

Design of Reversible Low Redox Potential Systems Using Five-Membered Trichalcogenaheterocycles Containing Heavy Chalcogens; Sulfur, Selenium, and Tellurium

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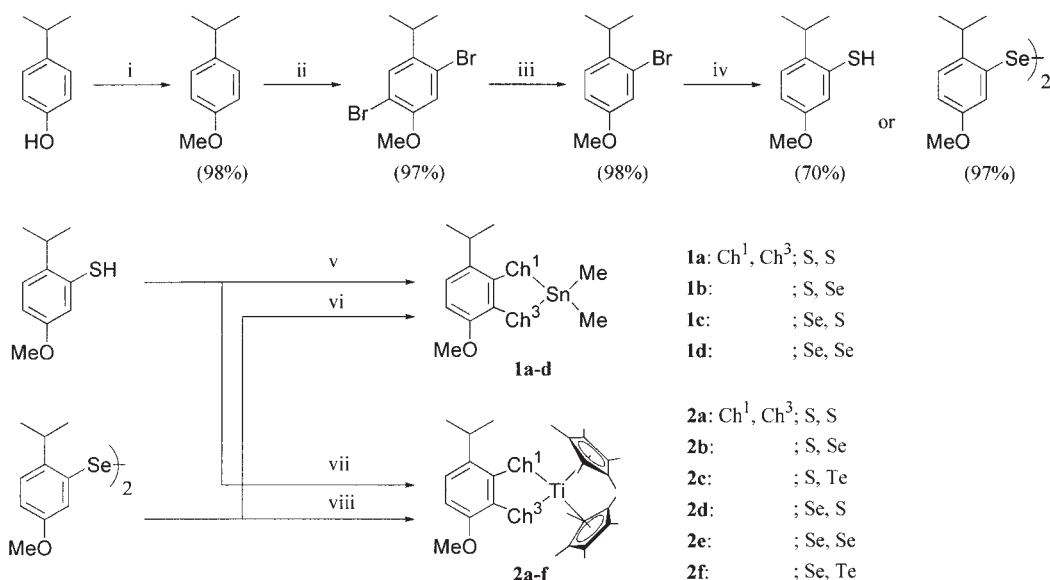
4-Isopropyl-7-methoxy-1,3,2-benzodichalcogenastannoles and 2,2-bis(η^5 -pentamethylcyclopentadienyl)-1,3,2-benzodichalcogenatitanoles, a synthetic equivalent of unstable *ortho*-benzenedichalcogenol, were prepared from 2-isopropyl-5-methoxybenzenechalcogenols in moderate yields by *ortho*-lithiation, chalcogenation, and protection with dichlorodimethylstannane and bis(η^5 -pentamethylcyclopentadienyl)titanocene dichloride, respectively. Some of the solid-state structures of the new-type stannoles and titanoles were confirmed by X-ray crystallographic analyses. Transformation into 4-isopropyl-7-methoxy-1,2,3-benzotrichalcogenoles was successfully carried out, namely by reacting the stannoles or titanoles with electrophiles containing one sulfur or selenium unit. The molecular structures of the new trichalcogenoles were determined by NMR, IR, mass spectra, X-ray crystallographic analyses, and theoretical calculations. In particular, it was elucidated that heavier multi-chalcogen linkages, selenium-selenium and selenium-tellurium bonds in the benzotrichalcogenoles were present in the five-membered ring by multi-nuclear NMR spectra in solution and confirmed by X-ray crystallographic analyses in the solid-state. The redox properties of the trichalcogenoles were studied by cyclic voltammetry. The voltammograms exhibited well-defined reversible one-electron redox couples. New type radical cations were isolated in quantitative yields in the one-electron oxidation of the trichalcogenoles with equimolar amounts of NOPF₆. The structures of the radical cation salts were analyzed by ³¹P-NMR, ESR spectra, elemental analyses, and theoretical calculations. One-electron reduction of the radical cations on treatment with one equivalent of samarium(II) iodide gave the neutral trichalcogenoles quantitatively.

Our study was aimed at the design of a reversible, one-electron reduction–oxidation (redox) system with a low redox potential using neutral trichalcogenoles incorporating sulfur, selenium, and/or tellurium atoms. In the past, such trichalcogenoles have received little attention due to their low stability, as they are known to be readily converted to oligomeric or polymeric forms.^{1,2} Recently, we reported a new efficient method for the synthesis of stable trichalcogenoles incorporating sulfur and/or selenium atoms fused to a benzene ring. These trichalcogenoles showed well-defined chemical and electrochemical redox behavior.^{3–7} On the other hand, in contrast to the sulfur or selenium ring system,^{1,2,8–11} there is no report for the synthesis of tellurium-containing trichalcogenoles fused to a benzene ring, while the compounds themselves have been predicted to have lower redox potentials.^{12–14} We reported a preliminary communication of a new efficient method via double-directing *ortho*-lithiation and stable metallacycles with bis(η^5 -pentamethylcyclopentadienyl)titanium for the synthesis of trichalcogenoles incorporating tellurium besides sulfur and selenium atoms in the five-membered ring.¹⁵ Here, we provide full details on the synthesis, structural characterization, and redox properties of novel benzotrichalcogenoles containing sulfur, selenium, and/or tellurium atoms, which have both isopropyl and methoxy groups at the appropriate positions on the benzene ring to stabilize the five-membered heterocycles. Furthermore, we performed calculations with the den-

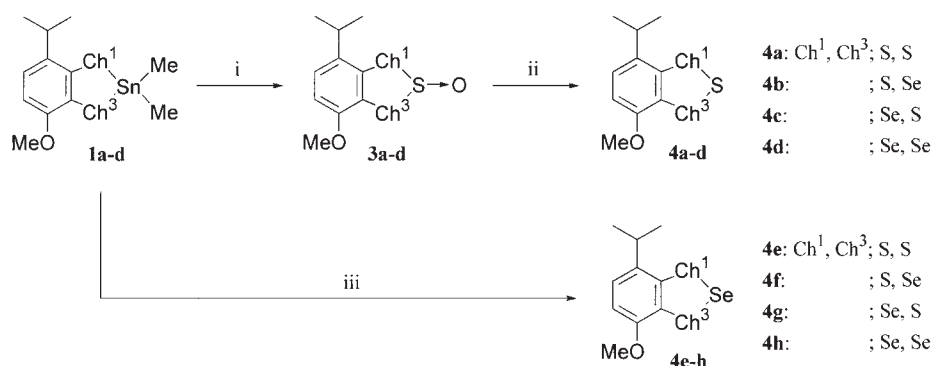
sity functional theory to gain understanding of the unusual stability of the corresponding radical cations with a 7π electron framework that would have pseudoaromaticity.

Results and Discussion

Synthesis of 1,3,2-Benzodichalcogenastannoles 1a–d and 1,3,2-Benzodichalcogenatitanoles 2a–f. 2,2-Dimethyl-1,3,2-benzodichalcogenastannoles **1a–d** and 2,2-bis(η^5 -pentamethylcyclopentadienyl)-1,3,2-benzodichalcogenatitanoles **2a–f**, synthetic equivalents of unstable benzene-1,2-dichalcogenols, were synthesized from commercially available 4-isopropylphenol by following the modified methods previously reported.⁷ The synthetic routes are shown in Scheme 1. The substituted bromobenzene, the precursor of dichalcogenastannoles **1a–d** and titanoles **2a–f**, was prepared in an excellent yield by a sequence of methylation, double-bromination, and selective halogen-metal exchange reactions. Then, a Grignard reaction and chalcogenation of the obtained bromobenzene gave the corresponding thiol and diselenide as isolated products in 70% and 97% yields, respectively.^{16,17} The novel sulfur- and/or selenium-containing dichalcogenastannoles **1a–d** were prepared through *ortho*-lithiation by the double-directing effect of the thiol (or selenol) and methoxy groups¹⁸ followed by chalcogenation^{18–20} and stannylation²¹ with dichlorodimethylstannane in moderate yields. Unfortunately, the tellurium-containing dichalcogenastannoles were



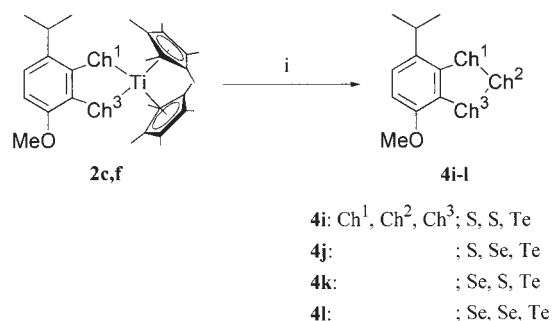
Scheme 1. Reagents and conditions: i. MeI, K_2CO_3 , acetone, reflux; ii. Br_2 , Fe, CCl_4 , room temperature; iii. (a) BuLi, Et_2O , room temperature, (b) H_3O^+ ; iv. (a) Mg, THF, (b) S_8 or Se, (c) H_3O^+ ; v. (a) BuLi, TMEDA, (b) S_8 or Se, (c) Me_2SnCl_2 (**1a**; 53%, **1b**; 23%); vi. (a) LiAlH_4 , THF, (b) BuLi, TMEDA, (c) S_8 or Se, (d) Me_2SnCl_2 (**1c**; 28%, **1d**; 21%); vii. (a) BuLi, TMEDA, (b) S_8 , Se, or Te, (c) $\text{Cp}^*_2\text{TiCl}_2$ (**2a**; 44%, **2b**; 70%, **2c**; 55%); viii. (a) LiAlH_4 , THF, (b) BuLi, TMEDA, (c) S_8 , Se, or Te, (d) $\text{Cp}^*_2\text{TiCl}_2$ (**2d**; 28%, **2e**; 41%, **2f**; 40%).



