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OKLAHOMA UNIV NORMAN DEPT OF CHEMISTRY
SYNTHESIS OF TETRAPHENYLSTANNACYCLOPENTADIENES (STANNOLES). II.--ETC(U)
APR 81 W A GUSTAVSON, L M PRINCIPE
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1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene and tin(II) chloride yields only the ring-opened products (4-bromo-1,2,3,4-tetraphenylbutadienyl)tin tribromide or (4-iodo-1,2,3,4-tetraphenylbutadienyl)tin triiodide. Even gentle chlorination of hexaphenylstannole by elemental chlorine cleaves the ring tin-carbon bonds to form cis-cis-1,4-dichloro-1,2,3,4-tetraphenylbutadiene-1,3 and diphenyltin dichloride, while the action of a glacial acetic acid/acetic anhydride mixture yields tetraphenylfuran and diphenyltin diacetate. The dihalostannoies form neutral adducts with pyridine, 2,2'-bipyridyl and 1,10-phenanthroline, and the double salt $[XSnC_4(C_6H_5)_4 \cdot terpy]^+ [X_2YS_nC_4(C_6H_5)_4]^-$ from 2,2',2''-terpyridine where X = Y = Br, I = F, Y = I. The structures of the substituted stannoies and the adducts of the dihalostannoies are discussed on the basis of tin-119m Mössbauer and infrared spectroscopic evidence.

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Synthesis of Tetraphenylstannacyclopentadienes (Stannoles).

II. Derivatives and Adducts of

1,1-Dihalo-2,3,4,5-tetraphenylstannoles^f

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W. A. Gustavson, L. M. Principe, W.-Z. Min Rhee
and J. J. Zuckerman

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Department of Chemistry

University of Oklahoma

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Synthesis of Tetraphenylstannacyclopentadienes (Stannoles).

II. Derivatives and Adducts of
1,1-Dihalo-2,3,4,5-tetraphenylstannoles¹

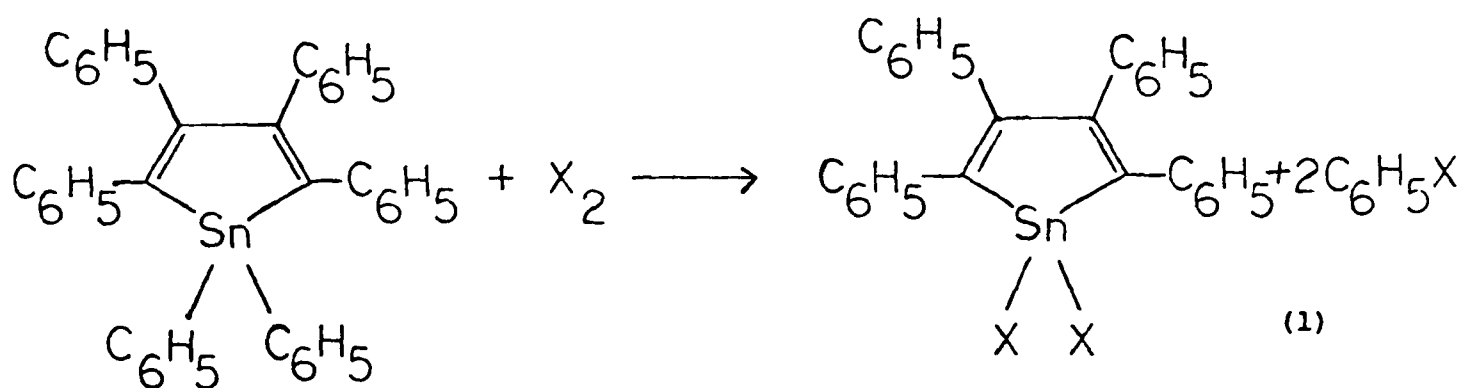
W. A. Gustavson, L. M. Principe, W.-Z. Min Rhee
and J. J. Zuckerman*

Department of Chemistry
University of Oklahoma
Norman, OK 73019

ABSTRACT

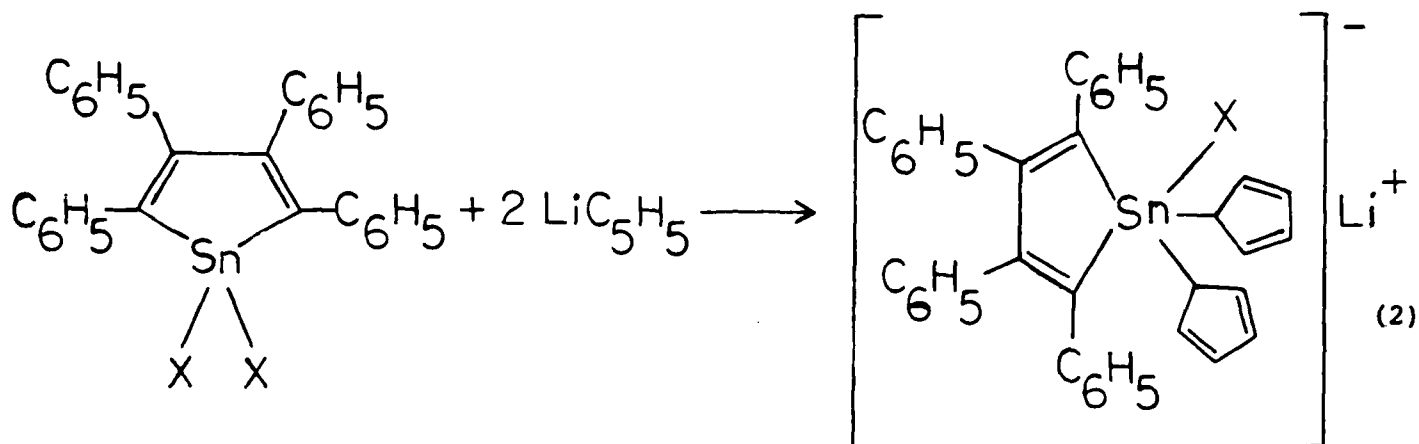
1,1-Dibromo- and 1,1-diiodo-2,3,4,5-tetraphenyl-1-stannacyclopentadiene, dihalotetraphenylstannoies, $\text{XYSn}(\text{C}_6\text{H}_5)_4$, can be derivatized to form a series of disubstituted products in which $\text{X} = \text{Y} = \text{N}_3$, iso-NCO, iso-SCN, $\text{OC}(\text{O})\text{CH}_3$, $\text{SC}(\text{S})\text{N}(\text{C}_2\text{H}_5)_2$, $\text{N}(\text{CH}_3)_2$ and $\text{P}(\text{C}_6\text{H}_5)_2$. Fluorination by KF in acetone results in the $\text{X} = \text{F}$, $\text{Y} = \text{Br}$ or $\text{Y} = \text{I}$ product only, and lithioamination by $\text{LiN}(\text{Si}(\text{CH}_3)_3)_2$ yields the $\text{X} = \text{N}(\text{Si}(\text{CH}_3)_3)_2$, $\text{Y} = \text{Br}$ product only. Attempted synthesis of the dihalostannoies by halogenation of the intermediate tin(II) stannole from 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene and tin(II) chloride yields only the ring-opened products (4-bromo-1,2,3,4-tetraphenylbutadienyl)tin tribromide or (4-iodo-1,2,3,4-tetraphenylbutadienyl)tin triiodide. Even gentle chlorination of hexaphenylstannole by elemental chlorine cleaves the ring tin-carbon bonds to form cis-cis-1,4-dichloro-1,2,3,4-tetraphenylbutadiene-1,3 and diphenyltin dichloride, while the action of a glacial acetic acid/acetic anhydride mixture yields tetraphenylfuran and diphenyltin diacetate. The dihalostannoies form neutral adducts with pyridine, 2,2'-bipyridyl and 1,10-phenanthroline, and the double salt $[\text{XSn}(\text{C}_6\text{H}_5)_4 \cdot \text{terpy}]^+ [\text{X}_2\text{Y}_n\text{Sn}(\text{C}_6\text{H}_5)_4]^-$ from 2,2',2''-terpyridine where $\text{X} = \text{Y} = \text{Br}$, $\text{I} = \text{F}$, $\text{Y} = \text{I}$. The structures of the substituted stannoies and the adducts of the dihalostannoies are discussed on the basis of tin-119m Mössbauer and infrared spectroscopic evidence.

In part one of this series we described the synthesis of the 1,1-dihalostannoles by phenyltin bond cleavage in hexaphenylstannole²⁻⁴ by the action of elemental bromine or iodine under controlled conditions:¹



The availability of 1,1-dihalostannoles by a convenient synthesis in high yield opens up the derivative chemistry of the stannole ring system for exploitation. Comparisons of the 1,1-disubstituted stannoles and their donor-acceptor adducts can be drawn with the analogous diorganotin(IV) derivatives and complexes whose number is vast.⁵⁻⁷ The stannole ring system is a special case, however, in that the carbon-tin-carbon bond vectors are constrained to the interior angles of the five-membered ring heterocycle, and so adducts of the formula $\text{R}_2\text{SnX}_2 \cdot 2\text{L}$ which adopt trans-diorganotin(IV) preferentially, will in the stannole series be forced into other structural forms. The unsaturated butadienoid residue of the stannacyclopentadiene will exert an electrical effect of unknown direction and power on the chemistry of the tin atom. In addition, the tetraphenyl substitution pattern and the presumably planar nature of the stannacyclopentadiene stannole ring will have a steric influence on the reactions of the

stannoles and the properties of the subsequent products. The formation of the lithium 1,1-di- η^1 -cyclopentadienyl-1-halo-2,3,4,5-tetraphenyl stannole salt, a five-coordinated tin(IV) heterocycle with pseudo-rotating axial- and equatorial-fluxional η^1 -cyclopentadienyl groups in a unique $[R_4SnX]^-$ anion described in part one of this series,¹ is a result of these simultaneous influences:⁸



In this paper we report the synthesis of the 1,1-disubstituted stannoles and the adducts of the stannole dihalides. For convenience stannole each time it is used is meant to mean the 1,1-disubstituted-2,3,4,5-tetraphenylstannole derivative.

Experimental Section

Organotin starting materials were of commercial grade and were used without further purification. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Boiling points were determined at constant pressure with a still head thermometer and are uncorrected. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5750 Laboratory Chromatograph equipped with a thermal conductivity detector using helium as the carrier gas. Volatiles were collected at -196°C in U-tubes. Elemental analyses were carried out by Galbraith Laboratory, Inc., Knoxville, TN and by Instranal Laboratory, Inc., Rensselaer, NY. Organotin compounds with high molecular weight (over 700) would often not give consistent analyses. Tin was determined gravimetrically as the oxide, and chlorine, bromine and iodine were determined by potentiometric titration with silver(I) nitrate. Molecular weights of (4-iodo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin triiodide, and (4-bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin tribromide were determined in benzene (a suspected carcinogen) on a Hewlett-Packard Model 301A Vapor Pressure Osmometer. The determination of the molecular weights of adducts did not give consistent results because of insufficient solubility. Mass spectra were recorded on A.E.I. MS-902 and Hewlett Packard 5985B GC/MS instruments at 70 eV. Nuclear magnetic resonance spectra were recorded on Varian A-60, HA-100 and XL-100 instruments. Tetramethylsilane was used as an external standard, and field width was calibrated with a solution of tetramethylsilane-benzene in carbon tetrachloride. Infrared spectra were recorded in the $4,000$ to 200 cm^{-1} range on Beckman IR-12 or 4250 infrared spectrophotometers and calibrated

with polystyrene. Samples were run as liquid smears or Nujol mulls on potassium bromide plates or in polyethylene cells. A Beckman IR-11 spectrophotometer was used to examine the far infrared region ($400\text{-}33\text{ cm}^{-1}$). Mössbauer spectra were recorded on a constant acceleration, cam-drive spectrometer previously described,⁹ with the sample mounted in a cryostat at liquid nitrogen temperature, or on a Ranger Engineering constant acceleration spectrometer equipped with an NaI scintillation counter using $\text{Ca}^{119\text{m}}\text{SnO}_3$ (New England Nuclear Corp.) as both source and standard reference material for zero velocity. Velocity calibration was based on both β -tin and natural iron foils. Data were fitted to Lorentzian curves by standard, non-linear, least squares techniques. The Mössbauer data are listed for the substituted stannole derivatives in Table I, and for the adducts of the dihalostannoles in Table II.

