Bromine Adducts of 9,10-Diheteratriptycene Derivatives

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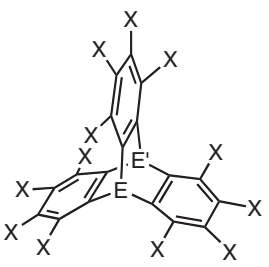
2,3,6,7,14,15-Hexamethyl-9,10-diphosphatriptycene (**1**), 2,3,6,7,14,15-hexamethyl-9-phospha-10-stibatriptycene (**2**), and 2,3,6,7,14,15-hexamethyl-9,10-distibatriptycene (**3**) were synthesized and their molecular structures were determined by X-ray crystallography. Reactions of **2** and **3** with bromine gave the corresponding adducts **8** and **9** with the compositions **2**·2Br_2 and **3**·2Br_2, respectively. Both of the adducts **8** and **9** have a zwitterionic structure composed of a hexacoordinate stiborate anion, ($R_3SbBr_3^-$) and a tetracoordinate phosphonium/stibonium cation (R_3MBr^+: M = P or Sb) in the crystalline state. ^{1}H and ^{31}P NMR spectra of the adduct **8** indicated that the structure is static in solution at room temperature. On the other hand, ^{1}H NMR spectra of the adduct **9** suggested fast topomerization at 27 °C, which becomes slow on the NMR time scale at −90 °C. Recrystallization of the adduct **9** from THF–mesitylene gave crystals with the composition of **3**·2Br_2·2THF, in which each antimony atom bonds to two bromine atoms and one THF oxygen to give an octahedral geometry.

Diheteratriptycenes (=9,10-dihydro-9,10-dihetera-9,10[1′,2′]-benzoanthracenes) with Group 15 elements (N, P, As, Sb, and Bi) at the bridgeheads are an intriguing series of compounds because of their highly symmetric structure and the possible interaction between the bridgehead atoms.[1] Hitherto, compounds shown in Chart 1 are known. Recently, theoretical and electron diffraction studies of perfluoro derivatives of 9,10-distibatriptycene and 9,10-dibismatriptycene have been reported to reveal the geometries around antimony and bismuth atoms and their valence shells.[13] These 9,10-diheteratriptycenes are expected to show interesting reactions at the bridgehead atoms including those with metal carbonyls, halogens, and alkyl halides to give compounds possessing structurally interesting properties.

Oxidation of 9,10-diphosphatriptycene gave the *P*,*P*′-dioxide quantitatively.[3] The reaction of 9,10-diphosphatriptycene with benzyl bromide gave a *P*-monobenzylphosphonium product, while that with methyl triflate gave a mixture of *P*-monomethyl and *P*,*P*′-dimethyl derivatives.[3,14] Complexes[15] of 9,10-diphosphatriptycene derivatives with palladium, tungsten, and molybdenum carbonyls were easily obtained and were shown to have similar properties as those of the corresponding triphenylphosphine–metal complexes. On the other hand, reactions[9] of 9,10-diheteratriptycenes with halogens have scarcely been investigated because the reaction products easily decompose under atmospheric conditions and are insoluble in common organic solvents. Perfluoro-9,10-distibatriptycene reacted with chlorine to give an adduct containing two molecules of chlorine, but its structure was not determined because it was easily hydrolyzed by moisture to give the corresponding dioxide.[9]



E	E'	X
N	N	H[2]
P	P	H,[3] F[8]
As	As	H,[4] F,[8,10,11] Cl[6]
Sb	Sb	H,[5] F,[8–11,13] Cl[6,9]
Bi	Bi	H,[6] F,[8,11,13] Cl[6]
N	P	H[7]
P	As	F[12]
P	Sb	F[8]
As	Sb	F[8,10]

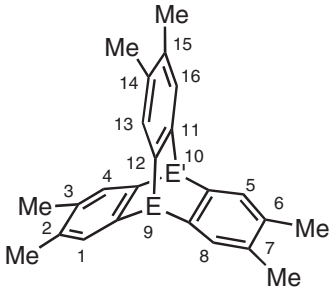
Chart 1.