Scheme 2. Reagents and conditions: i. SOCl_2 , THF, 0 °C (**3a**; 93%, **3b**; quant., **3c**; 99%, **3d**; quant.); ii. NaI, HClO_4 , THF, H_2O , room temperature (**4a**; 95%, **4b**; 99%, **4c**; 96%, **4d**; 99%); iii. (a) SeOCl_2 , THF, -78 °C, (b) $\text{CF}_3\text{SO}_3\text{SiMe}_3$, THF, -78 °C, (c) Sml_2 , THF, -78 °C (**4e**; 82%, **4f**; 82%, **4g**; 85%, **4h**; 92%).

not synthesized due to their tendency to be oxidized and form an oligomeric mixture without the metal protection. The dichalcogenatitanoles **2a-f** were also prepared by the *ortho*-lithiation and chalcogenation of the thiol and diselenide followed by titanylation²²⁻²⁶ with bis(η^5 -pentamethylcyclopentadienyl)titanium dichloride ($\text{Cp}^*_2\text{TiCl}_2$) in moderate yields.

Synthesis of 1,2,3-Benzotrithalcogenoles 4a-l. Transformation into trithalcogenoles **4a-l** was successfully carried out by following our original method,⁷ namely by the reaction of dichalcogenastannoles **1a-d** and titanoles **2a-f** with electrophiles containing one sulfur or selenium unit such as a thionyl chloride or seleninyl chloride. As shown in Scheme 2, treatment of dichalcogenastannoles **1a-d** with thionyl chloride and sodium iodide/perchloric acid afforded novel trithalcogenoles **4a-d** having a sulfur atom at the 2-position in excellent yields via the corresponding trithalcogenole 2-oxides **3a-d**. Furthermore, sequential treatment of dichalcogenastannoles **1a-d** with seleninyl chloride, trimethylsilyl trifluoromethanesul-

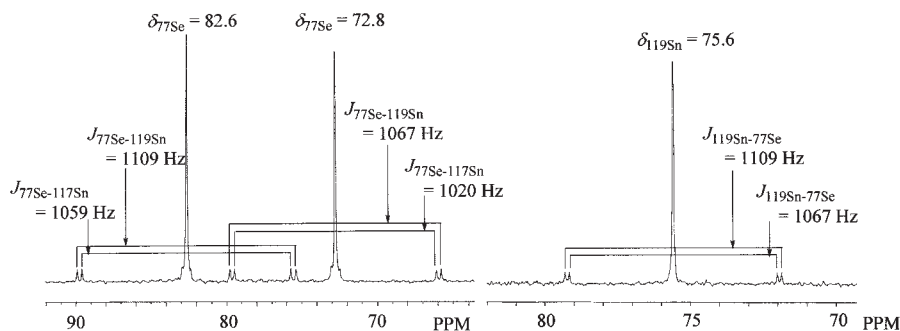


Scheme 3. Reagents and conditions: i. SCl_2 or SeOCl_2 , THF, room temperature (**4i**; 95%, **4j**; 29%, **4k**; 92%, **4l**; 23%).

fonate, and samarium(II) iodide gave novel trithalcogenoles **4e-h** having a selenium atom at the 2-position in excellent yields. In the case of tellurium-containing benzotrithalcogen-

Table 1. Multi-Nuclear NMR Data for 1,3,2-Benzodichalcogenastannoles **1a–d**

Compound	^{119}Sn NMR δ/ppm	^{77}Se NMR δ/ppm	$J_{^{117}\text{Sn}-^{77}\text{Se}}, J_{^{119}\text{Sn}-^{77}\text{Se}}/\text{Hz}$
1a	187.8	—	—
1b	134.1	17.0	1052, 1100
1c	135.3	31.0	1091, 1141
1d	75.6	82.6 72.8	1059, 1109 1020, 1067

Fig. 1. ^{77}Se NMR (left) and ^{119}Sn NMR (right) spectra of 1,3,2-benzodiselenastannole **1d**.Table 2. Multi-Nuclear NMR Chemical Shifts for 1,3,2-Benzodichalcogenatitanoles **2a–f**

Compound	^{77}Se NMR δ/ppm	^{125}Te NMR δ/ppm
2a	—	—
2b	772.7	—
2c	—	944.8
2d	775.0	—
2e	841.1, 844.0	—
2f	1003.2	1055.0

oles **4i–l** (Scheme 3), introduction of a sulfur or selenium atom at the 2-position was performed by the reactions of benzodichalcogenatitanoles **2c,f** with sulfur dichloride or seleninyl chloride, respectively.

Multi-Nuclear NMR Studies. Selenium has one, tin has two, and tellurium has one NMR-active spin 1/2 nuclei of relatively high natural abundance: ^{77}Se , ^{117}Sn , ^{119}Sn , and ^{125}Te . Therefore, the ^{77}Se - and ^{119}Sn -NMR spectra provided pertinent information on the new five-membered framework of dichalcogenastannoles **1a–d** (Table 1). With respect to benzodiselenastannole **1d**, the ^{77}Se -NMR spectrum (Fig. 1) showed two signals with ^{117}Sn and ^{119}Sn satellites, which were in accordance with the existence of two selenium atoms neighboring a tin atom in the five-membered ring. The ^{119}Sn -NMR spectra also showed ^{77}Se satellites. Similarly, the ^{77}Se - and ^{125}Te -NMR spectra also provided pertinent information on the new five-membered framework of dichalcogenatitanoles **2a–f** (Table 2). The ^{77}Se - and ^{125}Te -NMR spectra of trichalcogenoles **4a–l** indicated that each five-membered ring has the selenium atom(s) and a tellurium atom at the appropriate positions. The obtained spectral data are shown in Table 3. The spectra of thiadiselenole **4f,g** consisted of two equally with ^{77}Se satellites. The spectrum of triselenole **4h** consisted of three equally intense signals with ^{77}Se satellites. The data could be facily assigned to be the number of selenium–selenium bonds in the ring. In the case of diselenatellurolle **4i**

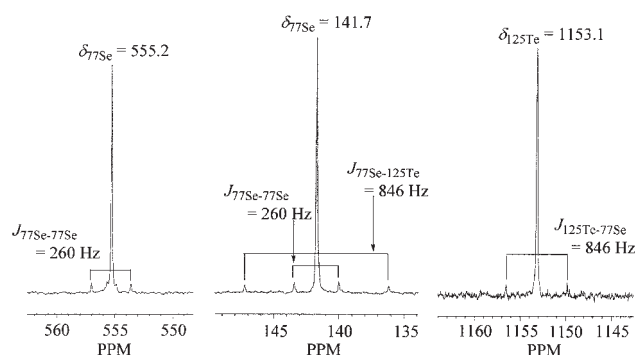
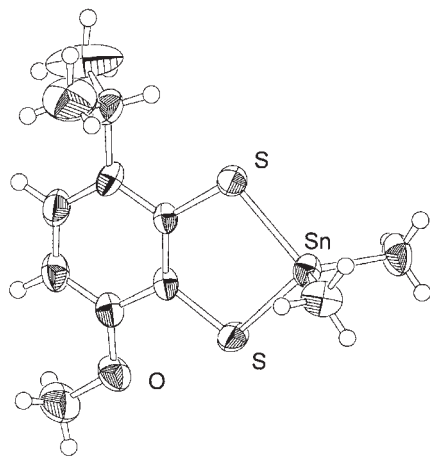
(Fig. 2), the ^{125}Te -NMR spectrum showed a signal with a ^{77}Se satellite, which could be assigned to the tellurium atom at the 3-position bound to a selenium atom. Furthermore, the ^{77}Se -NMR spectrum showed two resonances at 141.7 and 555.2 ppm. The former, with both ^{77}Se and ^{125}Te satellites, indicated the existence of a selenium atom at the 2-position bound to both selenium and tellurium atoms. The latter, with the ^{77}Se satellite, was assigned to the selenium atom at the 1-position bound to a selenium atom. Consequently, these multi-nuclear NMR data clearly indicate that selenium–tin bonding in benzodichalcogenastannoles, and selenium–selenium and selenium–tellurium bonding in benzotrichalcogenoles is present in their five-membered rings.

X-ray Crystallographic Analysis. The crystal structures of benzodithiastannole **1a** and benzothiaselenatitanole **2b** were confirmed by X-ray crystallographic analyses (Figs. 3 and 4, Tables 4 and 5). The five-membered ring of benzodithiastannole **1a** was almost coplanar with the benzene ring. The tin atom of benzodithiastannole **1a** has a tetrahedral structure, the bond angle of S(1)–Sn(2)–S(3) (89.62(6)°) was the most narrow around the tin atom. The sulfur–tin bond lengths are similar to those of reported crystal structures.^{27–30} Two chalcogen atoms of benzothiaselenatitanole **2b** were nearly coplanar with the benzene ring, while the titanium atom lay out of this plane (Ch–Ti–Ch–C torsion angles are ca. 35°). The stable five-membered dichalcogenametallacycles, a synthetic equivalent of unstable benzene-1,2-dichalcogenols, were readily prepared by protection with dichlorodimethylstannane or the corresponding titanocene dichloride.

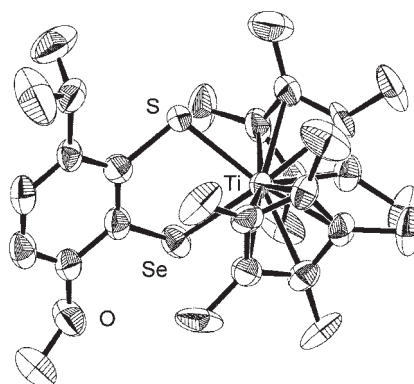
Fortunately, upon recrystallization, benzothiaselenatellurolle **4j** and benzodiselenatellurolle **4l** precipitated from the chloroform solution as brown and purple prisms, respectively. These crystal structures were confirmed by X-ray crystallographic analyses (Figs. 5 and 6, Tables 6 and 7). Two chalcogen atoms at the 1- and 3-positions were almost coplanar with the benzene ring, while the chalcogen atoms at the 2-position lay out of this plane (Ch–Ch–Ch–C torsion angles are ca. 40°).