(4-Bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin tribromide

Into 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (67.42 mmol) in ethyl ether (150 mL), tin(II) chloride (6.4 g, 34.04 mmol) in ethyl ether (150 mL) was added dropwise at 0°C . The yellowish-brown solution was stirred for two hrs, and bromine (5.1 g, 63.75 mmol) in carbon tetrachloride was added slowly at -50 to -40° hours. Stirring was continued overnight, and the solvent was removed in vacuo. The tin tribromide (6.3 g, 7.93 mmol) was obtained by recrystallization from methanol-methylene chloride with charcoal (m.p. $162.5^\circ\text{-}163.0^\circ\text{C}$ with some decomposition) in 23% yield based on tin(II) chloride.

The infrared spectrum contained bands at 3060 (w,d), 3020(w), 1600(m,sh), 1580(m), 1487(m), 1445(s), 1175(m,b), 1080(m,sh), 1030(m),

950(m), 740(s), 700(s), 572(m), 550(m), 520(w), 264(s), 258(s) and 247(s) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. of 1.35 ± 0.06 and Q.S. of 1.67 ± 0.12 mm/s. Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{SnBr}_4$: Sn, 14.93; mol. wt. 794.8. Found: Sn, 13.60%; mol. wt. 786.

(4-Iodo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin triiodide

Into 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (33.71 mmol) in ethyl ether (150 mL), tin(II) chloride (3.20 g, 17.02 mmol) in ethyl ether (80 mL) was added dropwise at 0°C . After stirring the yellowish-brown solution for two hours, iodine (4.0 g, 15.76 mmol) dissolved in ethyl ether (100 mL) was added slowly at 0° . The stirring was continued for one hour and the solvent was removed in vacuo. A crude yellow solid (2.1 g) was obtained when the residue was treated with methanol-methylene chloride. Crystallization gave 1.3 g (1.33 mmol) of yellow crystals (m.p. 166.0 - 166.5°C) in 7.8% yield based on tin(II) chloride.

The infrared spectrum showed prominent bands at 1600(w), 1580(w), 1480(m), 1440(m), 1169(w,sh), 1075(w,d), 1030(w), 770(w,d), 735(m), 695(s,sh), 565(m), 540(m), 270(w), 240(m), 226(m), 210(s) and 203(s) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. of 1.66 ± 0.06 and Q.S. of 1.80 ± 0.12 mm/s. Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{SnI}_4$: Sn, 12.08; mol. wt. 982.84. Found: Sn, 11.95%; mol. wt. 995.

1,2,3,4-Tetraphenylbuta-1,3-dienyl-1-phenyltin dichloride

Diphenylacetylene (5.35 g, 0.03 mol) was stirred for four hours in anhydrous diethyl ether (30 mL) under nitrogen with lithium (0.35 g, 0.05 mol) wire. A red solution formed after 10 minutes and a yellow solid precipitated. The slurry was added rapidly to a solution of phenyltin trichloride (4.52 g, 0.015 mol) in tetrahydrofuran (200 mL). An additional 100 mL of anhydrous diethyl ether was used to transfer

the dilithio reagent. The mixture was stirred under nitrogen for two hours at room temperature. The ether layers were then removed in vacuo to leave a green oil. The oil was then dissolved in methylene (200 mL) and the resulting suspension filtered. After concentration to 25 mL, absolute ethanol (50 mL) was added, and precipitation achieved by cooling the green solution to -78°C in Dry Ice.

The white solid product (m.p. $156-158^{\circ}\text{C}$) was identified as 1,2,3,4-tetraphenylbuta-1,3-dienyl-1-phenyltin dichloride. The Mössbauer spectrum of this compound contained a doublet with I.S. 1.15 ± 0.03 and Q.S. 1.70 ± 0.06 mm/s. The infrared spectrum contained prominent bands at 3065(w), 1050(w), 1595(w), 1432(m), 1060(m), 1020(m), 997(m), 915(m), 885(m), 764(w), 729(s), 695(s), 365(s), and $345(\text{m})\text{ cm}^{-1}$. The n.m.r. spectrum in CDCl_3 contained a singlet resonance at 5.2 ppm (relative to TMS) in addition to the phenyl group proton multiplet and calculated for $\text{C}_{34}\text{H}_{26}\text{Cl}_2\text{Sn}$: C, 65.49; H, 4.17; Cl, 11.24; Sn, 19.10% Found: C, 64.57; H, 3.52; Cl, 12.49; Sn, 18.64%.

1-Fluoro-1-bromo-tetraphenylstannole

Into dibromostannole^{1,5} (4.0 g, 6.30 mmol) in tetrahydrofuran (50 mL) potassium fluoride (0.73 g, 12.6 mmol) in ethanol (10 mL) was added dropwise at room temperature. After refluxing 45 minutes, a milky white precipitate was filtered, and the filtrate was concentrated to give a white precipitate (m.p. $189-190^{\circ}\text{C}$) (1.45 g, 2.90 mmol) in 45% yield based on the dibromostannole.

The infrared spectrum contained bands at 3060(s), 1597(m), 1575(m), 1179(w,b), 1158(w), 1072(s,sh), 1030(m), 998(w), 947(m), 915(m), 788(m), 761(s), 735(v,s), 700(v,s), 609(m,d), 550(s), 522(s), 448(m,d), 357(w), 325(w), 280(s) and $228(\text{s})\text{ cm}^{-1}$. The Mössbauer

spectrum was a doublet with I.S. 1.17 ± 0.06 and Q.S. of 2.82 ± 0.12 mm/s.

Anal. Calcd. for $C_{28}H_{20}SnFBr$: Sn, 20.71; C, 58.58; H, 3.49. Found; Sn, 19.85; C, 58.85; H, 3.71%.

1-Fluoro-1-iodo-2,3,4,5-tetraphenylstannole

Diiodostannole¹ (3.9 g, 5.3 mmol) was dissolved in tetrahydrofuran (50 mL), and potassium fluoride (0.62 g, 10.7 mmol) in absolute ethanol (10 mL) was added dropwise under a nitrogen atmosphere at room temperature. The mixture was allowed to reflux for 10 hours with continuous stirring to give a milky white solution which when filtered gave a clear, light yellow colored solution and a white solid. The solution was evaporated to dryness in vacuo. The resulting white oil was dissolved in tetrahydrofuran (15 mL) and then hexane (15 mL) was added. Precipitation occurred when the solution was cooled in Dry Ice. The white, fluoro-iodostannole (m.p. 182-184°C, 1.41 g) was obtained in 43% yield based on diiodostannole.

The infrared spectrum showed prominent bands at 3058(w), 1595(m), 1575(w), 1440(w), 1178(m), 1150(w), 1066(m), 1035(m), 1000(w), 930(m), 913(s), 786(m), 762(s), 735(s,b), 696(s), 611(s), 570(s), 550(s), 520(m), 449(s), 350(m), 315(m), and 275(w) cm^{-1} . The Mössbauer spectrum contained a doublet with I.S. of 1.22 ± 0.03 and Q.S. 2.74 ± 0.06 mm/s. Anal. Calcd. for $C_{28}H_{20}FISn$: C, 54.11; H, 3.22; I, 20.45; Sn, 19.16%. Found: C, 53.90; H, 3.58; I, 19.64; Sn, 18.32%.

Octaphenyl-1,1'-spirobistannole²⁻⁴

Into 1,4-dilithio-1,2,3,4-tetraphenylbutadene (89.53 mmol) in ethyl ether (150 mL) tin(IV) chloride (12.50 g, 45.65 mmol) was added dropwise at 0°. Stirring was continued overnight, and the solvent removed in vacuo. The spiro compound was obtained by re-

crystallization from methanol-methylene chloride (m.p. 275° vs. lit²⁻⁴ 270-280°C) in 25.4% yield based on tin(IV) chloride. The infrared spectrum is consistent with this formulation.³

1,1-Diazo-2,3,4,5-tetraphenylstannole

Lithium azide was prepared by a modification of the procedure of Huisgen and Ugi.¹⁰ Lithium chloride (0.35 g, 8.4 mmol) was dissolved in dry methanol (10 mL) and refluxed for 5 hours with sodium azide (0.6 g, 8.3 mmol) under nitrogen. The solution was allowed to cool and then filtered.

This solution was added slowly to a solution of diiodostannole (3.00 g, 4.1 mmol) in methylene chloride (50 mL), and the mixture stirred at room temperature under nitrogen for one hour after the addition was completed. The solvent was then removed in vacuo, toluene (50 mL) added, and the solution filtered. The addition of hexane precipitated a white solid (m.p. 153-154°C, 1.33 g) in 58% yield (based on diiodostannole).

The infrared spectrum contained prominent bands at 3050(w), 2090(s), 1600(w), 1570(w), 1445(m), 1320(w), 1275(w), 1072(s), 1030(m), 937(w), 767(m), 731(s), 690(s), 472(s), 400(w), and 270(s) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. of 1.18 ± 0.03 and Q.S. of 2.44 ± 0.06 mm/s. Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{N}_6\text{Sn}$: C, 60.11; H, 3.58; Sn, 21.29%. Found: C, 58.98; H, 3.92; Sn, 20.64%

1,1-Diisocyanato-2,3,4,5-tetraphenylstannole

Silver(I) cyanate was prepared by a modification of the procedure of Hassner and Heathcock.¹¹ Silver(I) nitrate (20.0 g, 0.12 mol) was dissolved in distilled water (600 mL) and an equimolar amount (7.8 g, 1.12 mol) of sodium cyanate added. The solution was then stirred at room temperature.

for one hour and filtered and washed with water, methanol and ether. The product was dried for 12 hours in vacuo, and stored in the dark until needed.

Diiodostannole (5.0 g, 6.86 mmol) in mixed absolute ethanol and benzene (a suspected carcinogen) (3:2) (100 mL) was allowed to reflux with silver(I) cyanate (2.06 g, 13.72 mmol) under nitrogen for one hour, and then stirred at room temperature for one hour to produce a clear solution and a white precipitate. The solvent was removed in vacuo, benzene added, and a white solid collected upon filtration. The diisocyanatostannole precipitated from solution with the addition of hexane and cooling in Dry Ice as a white solid (m.p. 163-165°C, 1.61 g) in 42% yield (based upon diiodostannole).

The infrared spectrum contained prominent bands at 3060(w), 2210(s), 1596(s), 1573(m), 1445(m), 1350(m), 1150(m), 1070(s), 1025(m), 995(w), 940(w), 785(w), 760(2), 728(s), 693(s), 610(w), 385(m), and 265(w) cm^{-1} . The Mössbauer spectrum contained a doublet with I.S. 1.05 ± 0.03 and Q.S. 2.47 ± 0.06 mm/s. Anal. Calcd. for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_2\text{Sn}$: C, 64.40; H, 3.58; N, 5.01; Sn, 21.29%. Found: C, 65.21; H, 2.96; N, 4.87; Sn, 20.86%.

1,1-Diisothiocyanato-2,3,4,5-tetraphenylstannole

1,1-Dibromo-2,3,4,5-tetraphenylstannole (5.2 g, 8.189 mmol) in mixed ethanol and benzene (a suspected carcinogen) (100 mL) 3:2 was allowed to reflux with potassium thiocyanate (1.6 g, 16.46 mmol) in ethanol (20 mL) for 30 minutes, then stirred at room temperature for an hour to produce a white precipitate which was filtered. The filtrate was concentrated in vacuo and benzene was added to obtain a crude white solid (1.9 g) which gave on recrystallization 0.6 g (1.01 mmoles) of white crystals (m.p. 152.5°-153.0°C) in 12.3% yield.

The infrared spectrum contained bands at 3075 (w,b), 2050(s), 1600(w,sh), 1480(m), 1465(s), 1452(s), 910(s), 770(s), 735(s), 695(s), 574(w), 553(m), 525(s), 442(m), 338(w,b) and 283(w,b) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. of 1.14 ± 0.06 and Q.S. of 2.81 ± 0.12 mm/s. Anal. Calcd. for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{S}_2\text{Sn}$: Sn, 20.07; mol. wt. 591.30. Found: Sn, 20.51%; mol. wt. 3330.

