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Registry No. I, 75311-40-9; II, 78514-11-1; III, 78514-10-0; IV, 78514-09-7; V, 78549-86-7; VI, 78514-15-5; VII, 78514-08-6; VIII, 78514-07-5; 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene, 36091-97-1; $Mo(CO)_6$, 13939-06-5; $Fe(CO)_5$, 13463-40-6; $(C_6H_7)Mn(CO)_3$, 12108-13-3; $(C_7H_8)Mo(CO)_4$, 12146-37-1; $Co_2(CO)_8$, 10210-68-1.

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Synthesis of Tetraphenylstannacyclopentadienes (Stannoles). 2. Derivatives and Adducts of 1,1-Dihalo-2,3,4,5-tetraphenylstannoles[1]

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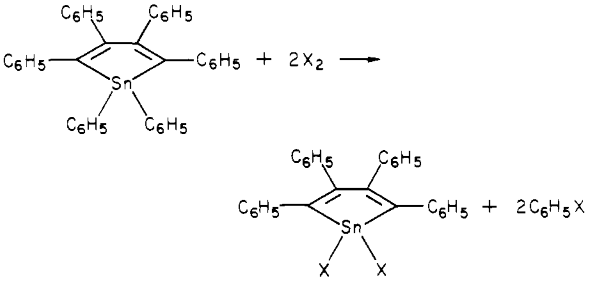
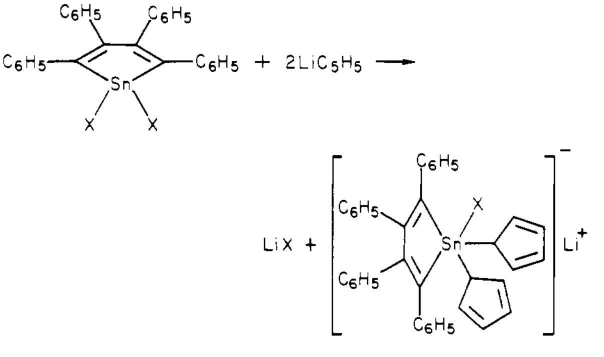
1,1-Dibromo- and 1,1-diiodo-2,3,4,5-tetraphenyl-1-stannacyclopentadiene, dihalotetraphenylstannoles $[XYSnC_4(C_6H_5)_4]$, can be derivatized to form a series of disubstituted products in which X = Y = N_3, *iso*-NCO, *iso*-SCN, $OC(O)CH_3$, $SC(S)N(C_2H_5)_2$, $N(CH_3)_2$, and $P(C_6H_5)_2$. Fluorination by KF in acetone results in the X = F, Y = Br, or Y = I product only, and lithioamination by $LiN[Si(CH_3)_3]_2$ yields the X = $N[Si(CH_3)_3]_2$, Y = Br product only. Attempted synthesis of the dihalostannoles 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-tetraphenyl-1,3-butadiene and diphenyltin(IV) dichloride, while the action of a glacial acetic acid–acetic anhydride mixture yields tetraphenylfuran and diphenyltin(IV) diacetate. The dihalostannoles form neutral adducts with pyridine, 2,2′-bipyridyl, and 1,10-phenanthroline and the double salt $[XSnC_4(C_6H_5)_4{\cdot}terpy]^+[X_2YSnC_4(C_6H_5)_4]^-$ from 2,2′,2″-terpyridine where X = Y = Br, I = F, and Y = I. The structures of the substituted stannoles and the adducts of the dihalostannoles are discussed on the basis of tin-119m Mössbauer and infrared spectroscopic evidence.

In part 1 of this series we described the synthesis of the 1,1-dihalostannoles by phenyltin bond cleavage of hexaphenylstannole[2–4] by the action of elemental bromine or iodine under controlled conditions[1] (eq 1).



(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 $R_2SnX_2{\cdot}2L$ 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-bis(η^1-cyclopentadienyl)-1-halo-2,3,4,5-tetraphenylstannole salt (eq 2), 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 1 of this series,[1] is a result of the simultaneous influences.[8]



(2)

In this paper we report the syntheses 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

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(1) For part 1 of this series see: Gustavson, W. A.; Principe, L. M.; Rhee, W.-Z. Min; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 4126.

(2) Leavitt, F. C.; Manuel, T. A.; Johnson, F. *J. Am. Chem. Soc.* **1959**, *81*, 3163.

(3) Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L. U.; Lehman, S. *J. Am. Chem. Soc.* **1960**, *82*, 5099.

(4) Zavistoski, J. G.; Zuckerman, J. J. *J. Org. Chem.* **1969**, *34*, 4197.

(5) Neumann, W. P. "The Organic Chemistry of Tin"; Wiley: New York, 1970.

(6) Poller, R. C. "The Chemistry of Organotin Compounds"; Logos Press: London, 1970.

(7) Sawyer, A. K. "Organotin Compounds"; Marcel Dekker: New York, 1972; Vol. 1–3.

(8) Rhee, W. Z. M.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 2291.

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Table I. Tin-119m Mössbauer Data (mm s^{-1}) for the Substituted Stannoles and Related Organotin(IV) Compounds at 77 K

compd	IS	QS	ρ^a
1,1-dibromostannole[b]	1.57	2.35	1.50
$(C_2H_5)_2SnBr_2$[c,d]	1.49-1.70	3.13-3.48	
1,1-diiodostannole[b]	1.61	2.32	1.44
$(C_2H_5)_2SnI_2$[c,d]	1.31-1.78	2.97-3.24	
1-fluoro-1-bromostannole[e]	1.17	2.82	2.41
1-fluoro-1-iodostannole[f]	1.22	2.74	2.25
(4-bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin(IV) tribromide[e]	1.35	1.67	1.24
$C_2H_5SnBr_3$[f]	1.49	1.85	1.24
(4-iodo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin(IV) triiodide[f]	1.66	1.80	1.08
$C_2H_5SnI_3$[d]	1.64	1.77	1.08
(1,2,3,4-tetraphenylbuta-1,3-dienyl)-phenyltin(IV) dichloride	1.15	1.70	1.48
$n\text{-}C_4H_9(C_6H_5)SnCl_2$[d]	1.47	3.25	2.21
1,1-diazidostannole[f]	1.18	2.44	2.07
$(C_2H_5)_2Sn(N_3)_2$[d]	1.23	2.94	2.39
1,1-bis(isothiocyanato)stannole[e]	1.05	2.47	2.35
$(C_2H_3)_2Sn(NCS)_2$[d]	1.52	4.28	2.82
1,1-bis(acetato)stannole[f]	1.09	2.87	2.63
$(n\text{-}C_4H_9)_2Sn(O_2CCH_3)_2$[c,d]	1.34-1.45	3.45-3.56	
1,1-bis(diethyldithiocarbamato)-stannole[e]	1.14	2.86	2.51
$(n\text{-}C_3H_7)_2Sn[S_2CN(C_2H_5)_2]_2$[d]	1.54	2.82	1.83
1,1-bis(dimethylamino)stannole[f]	1.25	0.72	0.58
$(CH_3)_2Sn[N(CH_3)_2]_2$[g]	1.20	1.35	1.13
1-bromo-1-[*N*,*N*-bis(trimethylsilyl)-amino]stannole[f]	1.18	1.99	1.18
1,1-bis(diphenylphosphino)stannole[f]	1.51	0.83	0.55
$(CH_3)_2Sn[P(t\text{-}C_4H_9)_2]_2$[h]	1.47	1.38	0.94

