 50 mg (0.19 mmol) of MCPBA in 20 mL of toluene. The reaction mixture was then stirred for 18 h, whereupon 20 mL of 5% aqueous sodium carbonate was added. The organic layer was separated and dried with anhydrous sodium sulfate and the solvent removed in vacuo to provide the crude material, which was purified by flash chromatography on silica gel (400 mesh) with *n*-hexane as the eluant to provide 181 mg (79% yield) of **7** as a white crystalline compound: ^{1}H NMR (300 MHz, benzene-d_6) δ 0.35 (s, 9 H), 0.39 (s, 9 H), 1.58 (br s, 1 H), 1.72 (br s, 1 H), 2.75 (m, 1 H); ^{13}C NMR (75 MHz, chloroform-*d*) δ 4.48 (q), 4.46 (q), 13.49 (d, ^1J(^{119,117}Sn–^{13}C) = 160.8 Hz), 25.89 (t), 28.99 (t), 34.86 (t, ^1J(^{119,117}Sn–^{13}C = 102.7 Hz), 164.29 (s); ^{119}Sn{^{1}H} NMR (112 MHz, chloroform-*d*) δ +49.2; IR (Nujol) 1025 (m), 1013 (m), 991 (w), 966 (w), 841 (br, s), 775 (m), 756 (m), 725 (w), 659 (s) cm^{-1}; UV (*n*-hexane) λ 225 nm (ϵ_{max} 33 900). Anal. Calcd for **7**: C, 43.28; H, 8.88. Found: C, 43.42; H, 8.62.

Table VII. Crystal, Data Collection, and Refinement Parameters for 6 and 9

	6	9
formula	$C_{36}H_{88}Si_8Sn_2$	$C_{36}H_{89}I_3OSi_8Sn_2$
syst	orthorhombic	monoclinic
a, Å	18.694 (1)	19.928 (4)
b, Å	19.053 (1)	12.198 (2)
c, Å	14.895 (1)	26.345 (5)
β, deg		111.09 (1)
V, Å^3	5305 (1)	5975 (2)
D(calcd), g cm^{-3}	1.23	1.54
space group	$P2_12_12_1$	$P2_1/n$
Z	4	4
temp, °C	23	20
radiation	Mo Kα (graphite monochromated)	
scan technique	ω	ω
μ, mm^{-1}	11.64	2.55
$2\theta_{max}$, deg	35	48
no. of data	8410	9541
no. of data in refinement	7787	6002
R	0.047	0.039
criteria	$I > 3\sigma(I)$	$I > 3\sigma(I)$

Reaction of 6 with Iodine. To a solution of 125 mg (0.13 mmol) of **6** in 10 mL of toluene was added a solution of 32 mg (0.13 mmol) of iodine in 15 mL of toluene dropwise over a period of 1 h under an inert atmosphere of N_2. After the addition was complete, the solvent was removed in a glovebox to give **8** as an air-sensitive crude material, which was purified by recrystallization in pentane at −40 °C to give 124 mg (79% yield): ^{1}H NMR (300 MHz, benzene-d_6) δ 0.41 (s, 9 H), 0.45 (s, 9 H), 1.43 (br s, 1 H), 1.70 (br s, 1 H), 2.72 (m, 1 H); ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6) δ 5.70, 5.86, 16.12, 26.03, 31.48, 37.97, 161.07; ^{119}Sn{^{1}H} NMR (112 MHz, benzene-d_6) δ −68.4 (broad). Chemical analysis gave results consistent with partial decomposition. Anal. Calcd for **8**: C, 34.96; H, 7.17; I, 20.52. Found: C, 36.34; H, 7.09; I, 13.24.

Reaction of 6 with Iodine and Moist Air. To a solution of 57 mg (0.058 mmol) of **6** in 5 mL of toluene was slowly added a solution of 44 mg (0.173 mmol) of iodine in 25 mL of toluene dropwise over a period of 1 h in an open reaction vessel. After the addition was complete, the solution was concentrated overnight by evaporation in an open beaker. Compound **9** was collected as bronze-colored crystals (50 mg), and an additional 10 mg of **9** could be isolated from the mother liquor through recrystallization from methylene chloride (76% combined yield): ^{1}H NMR (300 MHz, chloroform-*d*) δ 0.26 (s, 9 H), 0.33 (s, 9 H), 0.61 (s, 1 H), 1.62 (br s, 1 H), 1.814 (br s, 1 H), 2.77 (m, 1 H); ^{13}C{^{1}H} NMR (75 MHz, chloroform-*d*) δ 4.41, 4.59, 19.78, 25.41, 29.07, 35.15, 163.38; ^{119}Sn NMR (112 MHz, chloroform-*d*) δ +136.5; IR (Nujol) 3603 (w), 1310 (s), 1249 (s), 1158 (w), 1026 (m), 1005 (m), 982 (m), 840 (s), 769 (s), 726 (s) cm^{-1}; UV (ethanol) λ 225 nm (ϵ_{max} 47 600), 291 nm (ϵ_{max} 29 000), 361 nm (ϵ_{max} 16 800). Anal. Calcd for **9**: C, 31.31; H, 6.49; I, 27.57. Found: C, 30.83; H, 6.40; I, 27.96.