1,1-Diacetato-2,3,4,5-tetraphenylstannole

To a solution of diiodostannole (3.00 g, 4.1 mmol) in tetrahydrofuran (100 mL) was added silver(I) acetate (1.4 g, 8.4 mmol) in tetrahydrofuran (250 mL) in a flask wrapped with aluminum foil to prevent decomposition of the silver acetate by light. The mixture was stirred under nitrogen at reflux for two hours and then at room temperature for 10 h. The color of the slurry changed from yellow to white. The tetrahydrofuran was then removed in vacuo and toluene (100 mL) added. The resulting suspension was filtered and a clear yellow-orange colored solution obtained along with a light yellow solid (infusible to 400°C) which was assumed to be the silver(I) iodide product. The solution was concentrated to 25 mL and hexane (25 mL) was added. Precipitation occurred when the solution was cooled in Dry Ice to yield a white, air stable solid (m.p. $182\text{--}183^\circ\text{C}$) in 64% yield, based upon diiodostannole.

The infrared spectrum contained prominent bands at 3057(w), 1635(m), 1618(s), 1596(m), 1467(s), 1442(m), 1323(s), 1066(m), 933(m), 760(m), 728(s), 692(s), 615(s), 490(w), 295(m), and 279(w) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. of 1.09 ± 0.03 , and Q.S. of 2.87 ± 0.06 mm/s. The nmr spectrum in CDCl_3 contained a single resonance at 2.18 ppm, relative to TMS, in addition to the phenyl

group multiplet. The proton integration ratio was found to be 1:3.5 = $\text{CH}_3:\text{C}_6\text{H}_5$ vs. 1:3.3 calcd. Anal. Calcd. for $\text{C}_{32}\text{H}_{26}\text{O}_4\text{Sn}$: C, 64.76; H, 4.38; Sn, 20.07%. Found: C, 63.39; H, 4.26; Sn, 18.98%

2,3,4,5-Tetraphenylstannole bis-diethyldithiocarbamate

Into a saturated solution of sodium diethyldithiocarbamate trihydrate (1.8 g, 7.99 mmol) in benzene (a suspected carcinogen) was added 1,1-dibromotetraphenylstannole (2.53 g, 3.98 mmol) very slowly under nitrogen from a dropping funnel, and the reaction mixture allowed to reflux for 4 hrs and stirred 1 hr more until the solution became a yellowish color and the sodium bromide was precipitated. The solution was then filtered and the filtrate was concentrated in vacuo. The residue was left overnight under nitrogen to give yellow crystals of prismatic shape. The solution was filtered and washed with benzene several times to obtain the stannole bis-diethyldithiocarbamate (1.2 g, 1.55 mmol) (m.p. 145.5°-146°C) in 19.4% in yield.

The infrared spectrum contained bands at 3000(w), 1505(m), 1488(s), 1432(m,d), 1357(m), 1273(s), 1210(s), 1145(m), 995(m,b), 740(s,d), 702(s), 690(m,sh), 575(m,d), 552(m), 530(m), 445(m), 372(m,sh) and 255(m) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. of 1.14 ± 0.06 and Q.S. of 2.86 ± 0.12 mm/s. The nmr spectrum in CDCl_3 contained a triplet resonance at 9.27 and quartet resonance at 7.82 in addition to the phenyl group proton multiplet. The proton integration ratio was found to be 1:1.45:2.75 = $\text{CH}_2:\text{CH}_3:\text{Ph}$ vs. the calculated ratio of 1:1.5:2.5. Anal. Calcd. for $\text{C}_{38}\text{H}_{40}\text{N}_2\text{S}_4\text{Sn}$: C, 59.05; H, 5.22; Sn, 15.37%. Found: C, 56.44; H, 4.99; Sn, 13.02%.

1,1-Bis(dimethylamino)-2,3,4,5-tetraphenylstannole

Dimethylamino lithium was prepared by a modification of the procedure used by Foley and Zeldin.¹² A 100 mL three-necked flask was cooled to -78° in a Dry Ice/acetone bath and freshly distilled diethyl ether (25 mL) was added and stirred under nitrogen for 15 minutes. To this was added dimethylamine (0.45 mL, 6.86 mmol) followed by *n*-butyllithium (1.94 mL of 3.53 M in hexane, 6.86 mmol) to form a white precipitate. The mixture was stirred at -78°C for 30 minutes, and diiodostannole (2.5 g, 3.43 mmol) was added at -78°C via a solid addition tube, whereupon the milky white solution turned a yellow color and was stirred while warming to room temperature for eight hours. The ether was then removed in vacuo, toluene (25 mL) added, and the resulting solution filtered under nitrogen to give a white solid that was found to contain lithium by a flame test. The addition of hexane (20 mL) precipitated the product as a yellow colored, air-sensitive, solid (m.p. $158-169^{\circ}\text{C}$, 1.33 g) in 69% yield (based upon diiodostannole).

The Mössbauer spectrum contained a narrow doublet with I.S. 1.25 ± 0.03 and Q.S. 0.72 ± 0.06 mm/s. The infrared spectrum contained prominent bands at 3060(w), 3030(w), 1587(w), 1556(w), 1430(w), 1260(w), 1170(s), 1130(m), 1070(m), 1020(w), 959(m), 760(m), 725(s), 690(s) and 530(s) cm^{-1} . Anal. Calcd. for $\text{C}_{32}\text{H}_{32}\text{N}_2\text{Sn}$: C, 68.21; H, 5.68; Sn 21.14%. Found: C, 66.92; H, 4.97; Sn, 20.94%.

1,Bromo-1-N,N-bis(trimethylsilyl)amino-2,3,4,5-tetraphenylstannole

Into lithio-hexamethyldisilazane (3.55 g, 21.25 mmol) dissolved in tetrahydrofuran (250 mL), dibromotetraphenylstannole (5.4 g, 8.5 mmol) in the same solvent (20 mL) was added dropwise. Upon addition the solution turned a light gold color. Concentration of the solution for one hr at the water pump gave a white precipitate. Hexane was

added to the filtrate to give a light-tan colored solid (m.p. 178.0-178.5°) (1.5 g, 2.09 mmol) in 24.50% yield.

The infrared spectrum showed prominent bands at 3060(m), 1595(m), 1578(w), 1262(s), 1247(s,sh), 1072(w), 1030(w), 942(m), 912(s), 876(s), 840(s,d), 761(m), 733(s), 692(s), 629(w), 556(w), 362(w), 275(w) and 252(m) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. 1.18 ± 0.06 and Q.S. of 1.99 ± 0.12 mm/s. The nmr spectrum in THF contained a singlet resonance at 9.65 in addition to the phenyl group proton multiplet. The proton integration ratio was found to be 1.2:1 = phenyl:[N,N-bis(trimethylsilyl)]amino vs. the calculated ratio of 1.1:1. Anal. Calcd. for $\text{C}_{34}\text{H}_{38}\text{SnSi}_2\text{NBr}$: C, 57.06; H, 5.31%. Found: C, 55.28; H, 5.03%.

1,1-Bis(diphenylphosphino)-2,3,4,5-tetraphenylstannole

Into a three-necked, 100 mL flask was placed freshly distilled diethyl ether (50 mL) under a nitrogen atmosphere and cooled to -78°C in a Dry Ice/acetone bath. Diphenylphosphine (1.09 mL, 1.17 g, 6.30 mmol) was added and then n-butyllithium (1.91 mL of 3.3 M solution in hexane, 6.30 mmol) was added dropwise via syringe to turn the colorless solution a cloudy yellow color. The mixture was then stirred for one hour while warming to room temperature. The solution was then cooled again to -78°C and dibromostannole (2.00 g, 3.15 mmol) added via a solid addition tube, and the mixture was stirred at -78°C for one hour and allowed to warm to room temperature for three hours. Upon addition of the dibromostannole the solution passed from a yellow to gold to an orange color. The solution became yellow colored again as it was allowed to warm to room temperature, at which time a precipitation occurred. The ether was removed in vacuo, and toluene (50 mL) was added. A solid was filtered under

nitrogen and found to contain lithium by a flame test. The clear yellow colored filtrate was then concentrated to 30 mL and hexane (20 mL) was added to precipitate a yellow, air-sensitive, solid (m.p. 165-167°C, 1.52 g) in 57% yield (based upon dibromostannole).

The infrared spectrum contained bands at 3070(w), 3060(w), 1585(w), 1437(m), 1310(w), 1180(s), 1110(s), 1090(s), 1070(m), 1028(m), 998(m), 737(s), 715(s), 692(s), 552(m), 485(s), and 354(m,b) cm^{-1} .

The Mössbauer spectrum contained a narrow doublet with I.S. 1.51 ± 0.03 and Q.S. 0.83 ± 0.06 mm/s. Anal. Calcd. for $\text{C}_{52}\text{H}_{40}\text{P}_2\text{Sn}$: C, 73.85; H, 4.73; Sn, 14.08%. Found: C, 72.49; H, 4.81; Sn, 13.62%.

Adducts of 1,1-dibromo-2,3,4,5-tetraphenylstannole. With Pyridine:

1,1-Dibromo-2,3,4,5-tetraphenylstannole (2.00 g, 3.14 mmol) was dissolved in pyridine (25 mL, 0.31 mol) to give a clear yellow solution (no evolution of heat was noticed), which upon heating and refluxing for 10 min turned pale golden yellow. Excess pyridine was removed in vacuo. Golden yellow colored crystals (0.80 g, 1.01 mmol; 64.3% yield), which were obtained by addition of benzene (a suspected carcinogen), gave no sharp melting point; upon heating, these gradually darkened at 161.5°C, and liquified at 166.5-167.0°C.

The infrared spectrum showed bands at 3060(m), 3040(m), 1589(m), 1579(m), 1464(s,b), 1439(s), 1376(m), 1213(m), 1143(m), 1065(m), 1025(m), 998(m), 912(m), 800(m), 725(s), 695(s), 545(m,b), 443(m), 306(m), 282(m,b), and 230(m) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. 1.05 ± 0.06 and Q.S. 2.36 ± 0.12 mm/s. Anal. Calcd. for $\text{C}_{38}\text{H}_{30}\text{SnBr}_2\text{N}_2$: C, 57.54; H, 3.81; Sn, 14.96; N, 3.53; mol. wt., 793.17. Found: C, 59.31; H, 4.16; Sn, 19.12; N, 2.83%; mol. wt., 794.

With 2,2'-Bipyridine:

1,1-Dibromo-2,3,4,5-tetraphenylstannole (0.50 g, 0.79 mmol) was dissolved in benzene (10 mL) (a suspected carcinogen), and a solution of 2,2'-bipyridine (0.12 g, 0.79 mmol) in anhydrous ethyl ether (5 mL) was added with no apparent evolution of heat. The reaction mixture was allowed to stand at room temperature for 30 min to precipitate a fine white powder. As the solvent was removed the solution became a greenish-yellow color and a tan colored solid (0.45 g, 0.56 mmol, 71.4% yield) remained (m.p. 158.5-159.0°C with decomposition).

The infrared spectrum contained bands at 3060(m), 3040(m), 1679(m), 1449(s), 1377(s), 1285(m), 1150(m), 1065(m), 1018(m), 800(m), 755(s), 723(s), 688(s), 615(m), 552(s), 442(m), 306(s), 287(w), 276(w), 235(sh) and 228(m) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. 1.09 ± 0.06 and Q.S. 2.62 ± 0.12 mm/s. Anal. Calcd. for $\text{C}_{38}\text{H}_{28}\text{SnBr}_2\text{N}_2$: C, 57.69; H, 3.57; Sn, 15.00; N, 3.54; mol. wt., 791.15. Found: C, 60.36; H, 4.05; Sn, 15.55; N, 3.37%; mol. wt., 611.