Table 3. Multi-Nuclear NMR Data for 1,2,3-Benzotrichalcogenoles **4a–l**

Compound	^{77}Se NMR δ/ppm	^{125}Te NMR δ/ppm
4a	—	—
4b	633.6	—
4c	624.1	—
4d	655.9, 645.4	—
4e	701.3	—
4f	568.9, 507.6 ($J_{\text{Se-Se}} = 311$ Hz)	—
4g	581.8, 501.9 ($J_{\text{Se-Se}} = 279$ Hz)	—
4h	543.0 ($J_{\text{Se-Se}} = 292$ Hz), 533.6 ($J_{\text{Se-Se}} = 264$ Hz), 436.7 ($J_{\text{Se-Se}} = 292, 264$ Hz)	—
4i	—	1346.7
4j	295.3 ($J_{\text{Se-Te}} = 878$ Hz)	1095.2 ($J_{\text{Te-Se}} = 878$ Hz)
4k	657.1	1383.9
4l	555.2 ($J_{\text{Se-Se}} = 260$ Hz), 141.7 ($J_{\text{Se-Se}} = 260, J_{\text{Se-Te}} = 846$ Hz)	1153.1 ($J_{\text{Te-Se}} = 846$ Hz)

Fig. 2. ^{77}Se NMR (left and center) and ^{125}Te NMR (right) spectra of 1,2,3-benzodiselenatellurole **4l**.Fig. 3. ORTEP drawing of **1a**. Thermal ellipsoids are drawn at the 50% probability level.

The $\text{Ch}(1)\text{--Se}(2)\text{--Te}(3)\text{--C}(8)$ torsion angles of **4j** and **4l** were $35.98(7)$ and $37.33(9)^\circ$, respectively, which were smaller than those of the benzotrichalcogenoles previously reported.^{1,5–7} The $\text{Te}(3)\text{--Se}(2)\text{--Ch}(1)\text{--C}(9)$ torsion angles of **4j** and **4l** were $-42.83(9)$ and $-42.1(1)^\circ$, respectively. Thus, we investigated these distorted structures with the aid of density functional theory calculations using the Gaussian 98 program.³¹ The electronic structures of benzotrichalcogenoles bearing isopropyl

Fig. 4. ORTEP drawing of **2b** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are drawn at the 50% probability level.Table 4. Crystallographic Data for 1,3,2-Benzodithiastannole **1a** and 1,3,2-Benzothiaselenitanole **2b**

	1a	2b
Empirical formula	$\text{C}_{12}\text{H}_{18}\text{OS}_2\text{Sn}$	$\text{C}_{30}\text{H}_{42}\text{OSSeTi}$
Formula weight	361.08	577.58
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/a$	$P2_12_12_1$
$a/\text{\AA}$	11.5648(7)	10.109(4)
$b/\text{\AA}$	9.7060(9)	14.855(4)
$c/\text{\AA}$	13.5324(8)	16.680(4)
β/deg	103.080(5)	—
$V/\text{\AA}^3$	1479.6(2)	2805(1)
Z	4	4
$D_{\text{calc}}/\text{g cm}^{-3}$	1.621	1.367
λ (Cu $K\alpha$)/ $\text{\AA}$	1.54178	1.54178
Total reflections	3147	5630
Independent reflections	2997	2852
Residuals: R ; R_w	0.051; 0.081	0.055; 0.085
GOF	0.85	0.76

and methoxy groups on the benzene ring were optimized and characterized by frequency computations and a wave function stability check at the B3LYP/3-21G* level. Torsion angles of

Table 5. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°)

Dithiastannole 1a		Thiaselenatitanole 2b	
Bond lengths		Bond lengths	
S(1)–Sn(2)	2.413(2)	S(1)–Ti(2)	2.428(3)
S(3)–Sn(2)	2.407(2)	Se(3)–Ti(2)	2.553(2)
S(1)–C(9)	1.772(7)	S(1)–C(8)	1.77(1)
S(3)–C(8)	1.761(6)	Se(3)–C(9)	1.89(1)
Bond angles		Bond angles	
S(1)–Sn(2)–S(3)	89.62(6)	S(1)–Ti(2)–Se(3)	81.80(9)
C(15)–Sn(2)–C(16)	111.5(4)	Ti(2)–S(1)–C(8)	103.4(4)
Sn(2)–S(1)–C(9)	100.1(2)	Ti(2)–Se(3)–C(9)	94.9(4)
Sn(2)–S(3)–C(8)	101.2(2)		
Torsion angles		Torsion angles	
S(1)–Sn(2)–S(3)–C(8)	5.1(2)	S(1)–Ti(2)–Se(3)–C(9)	–34.2(4)
S(3)–Sn(2)–S(1)–C(9)	–6.0(2)	Se(3)–Ti(2)–S(1)–C(8)	36.0(4)
S(1)–C(9)–C(8)–S(3)	–2.9(8)	Ti(2)–S(1)–C(8)–C(9)	–28.5(9)
		Ti(2)–Se(3)–C(9)–C(8)	32.3(10)
		Se(3)–C(9)–C(8)–S(1)	–4(1)

Values in parentheses are the greater of the range or the estimated S. D.

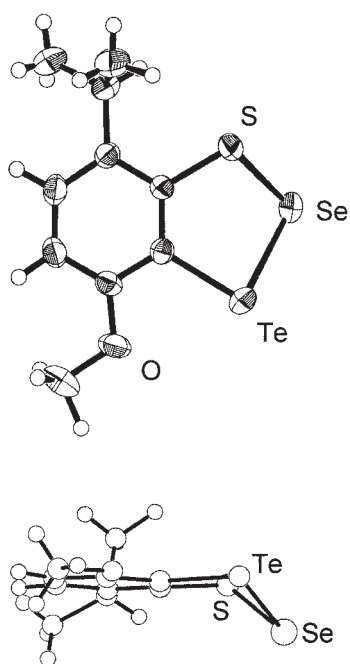


Fig. 5. ORTEP drawing (top) and side view (bottom) of **4j**. Thermal ellipsoids are drawn at the 50% probability level.

the optimized structures are summarized in Table 8, and are comparable with those of the solid-state structures (Table 7) determined by X-ray diffraction. Introduction of a heavier chalcogen atom at the 1- and 3-positions spread out the torsion angles of the trichalcogenole ring. The energies calculated for the distorted form of the five-membered trichalcogenole rings are lower than for the planar form. Consequently, the distorted geometry of the five-membered trichalcogenole rings implies the presence of lone pair-lone pair repulsion among the three divalent chalcogen atoms.

Electrochemical Studies. The solution redox properties of the trichalcogenoles **4a–l** were studied by cyclic voltammetry,

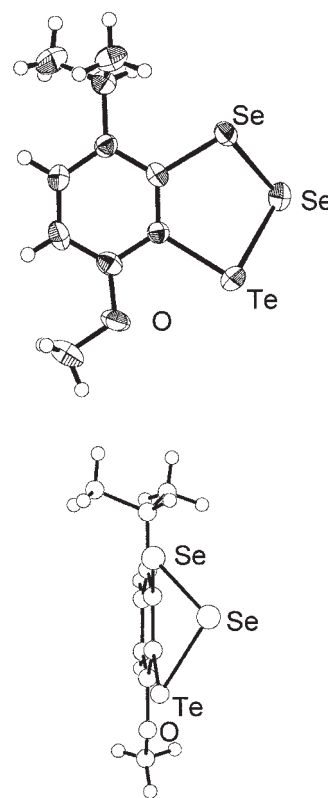


Fig. 6. ORTEP drawing (top) and side view (bottom) of **4l**. Thermal ellipsoids are drawn at the 50% probability level.

since little is known about the electrochemical behavior of polychalcogenide ring systems. Cyclic voltammograms were measured in acetonitrile (MeCN) containing 0.1 M (1 M = 1 mol dm^{–3}) Bu₄NClO₄ as a supporting electrolyte using a glassy-carbon working electrode and a Ag/0.01 M AgNO₃ couple in the electrolyte solution as a reference electrode at 20 °C under argon atmosphere. Interestingly, the typical voltammograms of trithiole **4a** and triselenole **4h** (Fig. 7) specify

Table 6. Crystallographic Data for 1,2,3-Benzothiaselenatellurole **4j** and 1,2,3-Benzodiselenatellurole **4l**

	4j	4l
Empirical formula	C ₁₀ H ₁₂ OSSeTe	C ₁₀ H ₁₂ OSe ₂ Te
Formula weight	386.82	433.72
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> /Å	7.373(5)	7.389(3)
<i>b</i> /Å	16.563(3)	16.581(3)
<i>c</i> /Å	10.046(2)	10.165(3)
β /deg	94.66(2)	93.14(3)
<i>V</i> /Å ³	1222.7(5)	1243.6(6)
<i>Z</i>	4	4
<i>D</i> _{calc} /g cm ⁻³	2.101	2.316
λ (Mo K α)/Å	0.71069	0.71069
Total reflections	2420	2467
Independent reflections	2240	2282
Residuals: <i>R</i> ; <i>R</i> _w	0.021; 0.037	0.033; 0.039
GOF	0.94	1.87

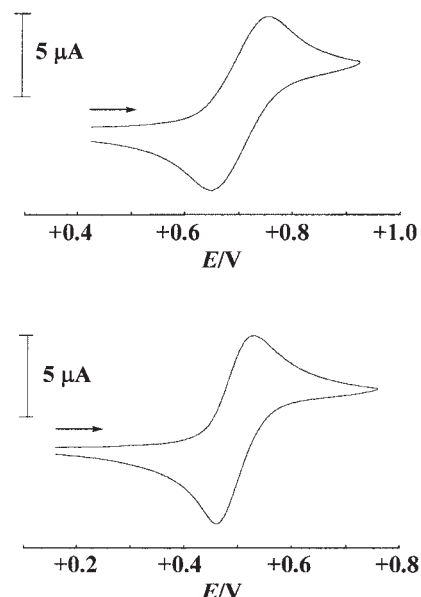
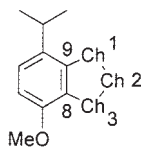
Fig. 7. Cyclic voltammograms of **4a** (top) and **4h** (bottom) in CH₃CN (0.1 M Bu₄NClO₄); scan rate, 100 mV s⁻¹.