We wanted to have deeper insight into the chemistry of 9,10-diheteratriptycenes and planned to introduce alkyl groups into the triptycene skeleton in order to increase the solubility in common solvents. Recently, we successfully synthesized 2,3,6,7,14,15-hexamethyl-9,10-distibatriptycene (**3**) under mild conditions, and found that compound **3** could be used for our purpose. We have therefore undertaken studies on a series of 2,3,6,7,14,15-hexamethyl-9,10-diheteratriptycenes.

In this article, we wish to report the synthesis and reactions with bromine of the 2,3,6,7,14,15-hexamethyl derivatives of 9,10-diphosphatriptycene **1**, 9-phospha-10-stibatriptycene **2**, and 9,10-distibatriptycene **3** (Chart 2), and discuss the X-ray molecular structures in the crystalline state and NMR behavior in solution of these compounds as well as their bromine adducts. Some of the previous results have been published.[16]

Results and Discussion

Synthesis of the 9,10-Diheteratriptycenes. Compounds **1**–**3** were synthesized as shown in Scheme 1. Treatment of 4,5-



1: E = E' = P
2: E = P, E' = Sb
3: E = E' = Sb

Chart 2.

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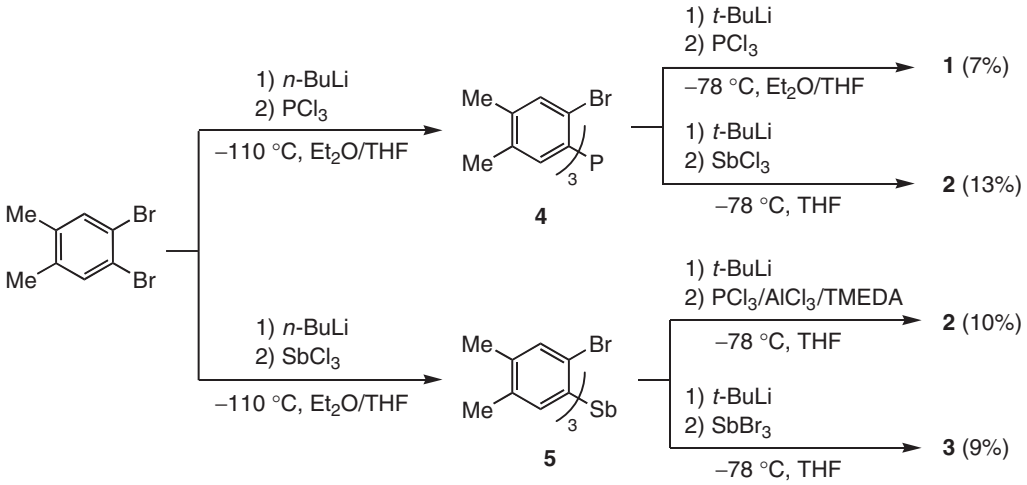


Scheme 1.

dibromo-*o*-xylene with *n*-BuLi at −110 °C[15,17] and subsequent reaction with PCl_3 or $SbCl_3$ gave tris(2-bromo-4,5-dimethylphenyl)phosphine (**4**) or tris(2-bromo-4,5-dimethylphenyl)-stibine (**5**) in 38% and 59% yields, respectively. Triarylphosphine **4** was reacted with *t*-BuLi and then with PCl_3 to give 9,10-diphosphatriptycene **1** in 7% yield. 9-Phospha-10-stibatriptycene **2** was synthesized by the reaction of compound **4** with *t*-BuLi and then addition of $SbCl_3$ in 13% yield. Compound **2** could be obtained by the reaction of compound **5** with *t*-BuLi followed by the addition of PCl_3 in the presence of TMEDA and $AlCl_3$ in 10% yield. Compound **5** was treated with *t*-BuLi and then with $SbBr_3$ to give 9,10-distibatriptycene **3** in 9% yield. These compounds **1**–**3** were obtained in very low yields because these compounds had to be separated from significant quantities of polymer-like side products which were recognized by GPC and ^{1}H NMR spectra to have large molecular weight and dimethylphenyl groups bridged by phosphorus and/or antimony. Suitable purifications of compounds **1**–**3** are shown in the experimental section in detail.