[a] ρ = QS/IS. [b] Reference 1. [c] Reference 23. [d] Reference 24. [e] This work: IS ± 0.06; QS ± 0.12 mm s^{-1}. [f] This work: IS ± 0.03; QS ± 0.06 mm s^{-1}. [g] Reference 45. [h] Reference 59.

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 (**caution**: 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 internal standard, and field width was calibrated with a solution of tetramethylsilane–benzene in carbon tetrachloride. Infrared spectra were recorded in the 4000–200 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 (400–33 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 $Ca^{119m}SnO_3$ (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, nonlinear, 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.

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

complex	IS	QS	ρ^a
dibromostannole·2py[b]	1.05	2.36	2.25
dibromostannole·2bpy[b]	1.09	2.62	2.40
dibromstannole·*o*-phen[b]	1.05	2.53	2.41
dibromostannole·terpy[b]	1.48	2.58	1.74
$(n\text{-}C_4H_9)_2SnBr_2$·bpy[c]	1.62	3.95	2.44
$(n\text{-}C_4H_9)_2SnBr_2$·*o*-phen[c]	1.63	3.94	2.42
diiodostannole·2py[d]	1.19	2.55	2.14
diiodostannole·bpy[d]	1.21	2.49	2.06
diiodostannole·*o*-phen[d]	1.14	2.61	2.29
diiodostannole·terpy[d]	1.49	2.49	1.67
$(n\text{-}C_4H_9)_2SnI_2$·bpy[c]	1.70	3.82	2.25
$(n\text{-}C_4H_9)_2SnI_2$·*o*-phen[c]	1.69	3.75	2.22
1-fluoro-1-iodostannole·terpy[d]	1.20	2.94	2.45

[a] ρ = QS/IS. [b] This work: IS ± 0.06; QS ± 0.12 mm s^{-1}. [c] Reference 23. [d] This work: IS ± 0.03; QS ± 0.06 mm s^{-1}.

(4-Bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin Tribromide. To 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (67.42 mmol) in ethyl ether (150 mL) was added dropwise at 0 °C tin(II) chloride (6.4 g, 34.04 mmol) in ethyl ether (150 mL). The yellowish brown solution was stirred for 2 h, and bromine (5.1 g, 63.75 mmol) in carbon tetrachloride was added slowly at −50 to −40 °C. 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 (mp 162.5°–163.0 °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, br), 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 an IS (isomer shift) of 1.35 ± 0.06 and QS (quadrupole splitting) of 1.67 ± 0.12 mm/s. Anal. Calcd for $C_{28}H_{20}SnBr_4$: Sn, 14.93. Found: Sn, 13.60. Molecular weight for $C_{28}H_{20}SnBr_4$: calcd, 794.8; found, 786.

(4-Iodo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin Triiodide. To 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (33.71 mmol) in ethyl ether (150 mL) was added dropwise at 0 °C tin(II) chloride (3.20 g, 17.02 mmol) in ethyl ether (80 mL). After the yellowish brown solution stirred for 2 h, iodine (4.0 g, 15.76 mmol) dissolved in ethyl ether (100 mL) was added slowly at 0 °C. The stirring was continued for 1 h, 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 (mp 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 an IS of 1.66 ± 0.06 and QS of 1.80 ± 0.12 mm/s. Anal. Calcd for $C_{28}H_{20}SnI_4$: Sn, 12.08. Found: Sn, 11.95. Molecular weight for $C_{28}H_{20}SnI_4$: calcd, 982.84; found, 995.

(1,2,3,4-Tetraphenyl-1,3-butadienyl)phenyltin Dichloride. Diphenylacetylene (5.35 g, 0.03 mol) was stirred for 4 h in anhydrous diethyl ether (30 mL) under nitrogen with lithium (0.35 g, 0.05 mol) wire. A red solution formed after 10 min 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 2 h at room temperature. The ether layers were then removed in vacuo to leave a green oil. The oil 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 precipitation achieved by cooling the green solution to −78 °C in dry ice.

The white solid product (mp 156–158 °C) was identified as (1,2,3,4-tetraphenyl-1,3-butadienyl)phenyltin dichloride. The Mössbauer spectrum of this compound contained a doublet with an IS of 1.15 ± 0.03 and QS of 1.70 ± 0.6 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 (m) cm^{-1}. The NMR spectrum in $CDCl_3$ contained a singlet resonance at 5.2 ppm (relative to Me_4Si) in addition

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[9] Debye, N. W. G.; Fenton, D. E.; Ulrich, S. E.; Zuckerman, J. J. *J. Organomet. Chem.* **1971**, *28*, 339.

to the phenyl group proton multiplet. Anal. Calcd for $C_{34}H_{26}Cl_2Sn$: 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-bromotetraphenylstannole. To dibromostannole[1,5] (4.0 g, 6.30 mmol) in tetrahydrofuran (50 mL) was added dropwise at room temperature potassium fluoride (0.73 g, 12.6 mmol) in ethanol (10 mL). After 45 min of refluxing, a milky white precipitate was filtered, and the filtrate was concentrated to give a white precipitate (mp 189–190 °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, br), 1158 (w), 1072 (s, sh), 1030 (m), 998 (w), 947 (m), 915 (m), 788 (m), 761 (s), 735 (vs), 700 (vs), 609 (m, d), 550 (s), 522 (s), 448 (m, d), 357 (w), 325 (w), 280 (s), and 228 (s) cm^{-1}. The Mössbauer spectrum was a doublet with an IS of 1.17 ± 0.06 and QS 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. Diiodostannole[1] (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 h, with continuous stirring to give a milky white solution which when filtered gave a clear, light yellow 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 fluoroiodostannole (mp 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, br), 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 an IS of 1.22 ± 0.03 and QS 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, 18.82.