With 1,10-Phenanthroline:

1,1-Dibromo-2,3,4,5-tetraphenylstannole (0.50 g, 0.79 mmol) was dissolved in benzene (10 mL) (a suspected carcinogen). A solution of 1,10-phenanthroline· H_2O (0.16 g, 0.79 mmol) in ethyl ether (20 mL) was combined to form a cloudy white colored slurry which was allowed to stand at room temperature for 30 min to precipitate to a fine white powder. The solvents were removed in vacuo to induce further precipitation of product complex (0.20 g, 0.24 mmoles, 30.5% yield) which melted sharply at 205.0°C,

The infrared spectrum contained bands at 3062(m), 3040(m), 1459(s,b), 1429(s), 1377(m), 854(m), 841(m), 727(s), 695(s), 556(m), 447(m), 306(m), 288(m), 263(s), 232(w), 223(m) and 180(w,b) cm^{-1} .

The Mössbauer spectrum was a doublet with I.S. 1.05 ± 0.06 and Q.S. 2.53 ± 0.12 mm/s. Anal. Calcd. for $C_{40}H_{28}SnBr_2N_2$: C, 58.94; H, 3.46; Sn, 14.56; N, 3.44. Found: C, 61.47; H, 4.02; Sn, 15.43; N, 3.55%.

With 2,2',2''-Terpyridine:

1,1-Dibromo-2,3,4,5-tetraphenylstannole (2.00 g, 3.15 mmol) was dissolved in benzene (8 mL) (a suspected carcinogen). A solution of 2,2',2''-terpyridine (0.40 g, 1.72 mmol) in benzene (2 mL) was mixed with no apparent evolution of heat. The reaction mixture was allowed to reflux for one hr under nitrogen to give a greenish-yellow colored solution with a brownish-white colored precipitate. The solvent was removed in vacuo to give a greenish yellow colored solid which was treated with toluene, filtered and recrystallized from methylene chloride-hexane to give needle shaped white crystals (m.p. 169.5° - 170.0° with some decomposition) (0.86 g, 0.572 mmol 36.3% yield).

The infrared spectrum showed bands at 3060(m), 3040(m), 2720(w), 1595(m), 1572(m), 1465(s), 1440(s), 1429(s), 1265(m), 1168(w,d), 1105(m), 1020(m), 997(m), 800(m,b), 780(m), 730(s,d), 690(s), 574(m,d), 550(s), 520(m), 445(m), 265(m), 251(s) and 232(s) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. 1.48 ± 0.06 and Q.S. 2.58 ± 0.12 mm/s. Anal. Calcd. for $C_{71}H_{51}Sn_2N_3Br_4$: C, 56.73; H, 3.42; Sn, 15.79%. Found: C, 56.78; H, 3.01; Sn, 14.89%.

Adducts of 1,1-Diiodo-2,3,4,5-tetraphenylstannole. With pyridine:

1,1-Diiodo-2,3,4,5-tetraphenylstannole (3.5 g, 4.8 mmol) was dissolved in pyridine (30 mL, 0.37 mol), and the resulting golden-brown colored solution was then allowed to reflux for one hr. The solution gradually darkened as the reaction proceeded. The pyridine was then removed in vacuo to give a red-brown oil

which was then dissolved in benzene (a suspected carcinogen) and hexane. A tan colored solid precipitated (m.p. 158-160°C, 2.47 g) in 58% yield (based on diiodostannole).

The infrared spectrum contained prominent bands at 3050(w), 1592(m), 1575(s), 1480(w), 1440(m), 1430(m), 1218(s), 1140(m), 1070(s), 1010(s,b), 996(s), 913(s), 805(s), 722(s), 690(s), 534(m), 440(s) and 310(s) cm^{-1} .

The Mössbauer spectrum contained a doublet with I.S. 1.19 ± 0.03 and Q.S. 2.55 ± 0.06 mm/s. Anal. Calcd. for $\text{C}_{38}\text{H}_{30}\text{SnI}_2\text{N}_2$: C, 51.41; H, 3.38; Sn, 13.42; I, 28.65. Found: C, 51.08; H, 3.52; Sn, 12.96; I, 29.13%.

With 2,2'-Bipyridine:

Diiodostannole (1.0 g, 1.4 mmol) was dissolved in benzene (a suspected carcinogen) (15 mL) and a solution of 2,2'-bipyridine (0.21 g, 1.4 mmol) in anhydrous diethyl ether (10 mL) was added dropwise with no apparent evolution of heat. The mixture was stirred at room temperature under a nitrogen atmosphere for 30 min, the solvent removed in vacuo, and the resulting material dissolved in benzene (20 mL). When the solution was cooled to 0°C a white solid [m.p. 163-164°C(d), 0.69 g] was obtained in 56% yield (based on diiodostannole).

The infrared spectrum contained prominent bands at 3050(w), 1590(w), 1565(w), 1440(w), 1378(s), 1285(m), 1150(m), 1065(m), 1020(m), 990(w), 905(w), 780(m), 755(m), 723(s), 690(s), 534(m), and 435(w) cm^{-1} . The Mössbauer spectrum was a doublet with I.S. 1.21 ± 0.03 and Q.S. 2.49 ± 0.06 mm/s. Anal. Calcd. for $\text{C}_{38}\text{H}_{28}\text{SnI}_2\text{N}_2$: C, 51.53; H, 3.16; Sn, 13.45; I, 28.70. Found: C, 51.85; H, 3.37; Sn, 13.30; I, 28.46%.

With 1,10-Phenanthroline:

Diiodostannole (1.0 g, 1.4 mmol) was dissolved in benzene (a suspected carcinogen) (20 mL) and 1,1-phenanthroline·H₂O (0.25 g, 1.4 mmol) dissolved in anhydrous diethyl ether (15 mL) added. The mixture was stirred at room temperature under nitrogen for 30 min, the solvent removed in vacuo, benzene (30 mL) added, and the resulting solution was then filtered. A white solid precipitated when the solution was cooled to 0°C [m.p. 169-171°C(d), 1.01 g] in 79% yield (based on diiodostannole).

The Mössbauer spectrum contained a doublet with I.S. 1.14 ± 0.03 and Q.S. 2.61 ± 0.06 mm/s. The infrared spectrum contained prominent bands at 3047(w), 1595(m), 1570(w), 1445(w), 1431(w), 1258(w), 1065(m), 1020(m), 990(w), 780(w), 729(s), 688(s) and 555(w) cm⁻¹. Anal. Calcd. for C₄₀H₂₈SnI₂N₂: C, 52.81; H, 3.08; Sn, 13.09; I, 27.94; Found: C, 53.06; H, 3.62; Sn, 12.42; I, 28.37%.

With 2,2',2''-Terpyridine:

Diiodostannole (1.0 g, 1.4 mmol) was dissolved in benzene (a suspected carcinogen) (15 mL) and a solution of 2,2',2''-terpyridine (0.16 g, 0.69 mmol) in benzene (5 mL) mixed with no apparent evolution of heat. The mixture was then allowed to reflux under nitrogen for 30 min, the solvent removed in vacuo, methylene chloride added, and the resulting solution was filtered. Dry methyl alcohol was then added and the solution cooled in an ice bath. A white solid [m.p. 167-169°C(d), 0.76 g] was isolated in 32% yield.

The infrared spectrum contained bands at 3070(w), 1595(m), 1570(w), 1478(w), 1440(w), 1428(w), 1210(m), 1065(m), 1020(m), 910(w), 785(s), 755(m), 721(s), 690(s), and 558(w) cm⁻¹. The Mössbauer spectrum contained a doublet with I.S. 1.49 ± 0.02 and Q.S. 2.49 ± 0.03

mm/s. Anal. Calcd. for $C_{71}H_{51}Sn_2N_3I_4$: C, 50.38; H, 3.06; Sn, 14.07; I, 30.48%. Found: C, 51.37; H, 3.39; Sn, 13.96; I, 28.83%.

Adduct of 1-fluoro-1-iodo-2,3,4,5-tetraphenylstannole with 2,2',2"-terpyridine

1-Fluoro-1-iodostannole (1.00 g, 1.61 mmol) was dissolved in freshly distilled benzene (a suspected carcinogen) (10 mL), and a solution of 2,2',2"-terpyridine (0.40 g, 1.72 mmol) in benzene (2 mL) mixed with no apparent evolution of heat. The mixture was then allowed to reflux under nitrogen for one hr. The milky solution cleared and turned a light yellow color upon refluxing. The solution was allowed to cool to room temperature and the benzene removed in vacuo. The resulting light yellow colored solid was then dissolved in methylene chloride (15 mL) and the solution filtered to give a clear, yellow solution. Hexane (10 mL) was then added and the solution cooled in Dry Ice. A white solid [m.p. 179-182°C(d)] was isolated in 39% yield (based on fluoroiodostannole).

The infrared spectrum contained bands at 3050(w), 3025(w), 1590(w), 1568(w), 1540(w), 1485(w), 1445(w), 1430(m), 1140(m), 1108(s), 1072(m), 1022(s), 998(s), 872(s), 805(s), 781(s), 768(m), 737(s), 695(s), 653(s), 617(s), 568(s), 545(s), 520(s), and 443(s) cm^{-1} .

The Mössbauer spectrum contained a doublet with I.S. 1.20 ± 0.03 and Q.S. 2.94 ± 0.06 mm/s. Anal. Calcd. for $C_{71}H_{51}Sn_2F_2I_2N_3$: C, 57.76; H, 3.46; Sn, 16.14; I, 17.22. Found: C, 55.97; H, 3.52; Sn, 15.98; I, 18.04%.

1,2,3,4-Tetraphenyl-cis, cis-1,3-butadienylphenyltin dichloride

Diphenylacetylene (tolan) (5.35 g, 0.03 mmol) was stirred for four hrs in anhydrous diethyl ether (30 mL) under nitrogen with

lithium (0.35 g, 0.05 mmol) wire. A red colored solution formed after 10 min and a yellow colored solid precipitated. The slurry was added rapidly to a solution of phenyltin trichloride (4.52 g, 0.015 mmoles) in tetrahydrofuran (200 mL). An additional 100 mL of anhydrous diethyl ether was used to transfer the dilithio reagent. The mixture was stirred under nitrogen for two hrs at room temperature, and the ether was then removed in vacuo to leave a green oil which was then dissolved in methylene chloride (200 mL) and the resulting suspension filtered. After concentration to 25 mL, absolute ethanol (50 mL) was added, and the green colored solution cooled to -78°C in Dry Ice to give a white solid product (m.p. $156-158^{\circ}\text{C}$) in 12.0% yield based on tolan.

The Mössbauer spectrum of this compound contained a doublet with I.S. 1.15 ± 0.02 and Q.S. 1.70 ± 0.04 mm/s. The infrared spectrum contained prominent bands at 3065(w), 3050(w), 1595(w), 1432(m), 1060(m), 1020(m), 997(m), 915(m), 885(m), 764(w), 729(s), 695(s), 365(s), and $345(\text{m})\text{ cm}^{-1}$. The nmr spectrum in CDCl_3 contained a singlet resonance at 5.2 ppm (relative to TMS) in addition to the phenyl group proton multiplet. Anal. Calcd. for $\text{C}_{34}\text{H}_{26}\text{Cl}_2\text{Sn}$: C, 65.49; H, 4.17; Cl, 11.24; Sn, 19.10%. Found: C, 64.57; H, 3.52; Cl, 12.49; Sn, 18.64%.

Attempted preparation of 1,1-dichloro-2,3,4,5-tetraphenylstannole

Hexaphenylstannole (2.0 g, 3.18 mmol) was dissolved in carbon tetrachloride (200 mL) and the system flushed with nitrogen and cooled to -78°C in a Dry Ice/acetone bath. Chlorine gas was condensed on a Dry Ice cold finger and a small amount was allowed to drip into the solution. The yellow solution darkened with the addition of chlorine. The reaction was then stirred for two hrs while warming

to room temperature. The solvent was then removed in vacuo, and methylene chloride added to the residue and the solution was then filtered. Addition of absolute ethanol precipitated a white solid (m.p. 163-164°C, 1.30 g) in 96% yield (based on hexaphenylstannole). This material, however, contained no tin. Its melting point, elemental analysis and infrared spectrum agree with its formulation as 1,4-dichloro-1,2,3,4-tetraphenylbutadiene¹³. Anal. Calcd. for $C_{28}H_{20}Cl_2$: C, 78.87; H, 4.69; Cl, 16.44%. Found: C, 77.71; H, 4.95; Cl, 17.67%.