The ^{1}H NMR spectrum of 9,10-diphosphatriptycene **1** in $CDCl_3$ showed a methyl signal at δ 2.18 as a singlet and an aromatic proton signal at δ 7.68 as a multiplet in an integral ratio of 3:1, reflecting the D_{3h} symmetry of the compound. ^{31}P NMR showed a multiplet at δ −46.1.

The ^{1}H NMR spectrum of 9-phospha-10-stibatriptycene **2** in $CDCl_3$ showed two signals at δ 2.14 and 2.18 as methyl groups, and two aromatic proton signals, a singlet at δ 7.68 and a doublet ($J = 12.1$ Hz) at δ 7.90, which were assigned to the 4/5/16-H and 1/8/13-H, respectively. The ^{13}C NMR spectrum gave two aliphatic and six aromatic signals, reflecting the C_{3v} symmetry. The ^{31}P NMR spectrum of **2** showed a quartet ($^3J_{HP} = 11.4$ Hz) at δ −10.1, which was at lower field than that of 9,10-diphosphatriptycene **1** (δ −46.1) and was close to that of triphenylphosphine (δ −4.83). This may be explained as follows: ^{31}P chemical shifts are known to depend on the bond angles of C–P–C,[18] and the phosphorus pyramid becomes flatter and closer to the tetrahedral geometry in the order of **1**, **2**, and triphenylphosphine, the C–P–C angles being 96.9, 100.2, and 102.8°, respectively, as described later.

The ^{1}H NMR spectrum of **3** in $CDCl_3$ showed only two signals at δ 2.18 and 7.81 due to the methyl groups and aromatic protons.

Crystals of compounds **1**–**3** were obtained by recrystallization from CH_2Cl_2, $CHCl_3$, and hexafluorobenzene, respectively, and were characterized by X-ray crystallography. The crystals of **3** contained solvent molecules. The molecular structures of these compounds are shown in Figure 1, and selected bond lengths and angles are compiled in Tables 1 and 2.

Both compounds **1** and **3** have nearly D_{3h} symmetry, while compound **2** shows almost C_{3v} structure. The average lengths of the P–C bonds in **1** and the Sb–C bonds in **3** are 1.840 and 2.152 Å, respectively, and are almost the same as those of Ph_3P (1.831 Å)[19] and Ph_3Sb (2.155 Å),[20] indicating that incorporation into a rigid skeleton does not largely affect the bond lengths. In contrast, the averaged C–P–C angles in **1**, 96.9°, and the C–Sb–C angles in **3**, 94.2°, are both somewhat smaller than the corresponding values in Ph_3P (102.8°)[19] and Ph_3Sb (96.3°)[20] due to the skeletal constraints.

The average P–C and Sb–C bond lengths in 9-phospha-10-stibatriptycene **2** are 1.846 and 2.150 Å, respectively, which are similar to those in **1** and **3**. In contrast, the average C–P–C angle in **2**, 100.1°, is larger than that in 9,10-diphosphatriptycene **1** (96.9°), while the average C–Sb–C angle, 90.3°, is smaller than that in 9,10-distibatriptycene **3** (94.2°). The phosphorus pyramid in **2** is flatter than in **1**, while the antimony pyramid in **2** is sharper than that of **3**, which is ascribed to skeletal constraints.