Octaphenyl-1,1′-spirobistannole.[2-4] To 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (89.53 mmol) in ethyl ether (150 mL) was added dropwise at 0 °C tin(IV) chloride (12.50 g, 45.65 mmol). Stirring was continued overnight and the solvent removed in vacuo. The spiro compound was obtained by recrystallization from methanol–methylene chloride (mp 275 °C; lit.[2-4] mp 270–280 °C) in 25.4% yield based on tin(IV) chloride. The infrared spectrum is consistent with this formulation.[3]

1,1-Diazido-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 h 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 1 h after the addition was completed. The solvent was then removed in vacuo, toluene (50 mL) was added, and the solution was filtered. The addition of hexane precipitated a white solid (mp 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 an IS of 1.18 ± 0.03 and QS of 2.44 ± 0.06 mm/s. Anal. Calcd for $C_{28}H_{20}N_6Sn$: C, 60.11; H, 3.58; Sn, 21.29. Found: C, 58.98; H, 3.92; Sn, 20.64.

1,1-Bis(isocyanato)-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 1 h and filtered and washed with water, methanol, and ether. The product was dried for 12 h in vacuo and stored in the dark until needed.

Diiodostannole (5.0 g, 6.86 mmol) in mixed absolute ethanol and benzene (3:2) (100 mL) was allowed to reflux with silver(I) cyanate (2.06 g, 13.72 mmol) under nitrogen for 1 h and then stirred at room temperature for 1 h 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 bis(isocyanato)stannole precipitated from solution with the addition of hexane and cooling in dry ice as a white solid (mp 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 (w), 728 (s), 693 (s), 610 (w), 385 (m), and 265 (w) cm^{-1}. The Mössbauer spectrum contained a doublet with an IS of 1.05 ± 0.03 and QS of 2.47 ± 0.06 mm/s. Anal. Calcd for $C_{30}C_{20}N_2O_2Sn$: 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-Bis(isothiocyanato)-2,3,4,5-tetraphenylstannole. 1,1-Dibromo-2,3,4,5-tetraphenylstannole (5.2 g, 8.189 mmol) in mixed ethanol and benzene (100 mL; 3:2) was allowed to reflux with potassium thiocyanate (1.6 g, 16.46 mmol) in ethanol (20 mL) for 30 min and then stirred at room temperature for 1 h 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 (mp 152.5–153.0 °C) in 12.3% yield.

The infrared spectrum contained bands at 3075 (w, br), 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, br), and 283 (w, br) cm^{-1}. The Mössbauer spectrum was a doublet with an IS of 1.14 ± 0.06 and QS of 2.81 ± 0.12 mm/s. Anal. Calcd for $C_{30}H_{20}N_2S_2Sn$: Sn, 20.07. Found: Sn, 20.51%. Molecular weight for $C_{30}H_{20}N_2S_2Sn$: calcd, 591.30; found, 3330.

1,1-Bis(acetato)-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 2 h 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 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 (mp 182–183 °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 an IS of 1.09 ± 0.03 and QS of 2.87 ± 0.06 mm/s. The NMR spectrum in $CDCl_3$ contained a single resonance at 2.18 ppm, relative to Me_4Si, in addition to the phenyl group multiplet. The proton integration ratio was found to be 1:3.5 = CH_3:C_6H_5 (calculated ratio 1:3.3). Anal. Calcd for $C_{32}H_{26}O_4Sn$: C, 64.76; H, 4.38; Sn, 20.07. Found: C, 63.39; H, 4.26; Sn, 19.88.

2,3,4,5-Tetraphenylstannole Bis(diethyldithiocarbamate). To a saturated solution of sodium diethyldithiocarbamate trihydrate (1.8 g, 7.99 mmol) in benzene was added 1,1-dibromotetraphenylstannole (2.53 g, 3.98 mmol) very slowly under nitrogen from a dropping funnel, and the reaction mixture was allowed to reflux for 4 h and stirred 1 h more until the solution became yellow 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 prismatic crystals. The solution was filtered and washed with benzene several times to obtain the stannole bis(diethyldithiocarbamate) (1.2 g, 1.55 mmol) (mp 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 an IS of 1.14 ± 0.06 and QS 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 ppm in addition to the phenyl group proton multiplet. The proton integration ratio was found to be 1:1.45:2.75 = CH_2:CH_3:Ph vs. the calculated ratio of

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(10) Huisgen, R.; Ugi, I. *Chem. Ber.* **1957**, *90*, 2914.

(11) Hassner, A.; Heathcock, C. *J. Org. Chem.* **1965**, *30*, 1748.

1:1.5:2.5. Anal. Calcd for $C_{38}H_{40}N_2S_4Sn$: 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 flash was cooled to −78 °C in a dry ice–acetone bath, freshly distilled diethyl ether (25 mL) was added; the resulting solution was stirred under nitrogen for 15 min. 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 min, and diiodostannole (2.5 g, 3.43 mmol) was added at −78 °C via a solid addition tube, whereupon the milky white solution turned yellow and was stirred while warming to room temperature for 8 h. The ether was then removed in vacuo, toluene (25 mL) was added, and the resulting solution was 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, air-sensitive, solid (mp 158–169 °C; 1.33 g) in 69% yield (based upon diiodostannole).

The Mössbauer spectrum contained a narrow doublet with an IS of 1.25 ± 0.03 and QS of 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 $C_{32}H_{32}N_2Sn$: 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. To lithiohexamethyldisilazane (3.55 g, 21.25 mmol) dissolved in tetrahydrofuran (250 mL) was added dropwise dibromotetraphenylstannole (5.4 g, 8.5 mmol) in the same solvent (20 mL). Upon addition the solution turned light gold. Concentration of the solution for 1 h at the water pump gave a white precipitate. Hexane was added to the filtrate to give a light tan solid (mp 178.0–178.5 °C) (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 an IS of 1.18 ± 0.06 and QS of 1.99 ± 0.12 mm/s. The NMR spectrum in THF contained a singlet resonance at 9.65 ppm 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 $C_{34}H_{38}SnSi_2NBr$: C, 57.06; H, 5.31. Found: C, 55.28; H, 5.03.