Another white solid isolated from this reaction (m.p. 39-41°C) contained tin, and gave a doublet Mössbauer spectrum with I.S. 1.32 ± 0.02 and Q.S. 2.79 ± 0.03 mm/s. From its melting point and Mössbauer spectrum this compound was identified as diphenyltin dichloride.

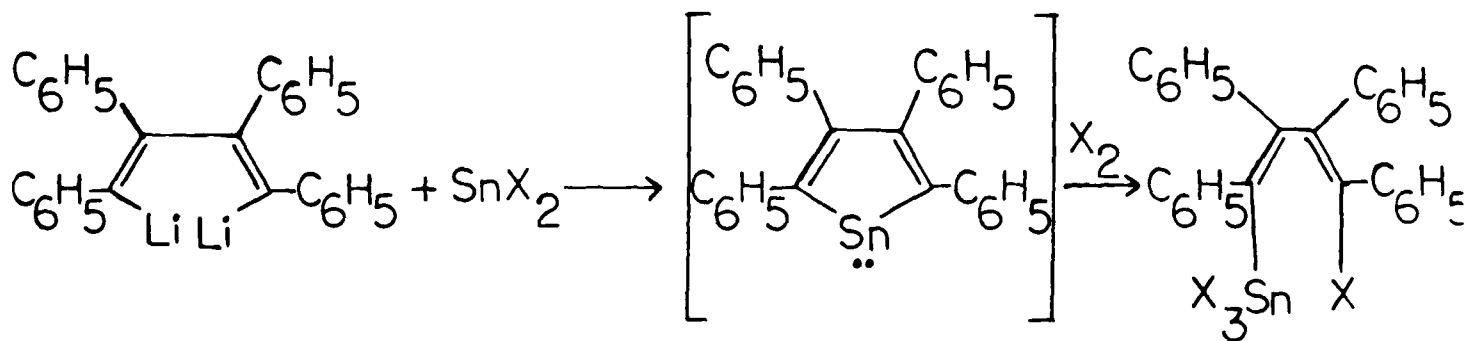
Reaction of Hexaphenylstannole and Acetic Acid

Hexaphenylstannole (4.0 g, 6.4 mmol) was dissolved in glacial acetic acid (50 mL, 0.87 mol), acetic anhydride (5 mL, 0.05 mol) was added and the solution allowed to reflux for 12 hrs under argon. The cloudy, intense yellow colored solution lightened and became clear on refluxing, and after 12 hrs of refluxing the solution was a clear, deep red color that lightened and precipitated a white solid when cooled. The solvent was removed in vacuo, methylene chloride added, and the resulting solution filtered. White needles were collected (m.p. 176-178°C, 1.40 g) after the addition of absolute ethanol (59% yield based on hexaphenylstannole). This material, however, contained no tin. The melting point, elemental analysis and infrared spectrum agree with the formulation of tetraphenylfuran. Anal. Calcd. for $C_{28}H_{20}O$: C, 90.32; H, 5.38. Found: C, 90.78; H, 6.43%. No pure tin-containing material could be isolated from this reaction.

Discussion

Like other diorganotin(IV) dihalides, the 1,1-dihalostannoles are easily handled covalent molecular solids, freely soluble in non-polar organic solvents, and convenient starting materials for synthesis.

Attempts to find other routes to the dihalostannanes, not requiring isolation of the hexaphenylstannole, failed. Using 1:1 molar ratios of the dilithio reagent with tin(IV) chloride, bromide and iodide give, in our hands, only the octaphenylspirobistannole. Neither did halogenation of the intermediate tin(II) stannole, or its tin(IV) metal-metal bonded oligomer, resulting from the action of the dilithio reagent on tin(II) chloride, yield the desired dihalostannoles. The green-colored oils from the first alkylation step solidified on drying in vacuo over long periods to give materials containing more than one tin(II) species with smaller amounts of tin(IV). Attempts to stabilize the tin(II) stannole by complexation with boron trifluoride by addition of the etherate also failed. The halogenation step resulted in the ring-opened product in each case:

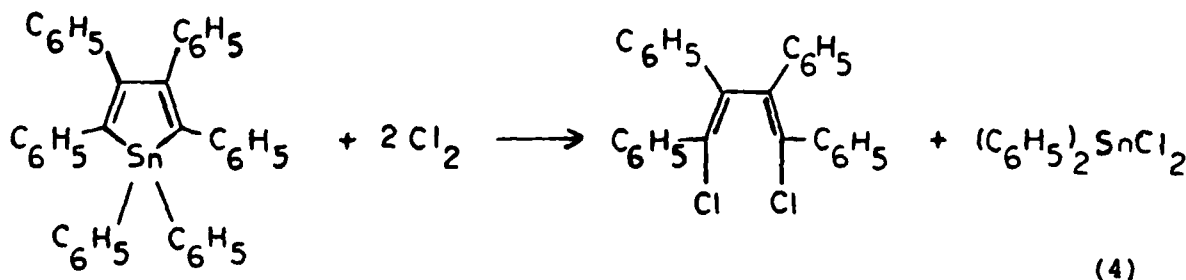


(3)

X = Br, I

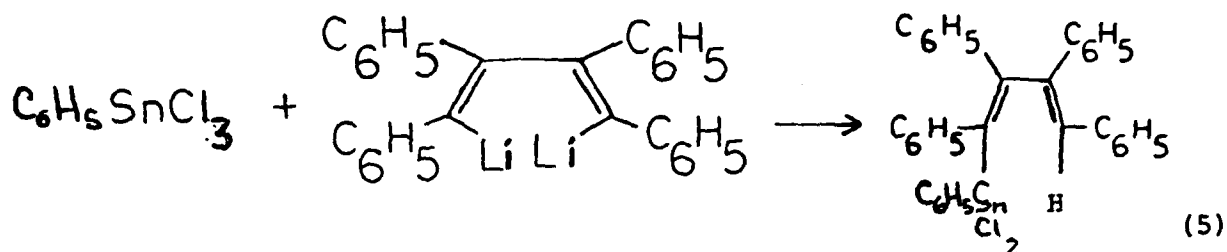
The product (4-halo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin trihalides which are formed in poor yields exhibit increase in relative intensities and shifts to higher energies in the far infrared spectra in agreement with previous findings.¹⁴ Thus, the $\nu_{\text{asym}}(\text{Sn-X})$ and $\nu_{\text{sym}}(\text{Sn-X})$ frequencies increase from 252 and 233 cm^{-1} for $\text{X}=\text{Br}$ and 184 and 180 cm^{-1} for $\text{X}=\text{I}$ in the dihalostannoles to 258 and 247 cm^{-1} for $\text{X}=\text{Br}$ and 210 and 203 cm^{-1} for $\text{X}=\text{I}$ in the open-chain trihalides. The Mössbauer Q.S. values are also diminished in comparison to the corresponding dihalostannoles as shown in Table I. The X-ray crystal structures of the related ring-opened compounds 4-chloro- and 4-bromo-1,2,3,4-tetraphenyl-1,3-butadienyldimethylphenyltin(IV)¹⁵ and 4-bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)dimethyltin bromide show that the latter adopts a cis-, cis-configuration to bring the tin and the 4-bromo atoms into contact for intramolecular coordination.¹⁶ Thus the transformation from the dihalostannane to the open-chain tin trihalide is probably accompanied by a change in solid state structure and coordination number at the tin atom.¹⁵⁻¹⁷

Gentle chlorination by elemental chlorine cleaves the tin-carbon bonds in the ring to form cis-,cis-1,4-dichloro-1,2,3,4-tetraphenylbuta-1,3-diene¹³ and diphenyltin dichloride:



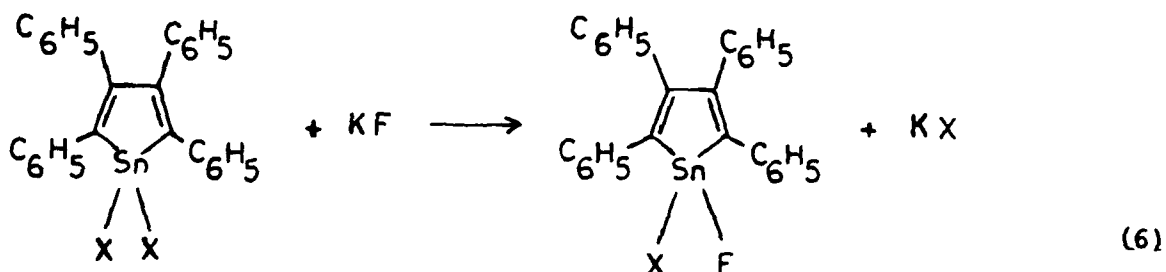
(4)

and an attempt to synthesize a monochloro derivative by the action of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene-1,3 on phenyltin trichloride gave only the ring-opened product:



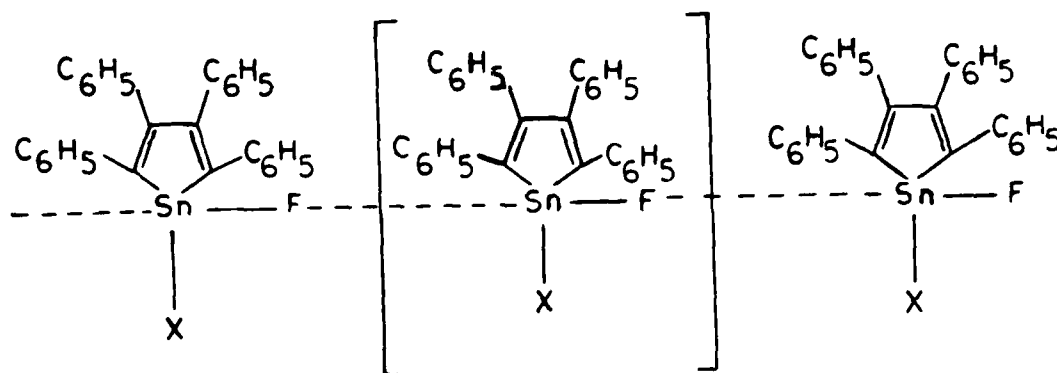
The 4-proton in the product gives rise to an nmr resonance at 5.2 ppm.

Attempts to convert the heavier dihalostannoles to the analogous dichloride with lead(II) chloride met with no success, but potassium fluoride in alcohol replaces one halogen of the dibromo- or diiodo-stannoles to the corresponding fluoride:



No halogen exchange took place with lead(II) or antimony(III) fluorides, nor could forcing conditions effect the fluorination of the remaining halogen by KF. The 1-bromo-1-fluoro-derivative retains a strong band at 228 cm^{-1} in the infrared spectrum which arises from the $\nu(\text{Sn-Br})$ mode, but adds a strong band at 570 cm^{-1} which can be assigned to the $\nu(\text{Sn-F})$ stretching mode. A second, broad absorption band at

357 cm^{-1} can be assigned to the $\nu(\text{Sn}\cdots\text{F})$ mode arising from the dative bridging interaction in the associated structure A:



A

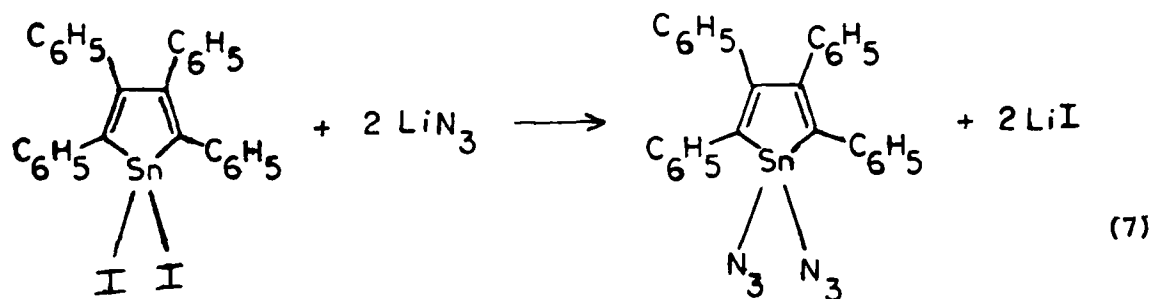
X=Br, I

The corresponding $\nu(\text{Sn}-\text{F})$ mode absorption bands in the 1-iodo-1-fluoro-derivative are found at 570 and 350 cm^{-1} , respectively.