Crystal Data for Compound 6. Crystals suitable for X-ray analysis were obtained from pentane at −40 °C. Crystallographic data are summarized in Table VII. Single crystals are (at 23 °C) orthorhombic, space group $P2_12_12_1$, with a = 18.694 (1) Å, b = 19.053 (1) Å, c = 14.895 (1) Å, V = 5305 (1) Å^3, and D_{calcd} = 1.23 g cm^{-3} (Z = 4). A total of 8410 symmetry-independent reflections having 2θ(Mo Kα) < 35° were collected on a CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained from least-squares refinements of the setting angles of 25 reflections (16° < 2θ < 23°). The non-hydrogen atom positions were determined by Harker vector analysis of three-dimensional Patterson maps, and hydrogen atoms were given calculated positions (C–H = 0.96 Å). The resulting structural parameters were refined to convergence R(unweighted) = 0.047 for 7787 reflections with use of block-diagonal least-squares refinement and a structural model that incorporated anisotropic

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thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.

Crystal Data for Compound 9. Crystals suitable for X-ray analysis were obtained by slow evaporation of toluene from the reaction mixture described above. Crystallographic data are summarized in Table VII. Single crystals are (at 20 °C) monoclinic, space group $P2_1/n$, with a = 19.928 (4) Å, b = 12.198 (2) Å, c = 26.345 (5) Å, β = 111.09 (1)°, V = 5975 (2) Å^3, and Z = 4 (D_{calcd} = 1.54 g cm^{-3}; μ_a(Mo Kα) = 2.55 mm^{-1}). A total of 9541 independent reflections having 2θ(Mo Kα) < 48.3° (the equivalent of 0.7 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo Kα radiation. The structure was solved by use of "direct methods" techniques with a Nicolet SHELXTL software package as modified at Crystalytics Co. The resulting structural parameters were refined to convergence (R_1 (unweighted, based on F) = 0.039 for 6002 independent absorption-corrected reflections having 2θ(Mo Kα) < 48.3° and $I > 3\sigma(I)$) with use of counterweighted cascade block-diagonal least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Hydrogen atom H_0 was located from a difference Fourier map and refined as an independent isotropic atom. The methyl groups were included in the refinement as idealized sp^3-hybridized rigid rotors and gave final values for the SiCH angles that ranged from 96 to 121°. The remaining hydrogen atoms were fixed at idealized sp^3-hybridized positions with a C–H bond length of 0.96 Å.

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Supplementary Material Available: Detailed information concerning the crystallographic analysis of **6** and **9**, which includes listings of anisotropic temperature factors and positional parameters of hydrogen atoms (14 pages); listings of observed and calculated structure factors (104 pages). Ordering information is given on any current masthead page.

Structure and Reactivity of a Titanocene η^2-Thioformaldehyde Trimethylphosphine Complex

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Bis(η^5-cyclopentadienyl)titanium titanocene η^2-thioformaldehyde trimethylphosphine (**3**) was prepared from titanocene methylidene trimethylphosphine and either sulfur-containing compounds (e.g., alkene sulfides, triphenylphosphine sulfide) or elemental sulfur. The product **3** crystallized in the orthorhombic system, in space group *Pnma* (No. 62), with a = 13.719 (3) Å, b = 12.384 (1) Å, c = 8.671 (1) Å, V = 1473.2 (6) Å^3; Z = 4. The reaction with *trans*-styrene sulfide-d_1 produced an equimolar mixture of *trans*- and *cis*-styrene-d_1 as byproducts, suggesting a stepwise reaction. The formation of a six-membered ring from titanocene methylidene trimethylphosphine and trimethylene sulfide also supports the stepwise mechanism. A biradical mechanism is preferred in view of the biradical mechanism observed in the analogous reaction with styrene oxide. The complex **3** reacted with methyl iodide to produce the cationic titanocene η^2-thiomethoxymethyl trimethylphosphine complex **5a**, which crystallized with acetonitrile in the orthorhombic system, space group *Pbca* (No. 61) with a = 14.839 (2) Å, b = 15.184 (14) Å, c = 18.461 (3) Å, V = 4159.5 (14)Å^3, Z = 8. Complexes **5b,c** having a less coordinating anion such as BF_4 or BPh_4 were obtained, and complex **5c** was converted to a trimethylphosphine-free complex by equilibration with copper(I) chloride. This cationic species (**7c**) does not catalyze the polymerization of ethylene or methyl vinyl ether in dichloromethane.

Titanocene metallacycles[1] react with a wide variety of organic and inorganic reagents. Methylene transfer to organic carbonyls, including enolizable carbonyls, is one of the most general reactions of these complexes.[2,3] Other important reactions include ring-opening polymerization of cyclic olefins,[4] complexation with metal halides,[5] and olefin metathesis.[6] All these reactions occur through a reactive intermediate that exhibits behavior consistent with that of a transition-metal methylene complex.[7] The titanocene methylidene trimethylphosphine complex, which is derived from titanocene metallacyclobutanes, reacts in a similar fashion.[8]

This family of compounds also provides a new route to thioformaldehyde complexes. Thioaldehydes are known to be stabilized through coordination to transition metals.[9] Although several thioaldehyde complexes of late transition metals have been reported, a zirconium complex is the only reported early-transition-metal analogue.[9a,b] The reaction of the titanocene methylidene trimethylphosphine complex with either organic sulfur compounds or elemental sulfur

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