1,1-Bis(diphenylphosphino)-2,3,4,5-tetraphenylstannole. In 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 aded dropwise via syringe to turn the colorless solution to a cloudy yellow. The mixture was then stirred for 1 h 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 solids addition tube, and the mixture was stirred at −78 °C for 1 h and allowed to warm to room temperature for 3 h. Upon addition of the dibromostannole, the solution passed from yellow to gold to orange. The solution became yellow again as it was allowed to warm to room temperature, at which time 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 filtrate was then concentrated to 30 mL, and hexane (20 mL) was added to precipitate a yellow, air-sensitive, solid (mp 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, br) cm^{-1}. The Mössbauer spectrum contained a narrow doublet with an IS of 1.51 ± 0.03 and QS of 0.83 ± 0.06 mm/s. Anal. Calcd for $C_{52}H_{40}P_2Sn$: 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. (a) 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 crystals (0.80 g, 1.01 mmol; 64.3% yield), which were obtained by addition of benzene, gave no sharp melting point; upon being heated, 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, br), 1439 (s), 1376 (m), 1213 (m), 1143 (m), 1065 (m), 1025 (m), 998 (m), 912 (m), 800 (m), 725 (s), 695 (s), 545 (m, br), 443 (m), 306 (m), 282 (m, br), and 230 (m) cm^{-1}. The Mössbauer spectrum was a doublet with an IS of 1.05 ± 0.6 and QS of 2.36 ± 0.12 mm/s. Anal. Calcd for $C_{38}H_{30}SnBr_2N_2$: C, 57.54; H, 3.81; Sn, 14.96; N, 3.53. Found: C, 59.31; H, 4.16; Sn, 19.12; N, 2.83. Molecular weight for $C_{38}H_{30}SnBr_2N_2$: calcd, 793.14; found, 794.

(b) 2,2′-Bipyridine. 1,1-Dibromo-2,3,4,5-tetraphenylstannole (0.50 g, 0.79 mmol) was dissolved in benzene (10 mL), 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 greenish yellow and a tan solid (0.45 g, 0.56 mmol; 71.4% yield) remained (mp 158.5–159.0 °C dec).

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), 422 (m), 306 (s), 287 (w), 276 (w), 235 (sh), and 228 (m) cm^{-1}. The Mössbauer spectrum was a doublet with an IS of 1.09 ± 0.06 and QS of 2.62 ± 0.12 mm/s. Anal. Calcd for $C_{38}H_{28}SnBr_2N_2$: C, 57.69; H, 3.57; Sn, 15.00; N, 3.54. Found: C, 60.36; H, 4.05; Sn, 15.55; N, 3.37. Molecular weight for $C_{38}H_{28}SnBr_2N_2$: calcd, 791.15; found, 611.

(c) 1,10-Phenanthroline. 1,1-Dibromo-2,3,4,5-tetraphenylstannole (0.50 g, 0.79 mmol) was dissolved in benzene (10 mL). A solution of 1,10-phenanthroline–water (0.16 g, 0.79 mmol) in ethyl ether (20 mL) was combined to form a cloudy white 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 mmol; 30.5% yield) which melted sharply at 205.0 °C.

The infrared spectrum contained bands at 3062 (m), 3040 (m), 1459 (s, br), 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, br) cm^{-1}. The Mössbauer spectrum was a doublet with an IS of 1.05 ± 0.06 and QS of 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.

(d) 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 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 1 h under nitrogen to give a greenish yellow solution with a brownish white precipitate. The solvent was removed in vacuo to give a greenish yellow solid which was treated with toluene, filtered, and recrystallized from methylene chloride–hexane to give needle-shaped white crystals (mp 169.5–170.0 °C 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, br), 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 an IS of 1.48 ± 0.06 and QS of 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. (a) 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 solution was then allowed to reflux for 1 h. 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 and hexane. A tan solid precipitated (mp 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, br), 996 (s), 913 (s), 805 (s), 722 (s), 690 (s), 534 (m), 440 (s), and 310 (s) cm^{-1}. The Mössbauer spectrum

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[12] Foley, P.; Zeldin, M. *Inorg. Chem.* **1975**, *14*, 2264.

contained a doublet with an IS of 1.19 ± 0.03 and QS of 2.55 ± 0.06 mm/s. Anal. Calcd for $C_{38}H_{30}SnI_2N_2$: 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.

(b) 2,2′-Bipyridine. Diiodostannole (1.0 g, 1.4 mmol) was dissolved in benzene (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 (mp 163–164 °C dec; 0.69 g) was obtained in 56% yield (based on diiodostannole).

The infrared spectrum contained prominent bands at 3050 (w), 1590 (w), 1565 (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 an IS of 1.21 ± 0.03 and QS of 2.49 ± 0.06 mm/s. Anal. Calcd for $C_{38}H_{28}SnI_2N_2$: 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.

(c) 1,10-Phenanthroline. Diiodostannole (1.0 g, 1.4 mmol) was dissolved in benzene (20 mL), and 1,1-phenanthroline–water (0.25 g, 1.4 mmol) dissolved in anhydrous diethyl ether (15 mL) was 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 (mp 169–171 °C dec; 1.01 g) in 79% yield (based on diiodostannole).

The Mössbauer spectrum contained a doublet with an IS of 1.14 ± 0.03 and QS of 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 $C_{40}H_{28}SnI_2N_2$: 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.

(d) 2,2′,2″-Terpyridine. Diiodostannole (1.0 g, 1.4 mmol) was dissolved in benzene (15 mL), and a solution of 2,2′,2″-terpyridine (0.16 g, 0.69 mmol) in benzene (5 mL) was 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 (mp 167–169 °C dec; 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 an IS of 1.49 ± 0.03 and QS of 2.49 ± 0.06 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 (10 mL), and 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 mixture was then allowed to reflux under nitrogen for 1 h. The milky solution cleared and turned light yellow upon refluxing. The solution was allowed to cool to room temperature and the benzene removed in vacuo. The resulting light yellow 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 (mp 179–182 °C dec) 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 an IS of 1.20 ± 0.03 and QS of 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.

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 2 h while warming to room temperature. The solvent was then removed in vacuo and methylene chloride added to the residue; the solution was then filered. Addition of absolute ethanol precipitated a white solid (mp 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-tetraphenylbutadiene.[13] 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.

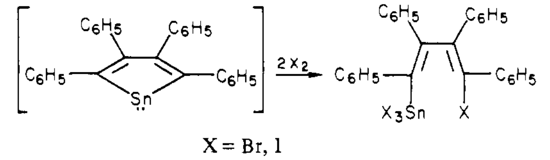
Another white solid isolated from this reaction (mp 39–41 °C) contained tin and gave a doublet Mössbauer spectrum with an IS of 1.32 ± 0.03 and QS of 2.79 ± 0.06 mm/s. From its melting point and Mössbauer spectrum, this compound was identified as diphenyltin dichloride.