Bridging fluorine is a structural feature of the trigonal bipyramidal trimethyltin(IV) fluoride¹⁸⁻¹⁹ as in tri-n-butyltin fluoride²⁰ where disorder in the crystals has prevented a completely satisfactory solution. It is clear, however, that infinite, non-linear, chain axes consisting of unsymmetrical $\text{F}-\text{Sn}\cdots\text{F}$ bridge bonds exists.²¹ Our 1-monofluoro-1-monohalo-derivatives are formally analogous to the diorganotin(IV) $(\text{CH}_3)_2\text{SnF}_2$, which forms trans-dimethyltin(IV) octahedra with four fluorine atoms at exactly equal distances from each of the tin atoms they bridge, but this structure requires opening the C-Sn-C angle to 180° which is impossible in our heterocycles. Additional bridging by bromine and iodine as seen in the weak (3.77 \AA) interactions in (4-bromo-1,2,3,4-tetraphenyl-cis-, cis-1,3-butadienyl)dimethyltin(IV) bromide¹⁵⁻¹⁶ discussed above, and in diethyltin(IV) dibromide and iodide,²² may also contribute to the cross-linking of the chains. We

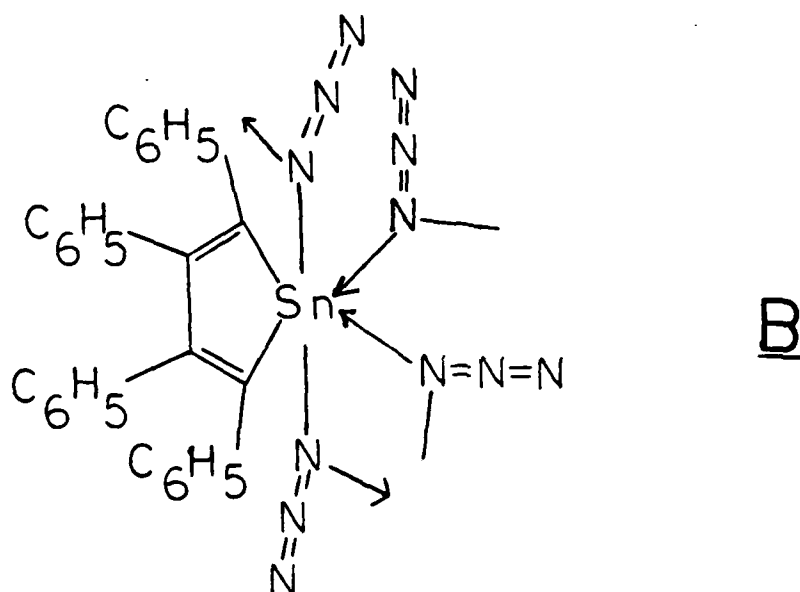
favor the predominantly fluorine-bridged trigonal bipyramidal structure depicted in A which could accommodate the stannole ring internal C-Sn-C angle requirements. From the variable temperature Mössbauer evidence, it would appear that the dibromostannole is completely molecular in its solid.¹ Unfortunately, the Mössbauer spectra of the simple compounds of the composition R_2SnXF where $X=Br, I$ are lacking.²³⁻²⁴ The formation of a stable structure such as A could be used to rationalize why the fluorination reaction does not proceed beyond monosubstitution. proceed beyond monosubstitution.

Disubstitution is effected, however, in derivatization by pseudohalides. Two moles of lithium azide are taken up by the diiodostannole:

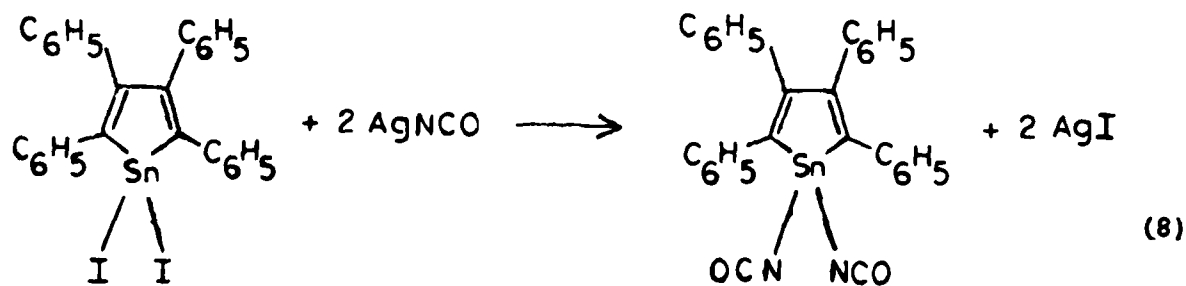


The infrared spectrum of this white solid product contains absorption bands at 2090 and 1275 cm^{-1} , which can be assigned to the $\nu_{\text{asym}}(\text{N}_3)$ and $\nu_{\text{sym}}(\text{N}_3)$ modes, and a sharp band at 690 cm^{-1} which is the azide bending mode, $\delta(\text{N}_3)$, respectively.²⁵ Absorption bands at 472 and 270 cm^{-1} can be assigned to the intra- and intermolecular $\nu(\text{Sn-N})$ modes, respectively.²⁶ The observation of the latter band suggests

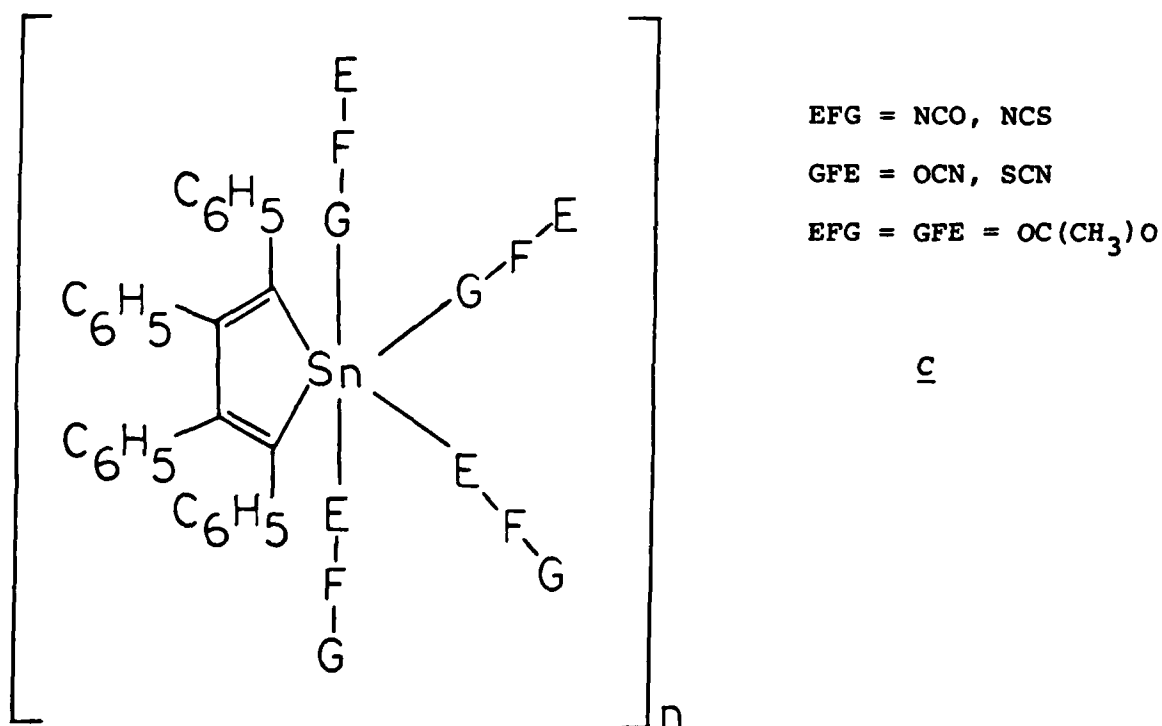
that the tin atoms are bridged by the azide groups in an unsymmetrical manner. In the analogous, simple fluoride and cyanide, $(\text{CH}_3)_2\text{SnX}_2$, where $\text{X} = \text{F}^{27}$ and CN^{28} trans-dimethyltin(IV) units are bridged by the halide or pseudohalide groups to form octahedra at tin. In our product, however, the tin-carbon bonds are confined to the interior angles of the stannole ring. The structure of trimethyltin(IV) azide²⁸⁻²⁹ shows that the bridging takes place through the α -nitrogen. The magnitudes of the Mossbauer Q.S. and ρ values²³ favor structure B in the solid:



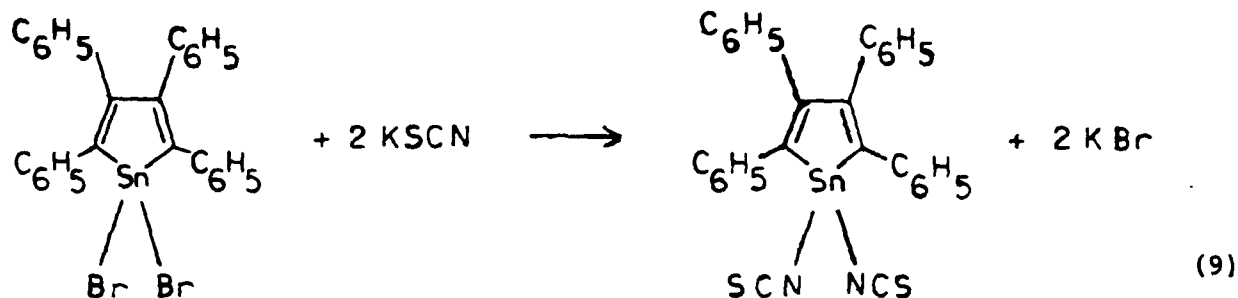
The dicyanato derivative, which is prepared by the action of two moles of silver(I) cyanate upon the diiodostannole:



is of interest since it can exist in either the cyanate, SnOCN , or isocyanate, SnNCO , form, as well as being either monomeric or associated in the solid state. Cyanato complexes exhibit very sharp $\nu(\text{C}=\text{O})$ absorptions below 1200 cm^{-1} , whereas the isocyanate derivatives show broad, more intense bands above 1200 cm^{-1} .³¹ The infrared spectrum of our product contains the strong NCO absorption band at 2210 and a medium band at 1350 cm^{-1} , both of which are absent in the starting material, specifying the isocyanato structure. Absorption bands at 610 and 385 cm^{-1} can be assigned to the $\delta(\text{NCO})$ and $\nu(\text{Sn-N})$ modes, respectively.³² The magnitudes of the Mössbauer Q.S. and ρ values are suggestive of a cis-octahedral geometry at the tin atom in the solid state,²³ but there are, unfortunately, no structural data available on diorganotin isocyanates.²¹ The SnNCO group in both $(\text{CH}_3)_3\text{SnOH} \cdot (\text{CH}_3)_3\text{SnNCO}$ ³³ and $(\text{C}_6\text{H}_5)_3\text{SnNCO}$ ³⁴ bridges the tin atoms by the γ -oxygen to form associated lattices, and we favor an analogous arrangement as in structure C.