Table 7. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°)

Thiaselenatellurole 4j		Diselenatellurole 4l	
Bond lengths		Bond lengths	
S(1)–Se(2)	2.2218(9)	Se(1)–Se(2)	2.3500(6)
Se(2)–Te(3)	2.5306(5)	Se(2)–Te(3)	2.5233(6)
Te(3)–C(8)	2.101(3)	Te(3)–C(8)	2.113(3)
S(1)–C(9)	1.779(3)	Se(1)–C(9)	1.929(3)
Bond angles		Bond angles	
Te(3)–Se(2)–S(1)	90.54(3)	Te(3)–Se(2)–Se(1)	90.52(3)
Se(2)–S(1)–C(9)	99.68(10)	Se(2)–Se(1)–C(9)	96.1(1)
Se(2)–Te(3)–C(8)	86.16(8)	Se(2)–Te(3)–C(8)	88.43(9)
S(1)–C(9)–C(8)	119.6(2)	Se(1)–C(9)–C(8)	119.4(3)
Te(3)–C(8)–C(9)	121.2(2)	Te(3)–C(8)–C(9)	122.2(3)
Torsion angles		Torsion angles	
Te(3)–Se(2)–S(1)–C(9)	–42.83(9)	Te(3)–Se(2)–Se(1)–C(9)	–42.1(1)
S(1)–Se(2)–Te(3)–C(8)	35.98(7)	Se(1)–Se(2)–Te(3)–C(8)	37.33(9)
Se(2)–S(1)–C(9)–C(8)	36.8(2)	Se(2)–Se(1)–C(9)–C(8)	36.1(3)
Se(2)–Te(3)–C(8)–C(9)	–25.8(2)	Se(2)–Te(3)–C(8)–C(9)	–27.1(3)

Values in parentheses are the greater of the range or the estimated S. D.

Table 8. Calculated Torsion Angles (°) of 1,2,3-Benzotrithalcogenoles **4a–l**

	4a	4b	4c	4d	4e	4f	4g	4h	4i	4j	4k	4l
Ch(3)–Ch(2)–Ch(1)–C(9)	–39.9	–41.5	–39.8	–42.0	–39.0	–40.7	–39.0	–41.3	–41.8	–41.5	–42.0	–41.9
Ch(1)–Ch(2)–Ch(3)–C(8)	38.7	37.5	41.0	40.6	37.8	36.7	40.3	39.6	34.4	34.0	36.9	36.6
Ch(2)–Ch(1)–C(9)–C(8)	–27.7	–25.7	–30.4	–28.8	–28.6	–26.6	–31.0	–29.3	–22.0	–23.5	–24.4	–25.7
Ch(2)–Ch(3)–C(8)–C(9)	30.2	32.8	29.5	32.5	31.4	33.9	30.8	33.7	35.3	36.2	35.0	36.0

Optimized structures were obtained B3LYP/3-21G* level.

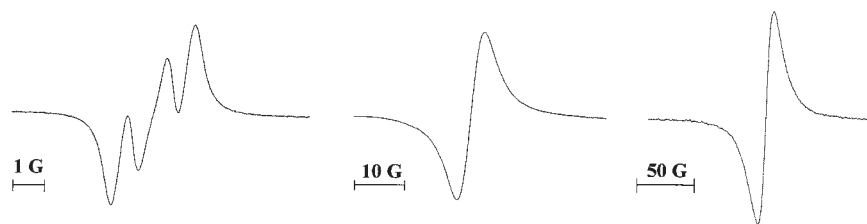
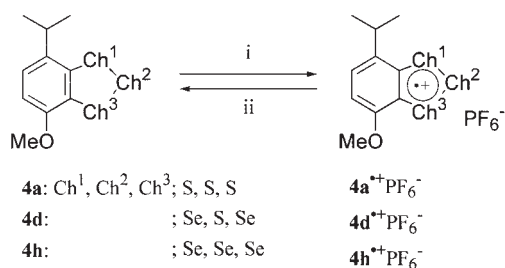


Fig. 8. ESR spectra of $4a^{\bullet+}PF_6^-$ at $-35\text{ }^{\circ}C$ (left), $4d^{\bullet+}PF_6^-$ at $-35\text{ }^{\circ}C$ (center), and $4h^{\bullet+}PF_6^-$ at $8\text{ }^{\circ}C$ in CH_3CN .

Table 9. Redox Potentials of 1,2,3-Benzotrichalcogenoles **4a–l**

Compound	E_{pa}/V	E_{pc}/V	$E_{1/2}/V$
4a	+0.76	+0.65	+0.71
4b	+0.71	+0.63	+0.67
4c	+0.69	+0.61	+0.65
4d	+0.66	+0.58	+0.62
4e	+0.60	+0.52	+0.56
4f	+0.56	+0.50	+0.53
4g	+0.58	+0.48	+0.53
4h	+0.53	+0.46	+0.50
4i	+0.44	—	—
4j	+0.39	—	—
4k	+0.39	+0.25	+0.32
4l	+0.36	+0.26	+0.31

Concentration, 2 mM sample MeCN/0.1 M Bu_4NClO_4 ; working electrode, glassy-carbon; reference electrode, $Ag/0.01\text{ M } AgNO_3$; counter electrode, Pt; scan rate, 100 mV s^{-1}



Scheme 4. Reagents and conditions: i. $NOPF_6$ (1 equiv. amt.), CH_3CN-Et_2O , $-78\text{ }^{\circ}C$ (**4a**; 94%, **4d**; 98%, **4h**; quant.); ii. SmI_2 (1 equiv. amt.), THF, $-78\text{ }^{\circ}C$ ($4a^{\bullet+}PF_6^-$; quant., $4d^{\bullet+}PF_6^-$; 98%, $4h^{\bullet+}PF_6^-$; quant.).

a well-defined reversible one-electron redox couple at $E_{1/2} = +0.71$ and $+0.50\text{ V}$, respectively. Moreover, most of the trichalcogenoles exhibited one reversible one-electron step with a low oxidation potential except for trichalcogenoles **4i,j** (Table 9). The peak potentials of the first oxidation peak (E_p) and half-wave ($E_{1/2}$) have been found to be governed by the atom present at the 2-position of the chalcogen ring, which is in good agreement with those of the trichalcogenoles previously reported.⁷ It is a well-known fact that increasing selenium and/or tellurium substitution normally leads to the lowering of the oxidation potential of a donor.^{12–14,32,33} As expected, with increasing selenium and/or tellurium substitution, lowered oxidation peaks were obtained. Thus, the present results suggest that the desired stable one-electron oxidized species, benzotrichalcogenolium radical cations, can be generated during the electrochemical or chemical oxidation.

One-Electron Redox Reactions and ESR Studies. The

Table 10. g -Values and Hyperfine Coupling Constants (hfc) of 1,2,3-Benzotrichalcogenolium Hexafluorophosphates

Compound	g -Value	hfc/mT
$4a^{\bullet+}PF_6^-$	2.013	0.110, 0.072
$4d^{\bullet+}PF_6^-$	2.025	—
$4h^{\bullet+}PF_6^-$	2.061	—

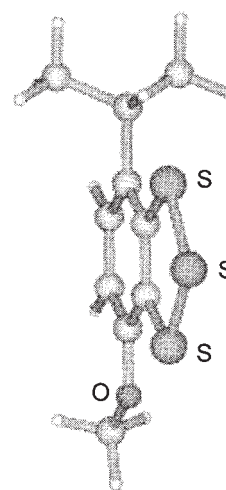


Fig. 9. Optimized structure of $4a^{\bullet+}$.

results of the reversibility observed in cyclic voltammetry described above clearly indicate that the trichalcogenoles provide stable radical cations even at room temperature. Several novel trichalcogenolium radical cation salts were readily isolated in the one-electron oxidation of trichalcogenoles with equimolar amount of $NOPF_6$ in ether–MeCN (Scheme 4). The dark-blue salts were stable at ambient temperature, and the structures of radical ions in solution were analyzed by ^{31}P -NMR and EPR spectroscopies. Each salt dissolved readily in MeCN to give a red-purple solution. The ESR spectra in the degassed MeCN solution showed the presence of a doublet of doublet peak with the hyperfine coupling constants aH of 0.110 and 0.072 mT ($4a^{\bullet+}PF_6^-$), and a broad singlet peak ($4d^{\bullet+}PF_6^-$ and $4h^{\bullet+}PF_6^-$) attributable to trichalcogenolium radical cations (Fig. 8, Table 10). The aH splitting due to two unequivalent protons of the fused-benzene ring ($4a^{\bullet+}PF_6^-$) suggests a partially spin-delocalized system over the benzene ring. This spin delocalization could be elucidated by the theoretical calculations. The electronic structure of the trithiolium radical cation was optimized and characterized by frequency computations and wave function stability checks at the UB3LYP/6-311+G(d,p) level. The optimized structure of the trithiolium radical cation (Fig. 9) was completely coplanar with the benz-