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 was allowed to reflux for 12 h under argon. The cloudy, intense yellow solution lightened and became clear on refluxing, and after 12 h of refluxing the solution was a clear, deep red 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 (mp 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 nonpolar organic solvents, and convenient starting materials for synthesis.

Attempts to find other routes to the dihalostannanes, not requiring isolation of the hexaphenylstannole, failed. With use of 1:1 molar ratios of the dilithio reagent with tin(IV) chloride, bromide, and iodide give, in our hands, only the octaphenyl-1,1′-spirobistannole. 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 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 (eq 3). The product (4-halo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin trihalides which are formed in poor yields exhibit increases in relative intensities and shifts to higher energies in the far-infrared spectra in agreement with previous findings.[14] Thus, the ν_{asym}(Sn–X) and ν_{sym}(Sn–X) frequencies increase from 252 and 233 cm^{-1} for X = Br and 184 and 180 cm^{-1} for X = I in the dihalostannoles to 258 and 247 cm^{-1} for X = Br and 210 and 203 cm^{-1} for X = I in the open-chain trihalides. The Mössbauer QS values are also diminished in



(3)

X = Br, I

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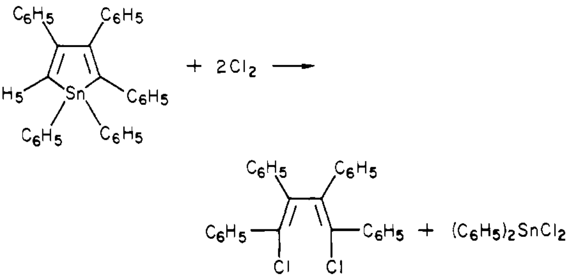
(13) Freedman, H. H. *J. Org. Chem.* **1962**, *27*, 2298.

(14) Lohmann, L. H. *J. Organomet. Chem.* **1965**, *4*, 382.

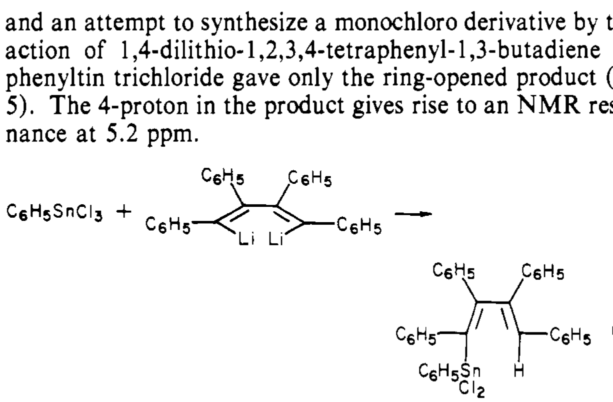
comparison to the corresponding dihalostannoles as shown in Table I. The X-ray crystal structures of the related ring-opened compounds (4-chloro-1,2,3,4-tetraphenyl-1,3-butadienyl)- and (4-bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)dimethylphenyltin(IV)[15] and (4-bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)dimethyltin 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 dihalostannole 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-tetraphenyl-1,3-butadiene[13] and diphenyltin dichloride (eq 4),



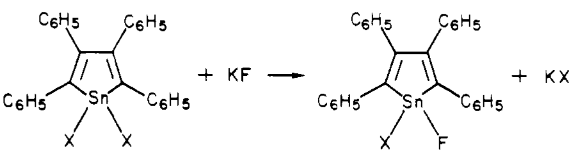
(4)

and an attempt to synthesize a monochloro derivative by the action of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene on phenyltin trichloride gave only the ring-opened product (eq 5). The 4-proton in the product gives rise to an NMR resonance at 5.2 ppm.

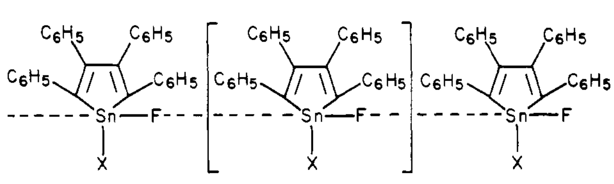


(5)

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 diiodostannoles with the corresponding fluoride (eq 6). 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 ν(Sn–Br) mode but adds a strong band at 570 cm^{-1} which can be assigned to the ν(Sn–F) stretching mode. A second, broad absorption band at 357 cm^{-1} can be assigned to the ν(Sn$\leftarrow$F) mode arising from the dative bridging interaction in the associated structure A. The corresponding ν(Sn–F) mode absorption bands in the 1-iodo-1-fluoro derivative are found at 570 and 350 cm^{-1}, respectively.



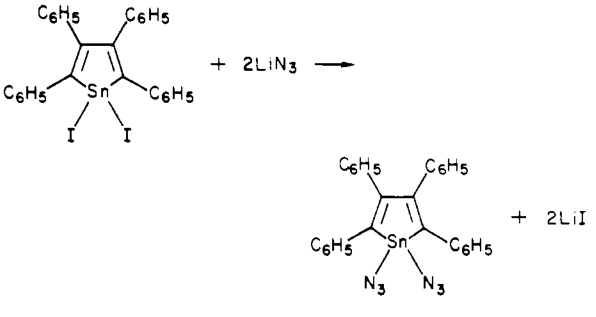
(6)



A, X = Br, I

Bridging fluorine is a structural feature of the trigonal-bipyramidal trimethyltin(IV) fluoride[18,19] as in tri-*n*-butyltin fluoride[20] where disorder in the crystals has prevented a completely satisfactory solution. It is clear, however, that infinite, nonlinear, chain axes consisting of unsymmetrical F–Sn···F bridge bonds exists.[21] Our 1-fluoro-1-halo derivatives are formally analogous to the diorganotin(IV) $(CH_3)_2SnF_2$, 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 of 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 Å) interactions in (4-bromo-1,2,3,4-tetraphenyl-*cis*,*cis*-1,3-butadienyl)dimethyltin(IV) bromide,[15,16] 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.

Disubstitution is effected, however, in derivatization by pseudohalides. Two moles of lithium azide are taken up by the diiodostannole (eq 7). The infrared spectrum of this white product contains absorption bands at 2090 and 1275 cm^{-1}, which can be assigned to the $\nu_{asym}(N_3)$ and $\nu_{sym}(N_3)$ modes, and a sharp band at 690 cm^{-1} which is the azide bending mode, $\delta(N_3)$, respectively.[25] Absorption bands at 472 and 270 cm^{-1} can be assigned to the intra- and intermolecular ν(Sn–N) modes, respectively.[26] The observation of the latter band suggests that the tin atoms are bridged by the azide groups



(7)

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(15) Boer, F. P.; van Remoortere, F. P.; North, P. P.; Reeke, G. N. *Inorg. Chem.* **1971**, *10*, 529.