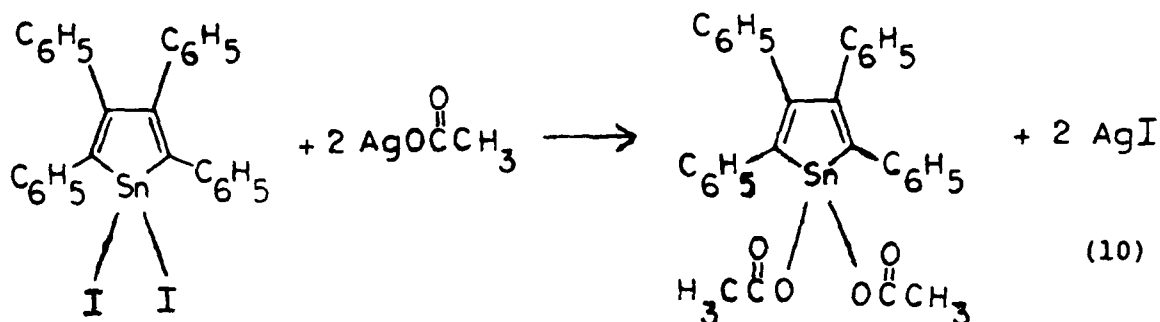
The structure of the diisothiocyanato derivatives have been much more extensively investigated.²¹ The diisothiocyanatostannole results from the action of two moles of KSCN on the dibromostannole:



Thiocyanate complexes exhibit a sharp $\nu(\text{N}=\text{C})$ stretching absorption above 2100 cm^{-1} , while the infrared spectra of their isothiocyanate isomers contain relatively broad, more intense bands at or below 2100 cm^{-1} . The $\nu(\text{C}=\text{S})$ absorption at 700 cm^{-1} is said to be indicative of attachment through sulfur, while absorption bands at $860\text{--}780 \text{ cm}^{-1}$ denote nitrogen bonding.³⁵ The infrared spectrum of our product contains a strong $\nu(\text{N}=\text{C})$ absorption at 2050 as well as the frequency at 770 cm^{-1} , both of which are absent in the starting materials. Solid diphenyltin(IV) isothiocyanate, which is presumed to be like its dimethyltin analogue,³⁶⁻³⁷ an associated solid, exhibits a strong band at 2100 cm^{-1} , while its monomeric molecular complexes with pyridine and *ortho*-phenanthroline exhibit bands in the $2040\text{--}2020 \text{ cm}^{-1}$ range.³⁸ We conclude that the stannole product is an isothiocyanate, bridged as in $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$ through the terminal sulfur atom to give an associated solid as in structure C, and unlike the dimethyltin(IV) derivative whose geometry is *trans*-octahedral.³⁶⁻³⁷ Osmometric molecular weight determinations suggest a pentamer or hexamer in solution, and the magnitude of the Mössbauer Q.S. and ρ values, support

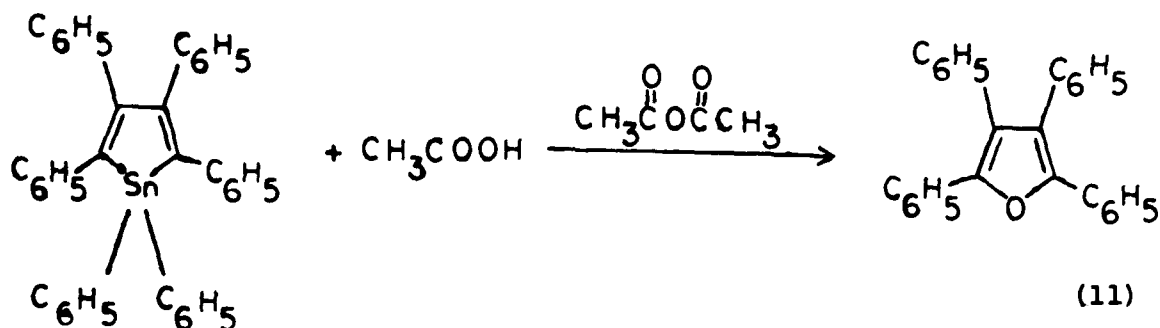
the suggestion that the tin atom is in a cis-octahedral environment in the solid.²³

Tin acetates also form associated solids.²¹ Silver (I) acetate converts the diiodostannole to its bis-acetato-derivative:

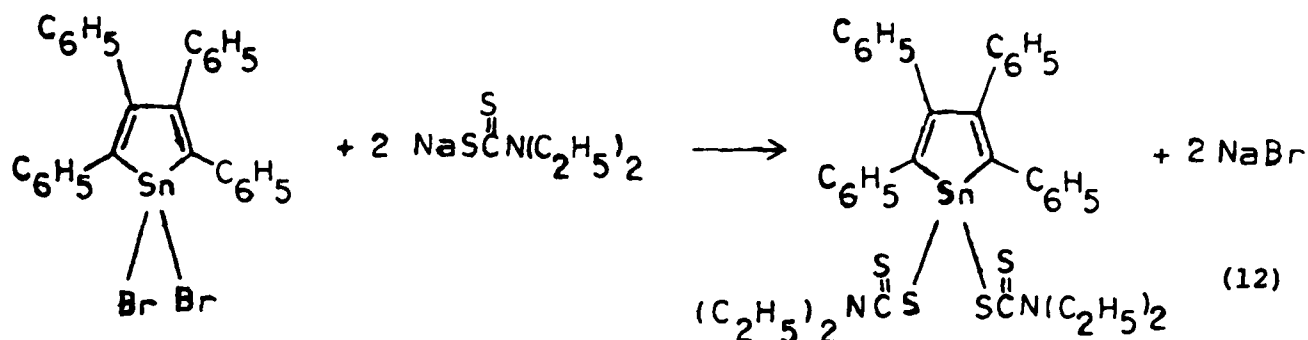


The infrared spectrum of the product stannole contains prominent absorption bands at 1567 and 1323 cm^{-1} which can be assigned to the $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$, respectively. Other bands arising from carboxylate group motions are the CO_2 scissor vibration which is a strong band at 760, the CO_2 out-of-plane deformation which is a medium band at 615 and the in-plane deformation which is a weak band at 490 cm^{-1} . A medium band observed at 295 cm^{-1} has been assigned to the $\nu(\text{Sn-O})$ mode.³⁹ Unfortunately, no structural data are available for diorganotin(IV) carboxylates, but all of the triorganotin(IV) derivatives excepting the tricyclohexyl⁴⁰ studied thus far have been shown to contain higher than four-coordinated tin atoms bound into associated lattices through bridging acetato groups.^{21,40} The magnitudes of the Mössbauer Q.S. and ρ values are in good agreement with the tin atoms in a cis-octahedral geometry²³ in an associated structure containing bridging acetoxy groups as in C.

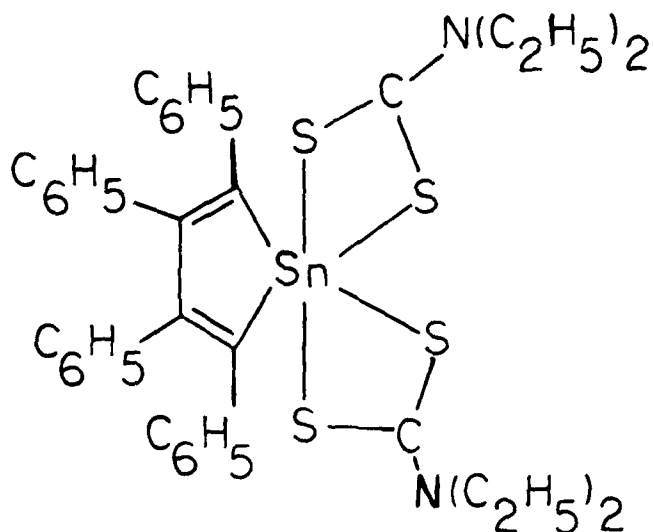
An attempt to reach the same product directly from hexaphenylstannole by reaction with glacial acetic acid and acetic anhydride resulted in cleavage of the ring to form tetraphenylfuran:



The bis-diethyldithiocarbamate is made from the dibromostannole and the sodium salt of the dithiocarbamate:

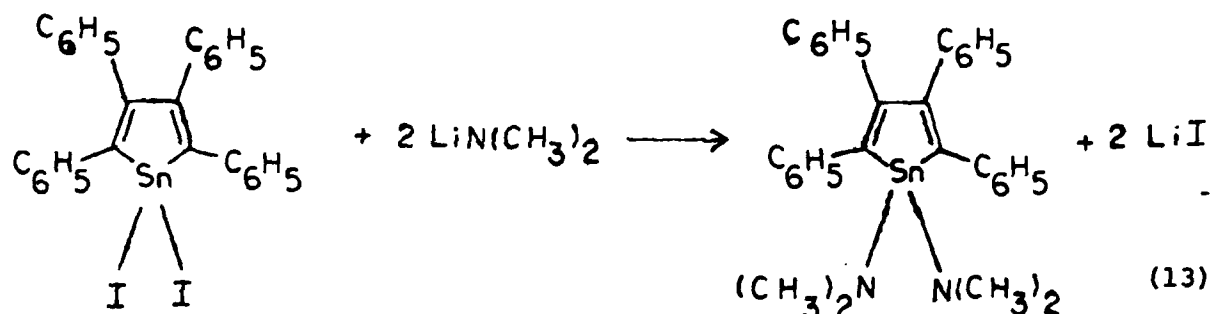


Similar solubility with the starting material makes clean separation difficult. Unlike the acetato or pseudohalide derivatives, the dithiocarbamate ligand has a known propensity to chelate organotin groups.²¹ The infrared spectrum of the product contains an absorption at 1505 cm^{-1} , the so-called "thioureide band," found in other chelated dithiocarbamate derivatives,⁴³ which arises from a $\nu(\text{C-N})$ mode with partial double-bond or polar character. Another prominent absorption at 995 cm^{-1} corroborates the suggested chelate structure which should exhibit a band in the 1000 cm^{-1} region, whereas the ester form should show twin absorptions at 1005 and 983 cm^{-1} .⁴⁴ The magnitudes of the Mössbauer Q.S. and ρ values are in agreement with the cis-diorganotin(IV) octahedral geometry²³ depicted in structure D.



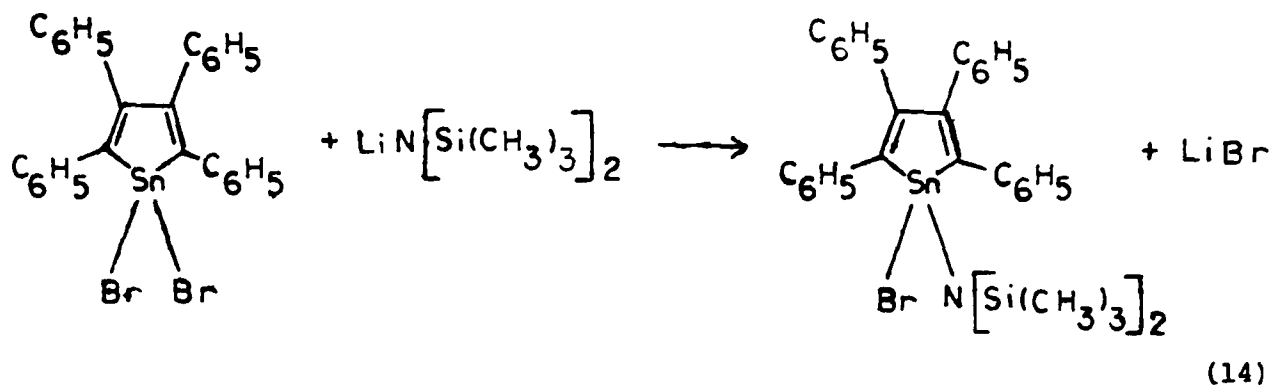
D

The preparation of two tin-nitrogen derivatives illustrate the steric limitations of the tetraphenylstannole system. Lithioamination by dimethylamine replaces both iodine substituents of the diiodostannole:



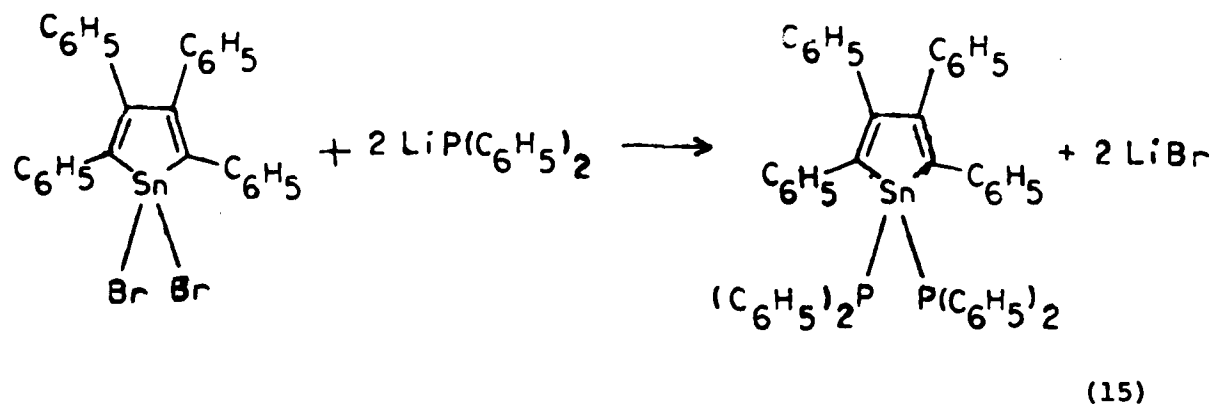
A band of medium intensity at 950 cm^{-1} in the infrared spectrum can be assigned to the $\nu_{\text{sym}}(\text{NC}_2)$ mode, and a strong band at 530 cm^{-1} to the $\nu(\text{Sn-N})$ mode.¹² The Mössbauer spectrum is a narrow doublet like that found for other tin-nitrogen derivatives,⁴⁵ and consistent with four-coordinated diorganotin(IV) systems.