Table 11. Calculated Nucleus-Independent Chemical Shift (NICS) Values (ppm) at the Individual Ring Center of 1,2,3-Benzotrichalcogenoles and Corresponding Radical Cations

Compound ^{a)}	NICS value ^{b)}	
	Six-membered ring	Five-membered ring
4a (C_1)	−8.3	—
4a ^{•+} (C_s)	−9.4 (−9.5) ^{c)}	−10.3 (−6.0) ^{c)}
4h (C_1)	−7.9	—
4h ^{•+} (C_s)	−9.8 (−9.9) ^{c)}	−8.6 (−5.0) ^{c)}

a) The point groups are described in parentheses. b) GIAO-B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) computed NICS values were obtained at the central point in the plane. c) NICS(1) values (ppm) are given in parentheses.

ene ring (C_s symmetry), which also predicted the π -systems consisted of the trithiolium and benzene ring. The spin distribution of the trithiolium radical cation revealed that the calculated aH values for the proton of the benzene ring were 0.149 and 0.058 mT, respectively, being in fair agreement with the observed values. The spin densities were mostly present in the five-membered trithiolium ring with the 7π electron system. Furthermore, this tendency of the spin delocalization is also the case for all trichalcogenolium frameworks. In addition, in order to evaluate computationally the ring current of these heterocyclic radical cations, nucleus-independent chemical shift³⁴ (NICS) values, which are known as an effective and simple probe of individual rings in polycyclic systems, were calculated with the density functional theory. The calculated NICS values of individual rings in trichalcogenoles and their radical cations are shown in Table 11. The NICS(1) and NICS(0) values for the six-membered ring of trichalcogenolium radical cations are close in magnitude to that for the benzene ring of the corresponding neutral trichalcogenole, providing evidence for the existence of a diatropic ring current. However, the NICS(1) values for the five-membered ring are even smaller in magnitude than those of the six-membered ring. These data suggest the radical cations with a 7π electron framework have pseudoaromaticity.

Interestingly, the radical cation salts undergo one-electron reduction to give trichalcogenoles quantitatively on treatment with samarium(II) iodide (Scheme 4). Thus, the facile inter-conversion between trichalcogenoles and their radical cations in the redox reactions is ascribed to the destabilization of the distorted neutral trichalcogenide framework by the lone pair-lone pair repulsion and the unusual stabilization of the oxidized radical cation by the 7π electron framework.

Experimental

General. Melting and decomposition points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra were measured on a Bruker AC-400 spectrometer using CDCl_3 as a solvent with Me_4Si as the internal standard. ^{31}P (162 MHz), ^{77}Se (76 MHz), ^{119}Sn (149 MHz), and ^{125}Te (126 MHz) NMR spectra used H_3PO_4 , Me_2Se , Me_4Sn , and Me_2Te as the external standard, respectively. IR spectra were recorded on a JASCO FT-7300 spectrometer. Mass spectra were determined on a Hitachi M-2000 spectrometer operating at 70 eV in the EI mode. Elemental

analyses were carried out by a Yanagimoto MT-5 CHN coder. High-resolution mass spectra were obtained using a JEOL JMS-SX 102 spectrometer. Cyclic voltammetry was carried out with a Cypress Systems CS-1090 galvanostat/potentiostat. A three-electrode system was used, consisting of a glassy-carbon working electrode, a platinum wire auxiliary electrode and a $\text{Ag}/0.01\text{ M AgNO}_3$ reference electrode. The measurements were carried out in MeCN solution containing 0.1 M Bu_4NClO_4 as a supporting electrolyte with scan rates $50\text{--}500\text{ mV s}^{-1}$ under an Ar atmosphere at 20 °C. ESR data were taken in a JEOL RE2X spectrometer working in the X-band with DPPH and Mn^{2+} on MgO as field markers. All solvents used in the reactions were purified by the general methods. All reactions were carried out under a nitrogen atmosphere, but the work-up was performed in air. Silica-gel column chromatography was performed with a Wakogel C-200.

Computational Methods. All calculations were carried out with Gaussian 98 program. The geometries were optimized with the restricted Becke hybrid (B3LYP) methods for the neutral compounds, and unrestricted B3LYP methods for the radical cations. The zero-point vibrational energies were computed at the same level and were not scaled. All stationary points were characterized by harmonic analysis. Nucleus-independent chemical shift (NICS) values were evaluated by using the gauge invariant atomic orbital (GIAO) approach and were obtained at a central point in the plane of the rings, and NICS(1) refers to calculations at 1.0 Å above the ring.

General Procedure for the Synthesis of 4-Isopropyl-7-methoxy-1,3,2-benzodichalcogenastannoles 1a–d. Butyllithium (42.3 mL of a 1.54 M solution in hexane, 65.2 mmol) was added to a stirred solution of 2-isopropyl-5-methoxybenzenethiol (2.93 g, 16.1 mmol) in N,N,N',N' -tetramethylethylenediamine (9.8 mL, 65.2 mmol) at 0 °C. After 2 h at room temperature, elemental sulfur (2.09 g, 65.2 mmol) was added at 0 °C, and the reaction mixture was stirred for 24 h at room temperature. The hexane was removed in vacuo and replaced with 10 mL of THF. The reaction mixture was treated with sodium borohydride (619 mg, 16.3 mmol) at 0 °C, and was stirred in reflux for 6 h. Then, the solution was poured into water. The solution was neutralized with diluted hydrochloric acid solution, treated with dichlorodimethylstannane (4.30 g, 19.6 mmol), and stirred for 0.5 h at room temperature. The mixture was extracted with dichloromethane. The organic layer was dried (MgSO_4), filtered, and concentrated in vacuo. Purification of the mixture by column chromatography on silica gel with chloroform as the eluent gave 3.10 g (8.58 mmol, 53%) of **1a** as colorless crystals: mp 201.0–202.0 °C; ^1H NMR (400 MHz) δ 0.98 (s, 6H, $\text{Sn}(\text{CH}_3)_2$), 1.25 (d, $J = 6.8\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 3.50 (sept, $J = 6.8\text{ Hz}$, 1H, $\text{CH}(\text{CH}_3)_2$), 3.88 (s, 3H, OCH_3), 6.61 (d, $J = 8.4\text{ Hz}$, 1H, ArH), 6.96 (d, $J = 8.4\text{ Hz}$, 1H, ArH); ^{13}C NMR (101 MHz) δ 2.3, 23.2, 33.4, 56.1, 107.0, 121.8, 127.0, 139.0, 140.9, 156.2; ^{119}Sn NMR (149 MHz) δ 187.7; IR (KBr) 2954, 1573, 1462, 1425, 1276, 1254, 1048, 791, 544 cm^{-1} ; MS (70 eV) m/z 362 (M^+); Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{OS}_2\text{Sn}$: C, 39.91; H, 5.02%. Found: C, 39.72; H, 5.01%.

7-Isopropyl-4-methoxy-2,2-dimethyl-1,3,2-benzothiaselenastannole (1b). Colorless crystals; mp 191.5–192.5 °C; ^1H NMR (400 MHz) δ 1.01 (s, 6H, $\text{Sn}(\text{CH}_3)_2$), 1.25 (d, $J = 6.8\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 3.56 (sept, $J = 6.8\text{ Hz}$, 1H, $\text{CH}(\text{CH}_3)_2$), 3.87 (s, 3H, OCH_3), 6.59 (d, $J = 8.4\text{ Hz}$, 1H, ArH), 7.02 (d, $J = 8.4\text{ Hz}$, 1H, ArH); ^{13}C NMR (101 MHz) δ 1.8, 23.2, 33.9, 56.2, 107.0, 122.9, 124.3, 141.2, 141.5, 156.7; ^{77}Se NMR (76 MHz) δ 17.0 ($J_{\text{Se-117Sn}} = 1052$, $J_{\text{Se-119Sn}} = 1100\text{ Hz}$); ^{119}Sn NMR (149

H δ 134.1 ($J_{\text{Sn-77Se}} = 1100$ Hz); IR (KBr) 2956, 1463, 1423, 1275, 1254, 1047, 793 cm^{-1} ; MS (70 eV) m/z 408 (M^+); Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{OSSeSn}$: C, 35.33; H, 4.45%. Found: C, 35.20; H, 4.55%.

4-Isopropyl-7-methoxy-2,2-dimethyl-1,3,2-benzothiaselenastannole (1c). Colorless crystals; mp 217.0–218.5 $^{\circ}\text{C}$; ^1H NMR (400 MHz) δ 1.02 (s, 6H, $\text{Sn}(\text{CH}_3)_2$), 1.26 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.38 (sept, $J = 6.7$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.88 (s, 3H, OCH_3), 6.67 (d, $J = 8.4$ Hz, 1H, ArH), 6.96 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 1.9, 23.4, 36.3, 56.2, 108.0, 122.0, 129.6, 136.8, 142.4, 156.7; ^{77}Se NMR (76 MHz) δ 31.0 ($J_{\text{Se-117Sn}} = 1091$, $J_{\text{Se-119Sn}} = 1142$ Hz); ^{119}Sn NMR (149 MHz) δ 135.3 ($J_{\text{Sn-77Se}} = 1142$ Hz); IR (KBr) 2957, 1571, 1458, 1425, 1274, 1252, 1215, 1036, 795, 768 cm^{-1} ; MS (70 eV) m/z 408 (M^+); Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{OSSeSn}$: C, 35.33; H, 4.45%. Found: C, 35.23; H, 4.50%.