(16) Boer, F. P.; Flynn, J. J.; Freedman, H. H.; McKinley, S. V.; Sandel, V. R. *J. Am. Chem. Soc.* **1967**, *89*, 5068.

(17) Boer, F. P.; Doorakian, G. A.; Freeman, H. H.; McKinley, S. V. *J. Am. Chem. Soc.* **1970**, *92*, 1225.

(18) Clark, H. C.; O'Brien, R. J.; Trotter, J. *J. Chem. Soc.* **1964**, 2332.

(19) Yasuda, K.; Kawasaki, Y.; Kasai, N.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1216.

(20) Wright, D. A. *Rep.—Def. Stand. Lab. (Aust.)* **1967**, **1968**, *37*. Quoted in: Smith, P. J. "A Bibliography of Organotin X-ray Crystal Structures"; Tin Research Institute: London, 1975.

(21) Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251.

(22) Alcock, N. W.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans.* **1977**, 1090.

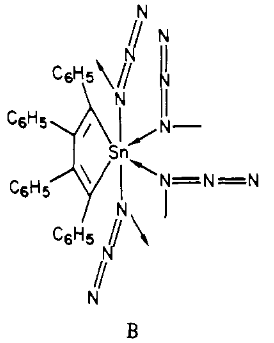
(23) Zuckerman, J. J. *Adv. Organomet. Chem.* **1970**, *9*, 21.

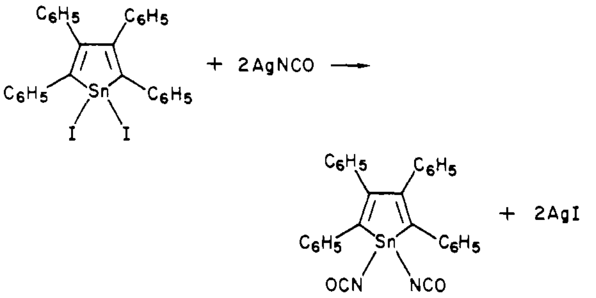
(24) Ruddick, J. N. R. *Rev. Silicon, Germanium, Tin, and Lead Compd.* **1976**, *2*, 115.

(25) Thayer, J. S.; West, R. *Inorg. Chem.* **1964**, *3*, 889.

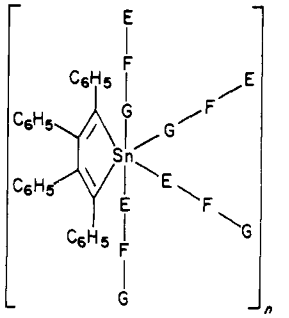
(26) Thayer, J. S.; Strommen, D. P. *J. Organomet. Chem.* **1966**, *5*, 383.

in an unsymmetrical manner. In the analogous, simple fluoride and cyanide $(CH_3)_2SnX_2$, where X = 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) azide[28,29] shows that the bridging takes place through the α-nitrogen. The magnitudes of the Mössbauer QS and ρ values[23] favor structure B in the solid.

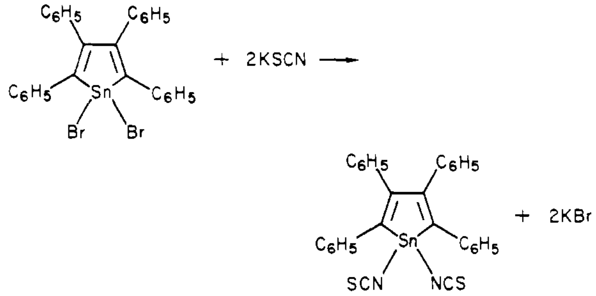

B


(8)

The bis(cyanato) derivative, which is prepared by the action of 2 mol of silver(I) cyanate upon the diiodostannole (eq 8), 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 ν(C═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 δ(NCO) and ν(Sn–N) modes, respectively.[32] The magnitudes of the Mössbauer QS 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 $(CH_3)_3SnOH{\cdot}(CH_3)_3SnNCO$[33] and $(C_6H_5)_3SnNCO$[34] bridges the tin atoms by the γ-oxygen to form associated lattices, and we favor an analogous arrangement as in structure C.


C

EFG = NCO, NCS
GFE = OCN, SCN
EFG = GFE = OC(CH$_3$)O


(9)

The structures of the bis(isothiocyanato) derivatives have been much more extensively investigated.[21] The bis(isothiocyanato)stannole results from the action of 2 mol of KSCN on the dibromostannole (eq 9). Thiocyanate complexes exhibit a sharp ν(N═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 ν(C═S) absorption at 700 cm^{-1} is said to be indicative of attachment through sulfur, while absorption bands at 860–780 cm^{-1} denote nitrogen bonding.[35] The infrared spectrum of our product contains a strong ν(N═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 *o*-phenanthroline exhibit bands in the 2040–2020-cm^{-1} range.[38] We conclude that the stannole product is an isothiocyanate, bridged as in $(CH_3)_2Sn(NCS)_2$ 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 QS and ρ values supports 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 (eq 10). The infrared spectrum of the product stannole contains prominent absorption bands at 1567 and 1323 cm^{-1} which can be assigned to the $\nu_{\mathrm{asym}}(CO_2)$ and $\nu_{\mathrm{sym}}(CO_2)$, 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 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 ν(Sn–O) mode.[39] Unfortunately, no structural data are

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(27) Schlemper, E. O.; Hamilton, W. C. *Inorg. Chem.* **1966**, *5*, 995.

(28) Konnert, J.; Britton, D.; Chow, Y. M. *Acta Crystallogr., Sect. B* **1972**, *B28*, 180.

(29) Allmann, R.; Rüdinger, H.; Waskowska, A.; Lorberth, J. *J. Organomet. Chem.* **1980**, *192*, 353.

(30) Cunningham, D.; Hossain, M. B.; Molloy, K. C.; van der Helm, D.; Zuckerman, J. J., unpublished work.

(31) Forster, D.; Goodgame, D. M. L. *J. Chem. Soc.* **1965**, 1286.

(32) See ref 26.

(33) Hall, J. B.; Britton, D. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2133.