The action of lithio-hexamethyldisilazane, on the other hand, results in the replacement of only one of the halogen atoms of the dibromostannole:



The infrared spectrum of the product contains the absorption band at 252 cm^{-1} arising from the remaining tin-bromine bond, and the large magnitude of the Mössbauer Q.S. rules out the disubstituted compound. The nmr integration ratio of trimethylsilyl to phenyl proton also establishes the singly substituted product. The steric bulk of the bis(trimethylsilyl)amino ligand is known to contribute to the kinetic stability of the metal-ligand bonds it forms.⁴⁶⁻⁴⁷

The corresponding phosphorus system, with its longer tin-phosphorus bond, can again accommodate disubstitution. Two moles of lithium diphenylphosphine react with the dibromostannole:



The infrared spectrum of the product contains bands at 1437 and 998 cm^{-1} which can be assigned to the $\nu_{\text{asym}}(\text{P-C}_6\text{H}_5)$ and $\nu_{\text{sym}}(\text{P-C}_6\text{H}_5)$ modes, respectively.⁴³ An additional band of medium intensity at 354 cm^{-1} can be assigned to the $\nu(\text{Sn-P})$ mode.⁴⁹ The Mössbauer spectrum is a narrow doublet like those observed for other organotin(IV) phosphines,⁵⁰ and consistent with a monomeric, molecular species in the solid state.

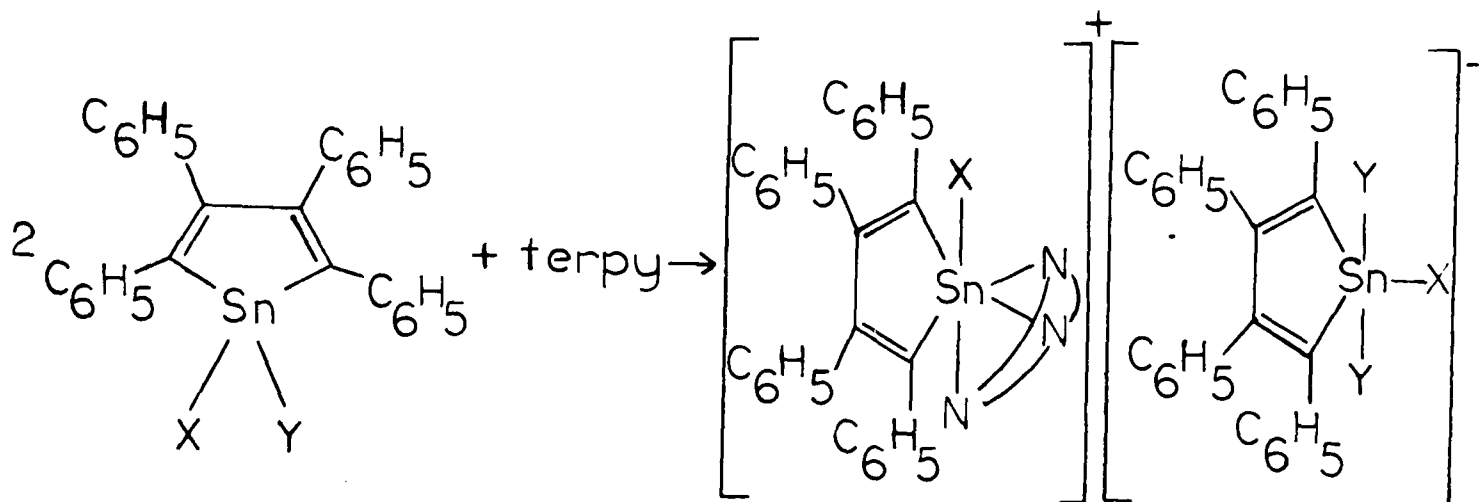
Adducts of the Dihalostannanes: Neutral Complexes

Diorganotin(IV) dihalides form neutral, cationic and anionic complexes, most commonly with nitrogenous bases, where the products have the formulation $\text{R}_2\text{SnX}_2 \cdot 2\text{B}$ with monodentate ligands, B. Structural data published to date²¹ for $(\text{CH}_3)_2\text{SnX}_2 \cdot 2\text{py}$ where $\text{X}=\text{Cl}$ ⁵¹ and Br ⁵² and for $(\text{C}_6\text{H}_5)_2\text{SnCl}_2 \cdot \text{bipy}$ ⁵³ show the expected trans-diorganotin(IV) octahedra. Complexes of the dihalostannoles, on the other hand, would be forced into another configuration because of the constraint of the ring, and for that reason are of especial interest. Information from Mössbauer spectroscopy can be utilized to assign the configuration of the organic groups about the tin atom,²³ which in these cases is fixed by the stannole ring, and of the ligand and halide groups from a combination of data from Mössbauer and vibrational spectroscopies in favorable cases.⁵⁴ However, in the product adducts the assignments of the tin-bromine and -iodine stretching frequencies are too insecure and the complexity of the vibrational spectra in the region of interest too great to risk drawing definite conclusions concerning which isomers are formed, especially since it is the absence of bands upon which these conclusions would be based. Pyridine, 2,2'-bipyridyl and ortho-phenanthroline were used to complex the dihalostannoles and form neutral adducts. Infrared data are listed for each adduct in the Experimental Section. The Mössbauer data are gathered in Table II.

Double Salts

The addition of 2,2',2''-terpyridyl (terpy) to dimethyltin dichloride precipitates an adduct which is the double salt $[(CH_3)_2SnCl \cdot terpy]^+ [(CH_3)_2SnCl_3]^-$, whose structure has been confirmed by an X-ray study which shows the trigonal bipyramidal anion and the bent trans-dimethyltin unit in the octahedral cation.⁵⁵ The Mössbauer spectra for the terpyridyl adducts of R_2SnCl_2 ($R = CH_3-$, $n-C_4H_9-$ and C_6H_5-) are surprisingly well-defined doublets in which both the five-coordinated tin atom in the cation and the six-coordinated tin atom in the anion give rise to I.S. and Q.S. values sufficiently similar to allow their respective resonances to fall within the envelope of the same doublet.^{56,57}

Terpyridyl adducts were prepared with dibromo-, diiodo- and fluoro-iodostannoles:



(16)

X = Y = Br, I

X = F, Y = I

By analogy with the products of terpyridyl adduct formation with the other diorganotin dihalides, and the similarities in the Mössbauer spectra,⁵⁶ we assign the double salt structure⁵⁵ shown in Eq. 16 to our products. An interesting choice arises in the product from the fluoro-iodostannole where two isomers are possible, depending upon whether the cation contains fluorine or not, but neither vibrational nor Mössbauer spectroscopy can definitively identify the isomer formed, and attempts to separate the double salt failed.

Acknowledgement

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Table I. Tin-119m Mössbauer Data for the Substituted Stannoies and Related Organotin(IV) Compounds at 77 K in mm s⁻¹

<u>Compound</u>	<u>IS</u>	<u>QS</u>	<u>ρ^a</u>
1,1-Dibromostannole ^b	1.57	2.35	1.50
(C ₂ H ₅) ₂ SnBr ₂ ^{c,d}	1.49-1.70	3.13-3.48	
1,1-Diodostannole ^b	1.61	2.32	1.44
(C ₂ H ₅) ₂ SnI ₂ ^{c,d}	1.31-1.78	2.97-3.24	
1-Fluoro-1-bromostannole ^e	1.17	2.82	
1-Fluoro-1-iodostannole ^f	1.22	2.74	
(4-Bromo-1,2,3,4-tetraphenyl-1,3-butadienyl) tin(IV) tribromide ^e	1.35	1.67	1.24
C ₂ H ₅ SnBr ₃ ^f	1.49	1.85	
4-Iodo-1,2,3,4-tetraphenyl-1,3-butadienyl) tin(IV) triiodide ^f	1.66	1.80	1.08
C ₂ H ₅ SnI ₃ ^d	1.64	1.77	
1,2,3,4-Tetraphenylbuta-1,3-dienyl-1-phenyltin(IV) dichloride ^f	1.15	1.70	1.48
<u>n</u> -C ₄ H ₉ (C ₆ H ₅)SnCl ₂ ^d	1.47	3.25	
1,1-Diazostannole ^f	1.18	2.44	2.07
(C ₂ H ₅) ₂ Sn(N ₃) ₂ ^d	1.23	2.94	
1,1-Diisothiocyanatostannole ^e	1.05	2.47	2.35
(C ₂ H ₃) ₂ Sn(NCS) ₂ ^d	1.52	4.28	
1,1-Diacetatostannole ^f	1.09	2.87	2.63
(<u>n</u> -C ₄ H ₉) ₂ Sn(O ₂ CCH ₃) ₂ ^{c,d}	1.34-1.45	3.45-3.56	
1,1-Bis(diethylthiocarbamate) stannole ^e	1.14	2.86	2.51
(<u>n</u> -C ₃ H ₇) ₂ Sn[S ₂ CN(C ₂ H ₅) ₂] ₂ ^d	1.54	2.82	
1,1-Bis(dimethylamino) stannole ^f	1.25	0.72	0.58

Table I (continued)

<u>Compound</u>	<u>IS</u>	<u>QS</u>	<u>ρ^a</u>
$(\text{CH}_3)_2\text{Sn}[\text{N}(\text{CH}_3)_2]_2^g$	1.20	1.35	
1-Bromo-1-N,N-bis(trimethylsilyl)aminostannole ^f	1.18	1.99	1.18
1,1-Bis(diphenylphosphino)stannole ^f	1.51	0.83	0.55
$(\text{CH}_3)_2\text{Sn}[\text{P}(\text{t-C}_4\text{H}_9)_2]_2^h$	1.47	1.38	

$\rho^a = \text{QS/IS}$.

^bRef. 1.

^cRef. 23.

^dRef. 24.

^eThis work; IS \pm 0.06; QS \pm 0.12 mm s⁻¹.

^fThis work; IS \pm 0.03; QS \pm 0.06 mm s⁻¹.

^gRef. 45.

^hRef. 59.

Table II. Tin-119m Mössbauer Data for the Adducts of the Dihalostannoles and Related Organotin(IV) Complexes at 77 K in mm s^{-1}

<u>Complex</u>	<u>IS</u>	<u>QS</u>	<u>ρ^a</u>
Dibromostannole·2py ^b	1.05	2.36	2.25
·2bipy ^b	1.09	2.62	2.40
·-phen ^b	1.05	2.53	2.41
·terpy ^b	1.48	2.58	1.74
(<u>n</u> -C ₄ H ₉) ₂ SnBr ₂ ·bipy ^c	1.62	3.95	
· <u>o</u> -phen ^c	1.63	3.94	
Diiodostannole·2py ^d	1.19	2.55	2.14
·bipy ^d	1.21	2.49	2.06
· <u>o</u> -phen ^d	1.14	2.61	2.29
·terpy ^d	1.49	2.49	1.67
(<u>n</u> -C ₄ H ₉) ₂ SnI ₂ ·bipy ^c	1.70	3.82	
· <u>o</u> -phen ^c	1.69	3.75	
1-Fluoro-1-iodostannole·terpy ^d	1.20	2.94	2.45

^a $\rho = \text{QS/IS}$.

^bThis work; IS±0.06; QS±0.12 mm s^{-1} .

^cRef. 23.

^dThis work; IS±0.03; QS±0.06 mm s^{-1} .

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