4-Isopropyl-7-methoxy-2,2-dimethyl-1,3,2-benzodiselenastannole (1d). Colorless crystals; mp 180.5–181.5 $^{\circ}\text{C}$; ^1H NMR (400 MHz) δ 1.05 (s, 6H, $\text{Sn}(\text{CH}_3)_2$), 1.26 (d, $J = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.45 (sept, $J = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.87 (s, 3H, OCH_3), 6.66 (d, $J = 8.4$ Hz, 1H, ArH), 7.04 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 1.4, 23.5, 36.8, 56.3, 108.0, 123.1, 127.3, 139.3, 143.1, 157.3; ^{77}Se NMR (76 MHz) δ 82.6 ($J_{\text{Se-117Sn}} = 1059$, $J_{\text{Se-119Sn}} = 1109$ Hz), 72.8 ($J_{\text{Se-117Sn}} = 1020$, $J_{\text{Se-119Sn}} = 1067$ Hz); ^{119}Sn NMR (149 MHz) δ 75.6 ($J_{\text{Sn-77Se}} = 1067$, 1109 Hz); IR (KBr) 2954, 1462, 1421, 1276, 1251, 1038, 794 cm^{-1} ; MS (70 eV) m/z 456 (M^+); Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{OSe}_2\text{Sn}$: C, 31.69; H, 3.99%. Found: C, 31.43; H, 3.88%.

General Procedure for the Synthesis of 4-Isopropyl-7-methoxy-1,3,2-benzodichalcogenatitanoles 2a–f. Butyllithium (3.12 mL of a 1.54 M solution in hexane, 4.80 mmol) was added to a stirred solution of 2-isopropyl-5-methoxybenzenethiol (360 mg, 1.97 mmol) in N,N,N',N' -tetramethylethylenediamine (5.0 mL, 33.0 mmol) at 0 $^{\circ}\text{C}$. After 2 h at room temperature, elemental sulfur (70 mg, 2.2 mmol) was added at 0 $^{\circ}\text{C}$. After the reaction mixture was stirred for 12 h at room temperature, it was treated with bis(pentamethylcyclopentadienyl)titanium(IV) dichloride (780 mg, 2.00 mmol) in THF (40 mL) at 0 $^{\circ}\text{C}$, and was stirred for 6 h at room temperature. The solution was concentrated in vacuo, and purified by column chromatography on silica gel with $\text{CCl}_4/\text{CHCl}_3$ (1:1 v/v) as the eluent to give 456 mg (0.86 mmol, 44%) of **2a** as deep green crystals; mp 242.5–243.0 $^{\circ}\text{C}$ (decomp.); ^1H NMR (400 MHz) δ 1.21 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.87 (s, 30H, CH_3), 3.69 (sept, $J = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.86 (s, 3H, OCH_3), 6.59 (d, $J = 8.2$ Hz, 1H, ArH), 6.94 (d, $J = 8.2$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 12.4, 23.5, 30.9, 55.7, 104.5, 119.9, 123.6, 140.6, 141.5, 154.8, 155.2; IR (KBr) 2900, 1552, 1449, 1378, 1254, 1209, 1047 cm^{-1} ; MS (70 eV) m/z 530 (M^+); Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{OS}_2\text{Ti}$: C, 67.90; H, 7.98%. Found: C, 67.64; H, 8.23%.

7-Isopropyl-4-methoxy-2,2-bis(pentamethylcyclopentadienyl)-1,3,2-benzothiaselenatitanole (2b). Deep green crystals; mp 230.0–230.5 $^{\circ}\text{C}$ (decomp.); ^1H NMR (400 MHz) δ 1.19 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.89 (s, 30H, CH_3), 3.67 (sept, $J = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.87 (s, 3H, OCH_3), 6.61 (d, $J = 8.3$ Hz, 1H, ArH), 6.97 (d, $J = 8.3$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 12.6, 23.5, 31.4, 55.7, 104.6, 120.7, 123.7, 137.5, 141.1, 155.86, 155.89; ^{77}Se NMR (76 MHz) δ 772.7; IR (KBr) 2904, 1550, 1443, 1419, 1377, 1275, 1252, 1047, 803 cm^{-1} ; MS (70 eV) m/z 578 (M^+); Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{OSSeTi}$: C, 62.39; H, 7.33%. Found: C, 62.22; H, 7.62%.

7-Isopropyl-4-methoxy-2,2-bis(pentamethylcyclopentadienyl)-1,3,2-benzothiatelluratitanole (2c). Deep green crystals; mp 171.0 $^{\circ}\text{C}$ (decomp.); ^1H NMR (400 MHz) δ 1.15 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.96 (s, 30H, CH_3), 3.54 (sept, $J = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.85 (s, 3H, OCH_3), 6.61 (d, $J = 8.2$ Hz, 1H, ArH), 7.00 (d, $J = 8.2$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 13.4, 23.4, 32.2, 56.0, 104.6, 122.1, 123.5, 125.1, 141.8, 157.7, 158.4; ^{125}Te NMR (126 MHz) δ 944.8; IR (KBr) 2904, 1418, 1377, 1251, 1177, 806 cm^{-1} ; MS (70 eV) m/z 628 (M^+); Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{OSTeTi}$: C, 57.54; H, 6.76%. Found: C, 57.24; H, 6.67%.

4-Isopropyl-7-methoxy-2,2-bis(pentamethylcyclopentadienyl)-1,3,2-benzothiaselenatitanole (2d). Deep green crystals; mp 206.5–207.0 $^{\circ}\text{C}$ (decomp.); ^1H NMR (400 MHz) δ 1.22 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.90 (s, 30H, CH_3), 3.71 (sept, $J = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.85 (s, 3H, OCH_3), 6.64 (d, $J = 8.3$ Hz, 1H, ArH), 6.99 (d, $J = 8.3$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 12.6, 23.8, 33.4, 55.7, 105.5, 120.4, 123.7, 142.0, 143.3, 151.4, 155.6; ^{77}Se NMR (76 MHz) δ 775.0; IR (KBr) 2900, 1554, 1420, 1253, 1038, 799 cm^{-1} ; MS (70 eV) m/z 578 (M^+); Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{OSSeTi}$: C, 62.39; H, 7.33%. Found: C, 62.05; H, 7.50%.

4-Isopropyl-7-methoxy-2,2-bis(pentamethylcyclopentadienyl)-1,3,2-benzodiselenatitanole (2e). Deep green crystals; mp 196.5–197.0 $^{\circ}\text{C}$ (decomp.); ^1H NMR (400 MHz) δ 1.21 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.93 (s, 30H, CH_3), 3.70 (sept, $J = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.86 (s, 3H, OCH_3), 6.67 (d, $J = 8.3$ Hz, 1H, ArH), 7.03 (d, $J = 8.3$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 12.8, 23.8, 34.0, 55.8, 105.5, 121.2, 123.8, 139.5, 142.6, 152.7, 156.3; ^{77}Se NMR (76 MHz) δ 841.1, 844.0; IR (KBr) 2902, 1449, 1420, 1378, 1253, 1040 cm^{-1} ; MS (70 eV) m/z 626 (M^+); Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{OSe}_2\text{Ti}$: C, 57.70; H, 6.78%. Found: C, 57.32; H, 6.91%.

7-Isopropyl-4-methoxy-2,2-bis(pentamethylcyclopentadienyl)-1,3,2-benzoselenatelluratitanole (2f). Deep green crystals; mp 155.0 $^{\circ}\text{C}$ (decomp.); ^1H NMR (400 MHz) δ 1.18 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.99 (s, 30H, CH_3), 3.60 (sept, $J = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.84 (s, 3H, OCH_3), 6.69 (d, $J = 8.3$ Hz, 1H, ArH), 7.07 (d, $J = 8.3$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 13.6, 23.8, 34.9, 56.0, 105.5, 122.4, 123.6, 125.0, 143.5, 155.5, 158.1; ^{77}Se NMR (76 MHz) δ 1003.2; ^{125}Te NMR (126 MHz) δ 1055.1; IR (KBr) 2904, 1449, 1377, 1308, 1252, 807 cm^{-1} ; MS (70 eV) m/z 674 (M^+).

General Procedure for the Synthesis of 4-Isopropyl-7-methoxy-1,2,3-benzotrichalcogenole 2-Oxides 3a–d. 4-Isopropyl-7-methoxy-2,2-dimethyl-1,3,2-benzodithiastannole (**1a**) (181 mg, 0.50 mmol) was dissolved in THF (10 mL) and cooled to 0 $^{\circ}\text{C}$. A solution of thionyl chloride (0.04 mL, 0.60 mmol) in THF (6 mL) was added at 0 $^{\circ}\text{C}$, and the reaction mixture was stirred for 2 h at 0 $^{\circ}\text{C}$. Then, the reaction mixture was poured into water. The organic layer was extracted with dichloromethane and dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo and purified by column chromatography on silica gel with tetrachloromethane as an eluent to give 121 mg (0.47 mmol, 94%) of 4-isopropyl-7-methoxy-1,2,3-benzotrichiole 2-oxide (**3a**) as a green oil: ^1H NMR (400 MHz) δ 1.23 (d, $J = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.34 (d, $J = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 3.00 (sept, $J = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.91 (s, 3H, OCH_3), 6.86 (d, $J = 8.4$ Hz, 1H, ArH), 7.24 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 22.6, 23.4, 34.8, 56.2, 110.0, 123.8, 125.8, 136.0, 137.5, 153.7; IR (neat) 2962, 2838, 1581, 1469, 1434, 1288, 1124, 1042, 807, 483, 437 cm^{-1} ; MS (70 eV) m/z 260 (M^+);

Anal. Calcd for $C_{10}H_{12}O_2S_3$: C, 46.13; H, 4.64%. Found: C, 46.29; H, 4.61%.