(34) Tarkhova, T. N.; Chuprunov, E. V.; Belov, N. V. *Kristallografiya* **1977**, *22*, 1004.

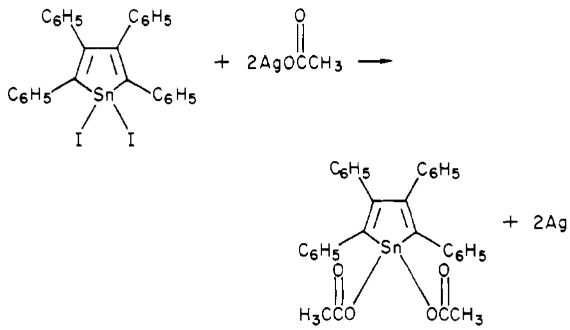
(35) Wada, M.; Okawara, R. *J. Organomet. Chem.* **1967**, *8*, 261.

(36) Chow, Y. M. *Inorg. Chem.* **1970**, *9*, 794.

(37) Forder, R. A.; Sheldrick, G. M. *J. Organomet. Chem.* **1970**, *22*, 611.

(38) Mullins, M. A.; Curran, C. *Inorg. Chem.* **1968**, *7*, 2584.

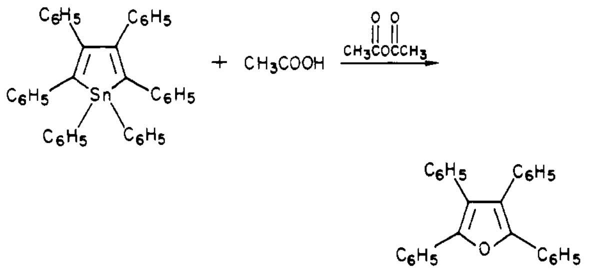
(39) Honnick, W. D.; Zuckerman, J. J. *J. Organomet. Chem.* **1979**, *178*, 133.



(10)

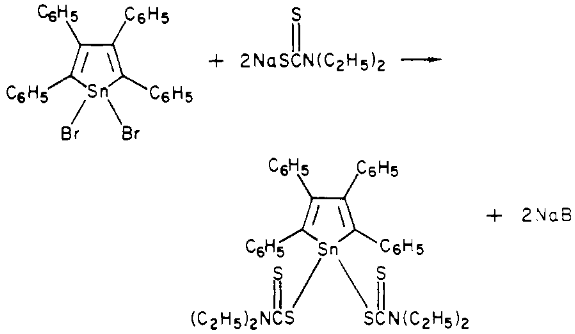
available for diorganotin(IV) dicarboxylates, but all of the triorganotin(IV) derivatives except the tricyclohexyl[40] studied thus far have been shown to contain higher than four-coordinated tin atoms bound into associated lattices through bridging acetato groups.[21,40] The magnitudes of the Mössbauer QS and ρ values are in good agreement with the tin atoms in a cis-octahedral geometry[23] 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 (eq 11).

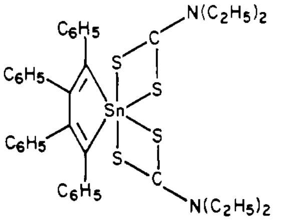


(11)

The bis(diethyldithiocarbamate) is made from the dibromostannole and the sodium salt of the dithiocarbamate (eq 12). Similar solubility with the staring 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 ν(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 QS and ρ values are in agreement with the *cis*-diorganotin(IV) octahedral geometry[23] depicted in structure D.

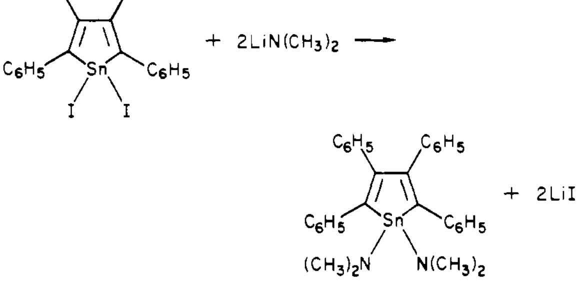


(12)



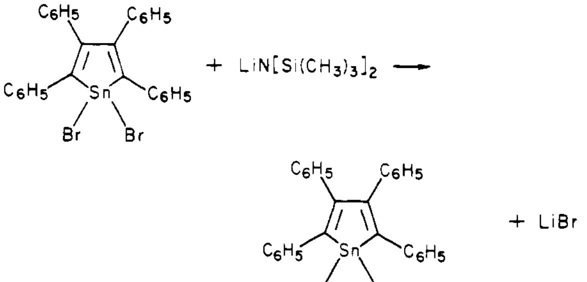
D

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 (eq 13). A band of medium intensity at 950 cm^{-1} in the infrared spectrum can be assigned to the $\nu_{sym}(NC_2)$ mode and a strong band at 530 cm^{-1} to the ν(Sn–N) mode.[12] The Mössbauer spectrum is a narrow doublet like that found for tin–nitrogen derivatives[45] and consistent with four-coordinated diorganotin(IV) systems.



(13)

The action of lithiohexamethyldisilazane, on the other hand, results in the replacement of only one of the halogen atoms of the dibromostannole (eq 14). 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 QS rule 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]



(14)

The corresponding phosphorus system, with its longer tin–phosphorus bond, can again accommodate disubstitution. Two moles of lithium diphenylphosphine react with the dibromostannole (eq 15). The infrared spectrum of the product contains bands at 1437 and 998 cm^{-1} which can be assigned to the $\nu_{asym}(P–C_6H_5)$ and $\nu_{sym}(P–C_6H_5)$ modes, respectively.[48]

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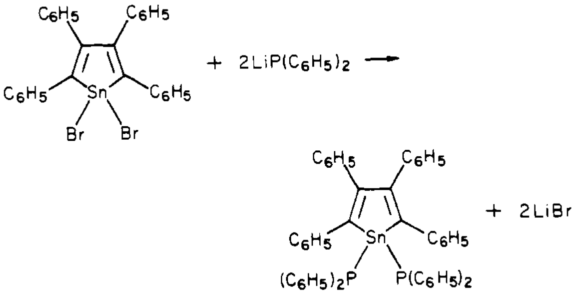
(40) Alcock, N. W.; Timms, R. E. *J. Chem. Soc. A* **1968**, 1876.
(41) Di-μ-acetato-bis(diphenyltin) is an exception in which the tin-tin bond is acetate bridged.[42]
(42) Bandoli, G.; Clemente, D. A.; Panattoni, C. *J. Chem. Soc. D* **1971**, 311.
(43) Chatt, J.; Duncanson, L. A.; Venanzi, L. M. *Nature (London)* **1956**, *177*, 1042.
(44) Bonati, F.; Ugo, R. *J. Organomet. Chem.* **1967**, *10*, 257.
(45) Harrison, P. G.; Zuckerman, J. J. *J. Organomet. Chem.* **1973**, *55*, 261.
(46) Bradley, D. C. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 259.
(47) Lundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253.
(48) Campbell, I. G. M.; Fowler, G. W. A.; Nixon, L. A. *J. Chem. Soc.* **1964**, 1389.



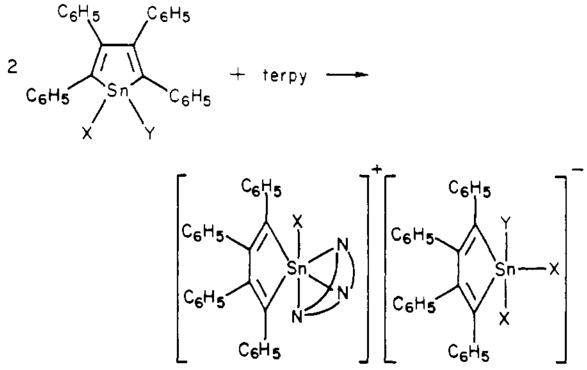
(15)

An additional band of medium intensity at 354 cm^{-1} can be assigned to the ν(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 $R_2SnX_2{\cdot}2B$ with monodentate ligand, B. Structural data published to date[21] for $(CH_3)_2SnX_2{\cdot}2py$ where X = Cl[51] and Br[52] and for $(C_6H_5)_2SnCl_2{\cdot}bpy$[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–bromie 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 *o*-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 IS and QS 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 fluoroiodostannoles (eq 16). By analogy with the products



(16)

X = Y = Br, I
X = F, Y = I

of terpyridyl adduct formation with the other diorganotin dihalides, and the similarities in the Mössbauer spectra,[56] we assign the double salt structure[55] shown in eq 16 to our products. An interesting choice arises in the product from the fluoroiodostannole 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.

Acknowledgment. Our work is supported by the Office of Naval Research and by the National Science Foundation through Grant CHE-78-26548. We thank M&T Chemicals for the donation of organotin starting materials.

Registry No. (4-Bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin tribromide, 77904-06-4; (4-iodo-1,2,3,4-tetraphenyl-1,3-butadienyl)tin dichloride, 77904-07-5; (1,2,3,4-tetraphenyl-1,3-butadienyl)phenyltin dichloride, 77904-08-6; $FBrSnC_4(C_6H_5)_4$, 77904-16-6; $FISnC_4(C_6H_5)_4$, 77904-18-8; octaphenyl-1,1′-spirobistannole, 21779-48-6; $(N_3)_2SnC_4(C_6H_5)_4$, 77904-20-2; (*iso*-NCO)$_2SnC_4(C_6H_5)_4$, 77904-09-7; (*iso*-SCN)$_2SnC_4(C_6H_5)_4$, 77904-10-0; $(OC(O)CH_3)_2SnC_4(C_6H_5)_4$, 77904-22-4; $(SC(S)N(C_2H_5)_2)_2SnC_4(C_6H_5)_4$, 77904-23-5; $(N(CH_3)_2)_2SnC_4(C_6H_5)_4$, 77904-11-1; $(N(Si(CH_3)_3)_2)BrSnC_4(C_6H_5)_4$, 77924-79-9; $(P(C_6H_5)_2)_2SnC_4(C_6H_5)_4$, 77904-12-2; $Br_2SnC_4(C_6H_5)_4{\cdot}2py$, 77904-24-6; $Br_2SnC_4(C_6H_5)_4{\cdot}bpy$, 77904-25-7; $Br_2SnC_4(C_6H_5)_4{\cdot}o\text{-phen}$, 77904-26-8; $Br_2SnC_4(C_6H_5)_4{\cdot}{}^1/_2terpy$, 77904-29-1; $I_2SnC_4(C_6H_5)_4{\cdot}2py$, 77904-30-4; $I_2SnC_4(C_6H_5)_4{\cdot}bpy$, 77904-31-5; $I_2SnC_4(C_6H_5)_4{\cdot}o\text{-phen}$, 77904-32-6; $I_2SnC_4(C_6H_5)_4{\cdot}{}^1/_2terpy$, 77904-35-9; terpy, 1148-79-4; 1,4-dilithio-1,2,3,4-tetraphenylbutadiene, 57956-30-6; $Br_2SnC_4(C_6H_5)_4$, 55690-98-7; $I_2SnC_4(C_6H_5)_4$, 77904-13-3; lithiohexamethyldisilazane, 4039-32-1; diphenylacetylene, 501-65-5; phenyltin trichloride, 1124-19-2; hexaphenylstannole, 21813-34-3; dichloro-1,2,3,4-tetraphenylbutadiene, 77904-14-4; diphenyltin dichloride, 1135-99-5; acetic acid, 64-19-7.

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(49) Schumann, H.; Schwabe, P.; Stelzer, O. *Chem. Ber.* **1969**, *102*, 2900.

(50) Schumann, H.; du Mont, W. W.; Kroth, H. J.; Newmann, H.; Corvan, P. J.; Zuckerman, J. J. *J. Organomet. Chem.* **1976**, *121*, 321.

(51) Harrison, P. G.; King, T. J.; Richards, J. A. *J. Chem. Soc., Dalton Trans.* **1976**, 2317.

(52) Clark, J. P.; Wilkins, C. J. *J. Chem. Soc. A* **1966**, 871.

(53) Srivastava, T. S. *J. Organomet. Chem.* **1967**, *10*, *373*, 375.

(54) Harrison, P. G.; Lane, B. C.; Zuckerman, J. J. *Inorg. Chem.* **1972**, *11*, 1537.

(55) Einstein, F. W. B.; Penfold, B. R. *J. Chem. Soc. A* **1968**, 3019.

(56) Debye, N. W. G.; Rosenberg, R.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1968**, *90*, 3234.

(57) We have recently observed the same phenomenon for the double salts derived from substituted (acetato)triorganotin(IV) cations and triphenyltin(IV) dichloride anions.[58]

(58) Ng, S.-W.; Zuckerman, J. J. "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, NY, Aug 1981; American Chemical Society: Washington, DC, 1981.

(59) Schumann, H.; du Mont, W.-W.; Wöbke, B.; Corvan, P. J.; Zuckerman, J. J. *J. Organomet. Chem.* **1977**, *128*, 187.