7-Isopropyl-4-methoxy-1,2,3-benzodithiaselenole 2-Oxide (3b). Orange crystals; mp 70.5–71.0 °C; 1H NMR (400 MHz) δ 1.23 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.34 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 3.09 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.90 (s, 3H, OCH_3), 6.87 (d, $J = 8.3$ Hz, 1H, ArH), 7.29 (d, $J = 8.3$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 22.8, 23.6, 34.9, 56.3, 109.6, 125.3, 126.3, 139.0, 154.5; ^{77}Se NMR (76 MHz) δ 1152.3; IR (neat) 2961, 1581, 1557, 1464, 1265, 1222, 1115, 1040, 907, 463 cm^{-1} ; MS (70 eV) m/z 308 (M^+); Anal. Calcd for $C_{10}H_{12}O_2S_2Se$: C, 39.09; H, 3.94%. Found: C, 39.18; H, 3.98%.

4-Isopropyl-7-methoxy-1,2,3-benzodithiaselenole 2-Oxide (3c). Yellow oil; 1H NMR (400 MHz) δ 1.23 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.35 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 2.77 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.90 (s, 3H, OCH_3), 6.90 (d, $J = 8.6$ Hz, 1H, ArH), 7.25 (d, $J = 8.6$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 22.9, 23.7, 37.9, 56.3, 110.2, 125.7, 127.4, 137.9, 139.1, 154.7; ^{77}Se NMR (76 MHz) δ 1149.0; IR (neat) 2960, 1578, 1461, 1430, 1286, 1105, 1030, 807 cm^{-1} ; MS (70 eV) m/z 308 (M^+); Anal. Calcd for $C_{10}H_{12}O_2S_2Se$: C, 39.09; H, 3.94%. Found: C, 39.42; H, 3.91%.

4-Isopropyl-7-methoxy-2,1,3-benzothiadiselenole 2-Oxide (3d). Orange crystals; mp 63.0–64.0 °C; 1H NMR (400 MHz) δ 1.22 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.35 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 2.85 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.89 (s, 3H, OCH_3), 6.91 (d, $J = 8.6$ Hz, 1H, ArH), 7.28 (d, $J = 8.6$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 155.4, 141.1, 140.4, 129.3, 126.1, 110.0, 56.3, 37.9, 23.9, 23.0; ^{77}Se NMR (76 MHz) δ 1159.3, 1156.4; IR (neat) 2960, 1578, 1461, 1430, 1286, 1264, 1105, 1030, 807 cm^{-1} ; MS (70 eV) m/z 356 (M^+); Anal. Calcd for $C_{10}H_{12}O_2SSe_2$: C, 33.91; H, 3.41%. Found: C, 34.24; H, 3.37%.

General Procedure for the Synthesis of 4-Isopropyl-7-methoxy-1,2,3-benzotrithalogenoles 4a–d. To a solution of 1,2,3-benzotrithiole 2-oxide **3a** (87 mg, 0.33 mmol) and sodium iodide (253 mg, 1.67 mmol) in THF (30 mL) and H_2O (3.1 mL) was added a 70% perchloric acid solution (4.0 mL) at 0 °C. After 6 h at room temperature, the reaction mixture was neutralized with aqueous sodium hydrogencarbonate solution and extracted with dichloromethane. The organic layer was washed with aqueous sodium hydrogensulfite solution and dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo and purified by column chromatography on silica gel with tetrachloromethane as an eluent to give 78 mg (0.32 mmol, 97%) of 1,2,3-benzotrithiole **4a** as an orange oil: 1H NMR (400 MHz) δ 1.23 (d, $J = 6.9$ Hz, 6H, $CH(CH_3)_2$), 2.95 (sept, $J = 6.9$ Hz, 1H, $CH(CH_3)_2$), 3.84 (s, 3H, OCH_3), 6.65 (d, $J = 8.4$ Hz, 1H, ArH), 6.97 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.1, 35.0, 56.1, 110.4, 125.3, 137.5, 141.7, 153.9; IR (neat) 2960, 2836, 1582, 1473, 1435, 1279, 1236, 1094, 1039, 803, 580 cm^{-1} ; MS (70 eV) m/z 244 (M^+); Anal. Calcd for $C_{10}H_{12}OS_3$: C, 49.15; H, 4.95%. Found: C, 49.51; H, 4.97%.

7-Isopropyl-4-methoxy-1,2,3-benzodithiaselenole (4b). Reddish brown oil; 1H NMR (400 MHz) δ 1.22 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 3.02 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.83 (s, 3H, OCH_3), 6.66 (d, $J = 8.4$ Hz, 1H, ArH), 7.03 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.3, 35.1, 56.1, 110.4, 125.7, 127.2, 138.3, 142.7, 155.0; ^{77}Se NMR (76 MHz) δ 633.6; IR (neat) 2959, 2835, 1582, 1469, 1434, 1278, 1231, 1181, 1082, 1038, 803 cm^{-1} ; MS (70 eV) m/z 292 (M^+); Anal. Calcd

for $C_{10}H_{12}OS_2Se$: C, 41.23; H, 4.15%. Found: C, 41.52; H, 4.28%.

4-Isopropyl-7-methoxy-1,2,3-benzodithiaselenole (4c). Orange oil; 1H NMR (400 MHz) δ 1.23 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 2.77 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.84 (s, 3H, OCH_3), 6.70 (d, $J = 8.4$ Hz, 1H, ArH), 7.01 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.5, 38.0, 56.2, 110.8, 125.3, 130.1, 140.9, 154.7; ^{77}Se NMR (76 MHz) δ 624.1; IR (neat) 2960, 2835, 1579, 1470, 1433, 1278, 1090, 1031, 804 cm^{-1} ; MS (70 eV) m/z 292 (M^+); Anal. Calcd for $C_{10}H_{12}OS_2Se$: C, 41.23; H, 4.15%. Found: C, 41.52; H, 4.12%.

4-Isopropyl-7-methoxy-2,1,3-benzothiadiselenole (4d). Red oil; 1H NMR (400 MHz) δ 1.22 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 2.83 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.82 (s, 3H, OCH_3), 6.71 (d, $J = 8.4$ Hz, 1H, ArH), 7.06 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.6, 38.0, 56.2, 110.6, 125.7, 129.0, 140.2, 141.7, 155.7; ^{77}Se NMR (76 MHz) δ 655.9, 645.4; IR (neat) 2959, 1578, 1464, 1432, 1278, 1078, 1030, 804 cm^{-1} ; MS (70 eV) m/z 340 (M^+); Anal. Calcd for $C_{10}H_{12}OSSe_2$: C, 35.52; H, 3.58%. Found: C, 35.67; H, 3.34%.

General Procedure for the Synthesis of 4-Isopropyl-7-methoxy-1,2,3-benzotrithalogenoles 4e–h. To a solution of 4-isopropyl-7-methoxy-2,2-dimethyl-1,3,2-benzodithiastannole (**1a**) (181 mg, 0.50 mmol) in THF (10 mL) was added seleninyl chloride (0.042 mL, 0.60 mmol) in THF (6 mL) at -78 °C. After 40 min at -78 °C, the reaction mixture was treated with trimethylsilyl trifluoromethanesulfonate (0.11 mL, 0.6 mmol) in THF (2 mL) at -78 °C. After 30 min at -78 °C, 0.1 M samarium(II) iodide THF solution (12.0 mL, 1.2 mmol) was added at -78 °C. The resulting solution was stirred for 45 min at -78 °C, then was stirred for 90 min at room temperature, and then poured into water. The organic layer was extracted with dichloromethane, washed with sodium chloride solution, and dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo and purified by column chromatography on silica gel with hexane as an eluent to give 119 mg (0.41 mmol, 82%) of 4-isopropyl-7-methoxy-1,3,2-benzodithiaselenole (**4e**) as a reddish brown oil: 1H NMR (400 MHz) δ 1.22 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 3.09 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.84 (s, 3H, OCH_3), 6.60 (d, $J = 8.5$ Hz, 1H, ArH), 6.93 (d, $J = 8.5$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.2, 34.7, 56.1, 110.5, 125.2, 129.9, 138.5, 142.8, 154.7; ^{77}Se NMR (76 MHz) δ 701.3; IR (neat) 2963, 1712, 1577, 1468, 1432, 1275, 1039, 903 cm^{-1} ; MS (70 eV) m/z 292 (M^+); Anal. Calcd for $C_{10}H_{12}OS_2Se$: C, 41.23; H, 4.15%. Found: C, 41.03; H, 4.16%.

7-Isopropyl-4-methoxy-1,2,3-benzothiadiselenole (4f). Brown oil; 1H NMR (400 MHz) δ 1.22 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 3.15 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.83 (s, 3H, OCH_3), 6.61 (d, $J = 8.4$ Hz, 1H, ArH), 7.00 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.4, 34.9, 56.1, 110.4, 125.7, 128.0, 139.4, 143.6, 155.5; ^{77}Se NMR (76 MHz) δ 568.9, 507.6 ($J_{Se-Se} = 311$ Hz); IR (neat) 2958, 1579, 1463, 1432, 1274, 1039, 802 cm^{-1} ; MS (70 eV) m/z 340 (M^+); HRMS m/z Calcd for $C_{10}H_{12}OSSe_2$: 339.8939. Found: 339.8950.

4-Isopropyl-7-methoxy-1,2,3-benzothiadiselenole (4g). Reddish-brown oil; 1H NMR (400 MHz) δ 1.23 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 2.90 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.84 (s, 3H, OCH_3), 6.66 (d, $J = 8.4$ Hz, 1H, ArH), 6.97 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.5, 37.8, 56.2, 110.8, 125.2, 131.4, 140.0, 141.4, 155.6; ^{77}Se NMR (76 MHz) δ 581.8, 501.9 ($J_{Se-Se} = 279$ Hz); IR (neat) 2958, 1575, 1464, 1431, 1274, 1087, 1030, 804 cm^{-1} ; MS (70 eV) m/z 340 (M^+); HRMS

m/z Calcd for $C_{10}H_{12}OSSe_2$: 339.8939. Found: 339.8940.

4-Isopropyl-7-methoxy-1,2,3-benzotriselenole (4h). Dark brown oil; 1H NMR (400 MHz) δ 1.23 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 2.96 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.83 (s, 3H, OCH_3), 6.67 (d, $J = 8.4$ Hz, 1H, ArH), 7.04 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.7, 37.9, 56.2, 110.7, 125.7, 129.7, 141.0, 142.1, 156.3; ^{77}Se NMR (76 MHz) δ 543.0 ($J_{Se-Se} = 292$ Hz), 533.6 ($J_{Se-Se} = 265$ Hz), 436.7 ($J_{Se-Se} = 292$, 265 Hz); IR (neat) 2957, 1576, 1459, 1430, 1275, 1029, 803 cm^{-1} ; MS (70 eV) m/z 386 (M^+ , $C_{10}H_{12}O^{78}Se^{80}Se_2$); HRMS m/z Calcd for $C_{10}H_{12}OS_3$: 387.8384. Found: 387.8389.

General Procedure for the Synthesis of Tellurium-Containing 7-Isopropyl-4-methoxy-1,2,3-benzotrichalcogenoles 4i-l.

To a solution of 2,2-bis(η^5 -pentamethylcyclopentadienyl)-7-isopropyl-4-methoxy-1,3,2-benzothiatelluratitanole (**2c**) (532 mg, 0.85 mmol) in THF (10 mL) was added sulfur dichloride (0.1 mL, 1.7 mmol) at 0 °C. After 30 min at room temperature, the reaction mixture was poured into water. The organic layer was extracted with dichloromethane and dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo and purified by column chromatography on silica gel with hexane as an eluent to give 274 mg (0.81 mmol, 95%) of 7-isopropyl-4-methoxy-1,2,3-benzodithiatellurole (**4i**) as a red oil: 1H NMR (400 MHz) δ 1.21 (d, $J = 6.9$ Hz, 6H, $CH(CH_3)_2$), 3.10 (sept, $J = 6.9$ Hz, 1H, $CH(CH_3)_2$), 3.82 (s, 3H, OCH_3), 6.70 (d, $J = 8.4$ Hz, 1H, ArH), 7.05 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.5, 35.3, 56.2, 109.8, 118.3, 126.7, 139.6, 147.6, 158.2; ^{125}Te NMR (126 MHz) δ 1346.7; IR (neat) 2958, 1577, 1460, 1431, 1261, 1036, 803 cm^{-1} ; MS (70 eV) m/z 342 (M^+); Anal. Calcd for $C_{10}H_{12}OS_2Te$: C, 35.33; H, 3.56%. Found: C, 35.12; H, 3.34%.

7-Isopropyl-4-methoxy-1,2,3-benzothiaselenatellurole (4j). Red crystals; mp 96.0–96.5 °C; 1H NMR (400 MHz) δ 1.21 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 3.22 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.82 (s, 3H, OCH_3), 6.64 (d, $J = 8.4$ Hz, 1H, ArH), 7.05 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.5, 35.2, 56.2, 109.7, 117.9, 126.6, 140.7, 147.9, 158.3; ^{77}Se NMR (76 MHz) δ 295.3 ($J_{77Se-125Te} = 878$ Hz); ^{125}Te NMR (126 MHz) δ 1095.2 ($J_{125Te-77Se} = 878$ Hz); IR (KBr) 2954, 1460, 1275, 1223, 1038, 584 cm^{-1} ; MS (70 eV) m/z 388 (M^+); Anal. Calcd for $C_{10}H_{12}OSSeTe$: C, 31.05; H, 3.13%. Found: C, 30.72; H, 2.93%.

7-Isopropyl-4-methoxy-2,1,3-benzothiaselenatellurole (4k). Red oil; 1H NMR (400 MHz) δ 1.21 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 2.91 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.81 (s, 3H, OCH_3), 6.74 (d, $J = 8.3$ Hz, 1H, ArH), 7.09 (d, $J = 8.3$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.8, 38.2, 56.3, 110.0, 120.6, 126.6, 141.6, 146.8, 158.7; ^{77}Se NMR (76 MHz) δ 657.1; ^{125}Te NMR (126 MHz) δ 1383.9; IR (neat) 2957, 1459, 1429, 1259, 1027, 804 cm^{-1} ; MS (70 eV) m/z 388 (M^+); Anal. Calcd for $C_{10}H_{12}OSSeTe$: C, 31.05; H, 3.13%. Found: C, 31.19; H, 3.13%.

7-Isopropyl-4-methoxy-1,2,3-benzodiselenatellurole (4l). Red crystals; mp 96.0–96.5 °C; 1H NMR (400 MHz) δ 1.21 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 3.04 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.81 (s, 3H, OCH_3), 6.70 (d, $J = 8.3$ Hz, 1H, ArH), 7.09 (d, $J = 8.3$ Hz, 1H, ArH); ^{13}C NMR (101 MHz) δ 23.9, 38.1, 56.3, 110.0, 120.2, 126.6, 142.4, 146.6, 159.0; ^{77}Se NMR (76 MHz) δ 555.2 ($J_{77Se-77Se} = 260$ Hz), 141.7 ($J_{77Se-77Se} = 260$ Hz, $J_{77Se-125Te} = 846$ Hz); ^{125}Te NMR (126 MHz) δ 1153.1 ($J_{125Te-77Se} = 846$ Hz); IR (KBr) 2954, 1573, 1457, 1426, 1272, 1025 cm^{-1} ; MS (70 eV) m/z 433 (M^+); Anal. Calcd for

$C_{10}H_{12}OS_2SeTe$: C, 27.69; H, 2.79%. Found: C, 27.96; H, 2.80%.

General Procedure for the Synthesis of 4-Isopropyl-7-methoxy-1,2,3-benzotrichalcogenolium Hexafluorophosphate $4a^{++}PF_6^-$, $4d^{++}PF_6^-$, and $4h^{++}PF_6^-$. A solution of 4-isopropyl-7-methoxy-1,2,3-benzotriethiole (**4a**) (80 mg, 0.33 mmol) in Et_2O (10 mL) under argon was treated with nitrosonium hexafluorophosphate (60 mg, 0.33 mmol) in acetonitrile (2 mL) at –78 °C. The solution immediately changed from orange to dark blue. After stirring for 30 min at –78 °C, the dark blue product was separated from the solution by filtration. The product was washed with ether and dried under reduced pressure to give 120 mg (0.31 mmol, 94%) of 4-isopropyl-7-methoxy-1,2,3-benzotricholium hexafluorophosphate (**4a⁺⁺PF₆[–]**): Dark blue powder (from ether); mp 95.0–96.5 °C (decomp.); ^{31}P NMR (162 MHz, CD_3CN) δ –143.6 (sept, $J_{P-F} = 706$ Hz); Anal. Calcd for $C_{10}H_{12}OS_3PF_6$: C, 30.85; H, 3.11%. Found: C, 30.90; H, 3.29%; X-band ESR (MeCN, 238 K) $g = 2.013$ ($a_{H1} = 0.110$, $a_{H2} = 0.072$ mT).

4-Isopropyl-7-methoxy-2,1,3-benzothiadiiselenolium Hexafluorophosphate ($4d^{++}PF_6^-$). Dark blue powder (from ether); mp 107.5–108.0 °C (decomp.); ^{31}P NMR (162 MHz, CD_3CN) δ –143.7 (sept, $J_{P-F} = 706$ Hz); X-band ESR (MeCN, 238 K) $g = 2.025$.

4-Isopropyl-7-methoxy-1,2,3-benzotriselenolium Hexafluorophosphate ($4h^{++}PF_6^-$). Dark blue powder (from ether); mp 195.0–197.0 °C (decomp.); ^{31}P NMR (162 MHz, CD_3CN) δ –143.6 (sept, $J_{P-F} = 707$ Hz); Anal. Calcd for $C_{10}H_{12}OS_3PF_6$: C, 22.66; H, 2.28%. Found: C, 22.82; H, 2.26%; X-band ESR (MeCN, 281 K) $g = 2.061$.

General Procedure for the Reduction with Samarium(II) Iodide of 1,2,3-Benzotricholium Hexafluorophosphate ($4a^{++}PF_6^-$).

A solution of 4-isopropyl-7-methoxy-1,2,3-benzotricholium hexafluorophosphate (**4a⁺⁺PF₆[–]**) (47 mg, 0.12 mmol) in THF (5 mL) at –78 °C under argon was treated with 0.1 M samarium(II) iodide THF solution (1.2 mL, 0.12 mmol). The solution was stirred for 30 min at –78 °C, and poured into water. The organic layer was extracted with dichloromethane and dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo and purified by column chromatography on silica gel with tetrachloromethane as an eluent to give 29 mg (0.12 mmol, quant.) of 4-isopropyl-7-methoxy-1,2,3-benzotriethiole (**4a**) as an orange oil.

X-ray Crystal Structure Analyses. Diffraction data were collected on a Rigaku AFC7R diffractometer employing $MoK\alpha$ or $CuK\alpha$ radiation using the $\omega/2\theta$ scan technique. The structure was determined by direct methods (SHELXS86³⁵ or SIR92³⁶) and expanded using Fourier technique (DIRDIF94³⁷). All calculations were performed using the teXsan³⁸ crystallographic software package of Molecular Structure Corporation.

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