The cyclic voltammograms of compounds **1**, **2**, and **3** are depicted in Figure 2 together with that of Ph_3P, and $(p\text{-Tol})_3Sb$ (p-Tol = p-tolyl) and the data are summarized in Table 3. In compounds **1**, **2**, and **3** irreversible oxidation waves were observed similar to those of Ph_3P, and $(p\text{-Tol})_3Sb$. Only one irreversible oxidation wave of 9,10-diphosphatriptycene **1** ($E_{1/2} = 0.75$ V vs. Fc/Fc^+) was found at a slightly higher potential than that of Ph_3P ($E_{1/2} = 0.66$ V). On the other hand, two irreversible oxidation waves of 9,10-distibatriptycene **3** were observed at 0.68 and 1.1 V, showing that the first oxidation occurred at somewhat lower potential and the second oxidation occurred at higher potential compared with that of $(p\text{-Tol})_3Sb$ ($E_{1/2} = 0.79$ V vs. Fc/Fc^+). For 9-phospha-10-stibatriptycene **2** the first potential was observed at 0.72 V located between the first potentials of **1** and Ph_3P and the

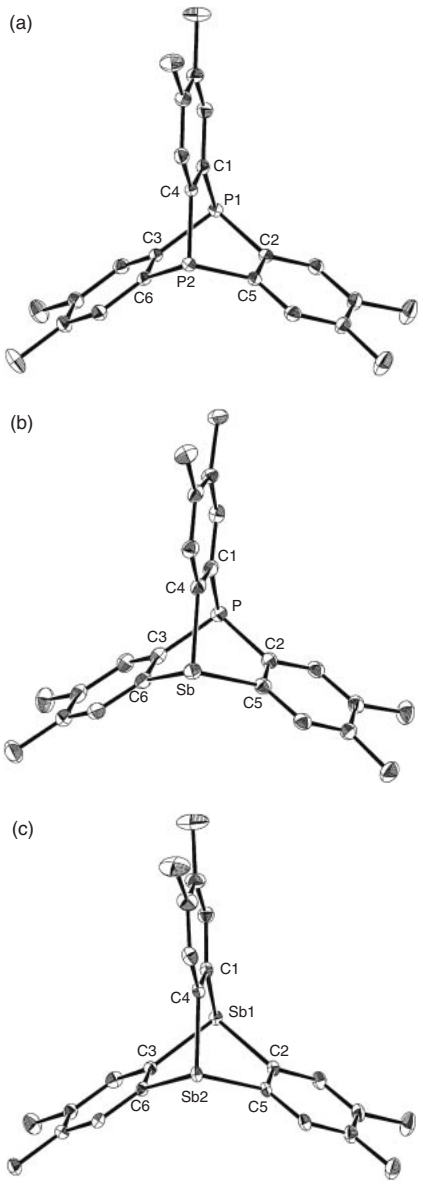


Figure 1. Molecular structures of (a) 9,10-diphosphatriptycene **1**, (b) 9-phospha-10-stibatriptycene **2**, and (c) 9,10-distibatriptycene **3** drawn with 50% probability.

Table 1. Selected Bond Lengths (Å) of Compounds **1**, **2**, and **3**

	1 (E1 = E2 = P)	**2** (E1 = P, E2 = Sb)	**3** (E1 = E2 = Sb)
E1–C1	1.838(1)	1.844(5)	2.151(2)
E1–C2	1.839(1)	1.844(5)	2.150(2)
E1–C3	1.842(1)	1.849(5)	2.154(3)
E2–C4	1.842(1)	2.149(4)	2.156(3)
E2–C5	1.839(1)	2.151(5)	2.149(2)
E2–C6	1.838(1)	2.151(4)	2.151(2)
E1···E2	3.248	3.482	3.692

Table 2. Selected Bond Angles (deg) of Compounds **1**, **2**, and **3**

	1 (E1 = E2 = P)	**2** (E1 = P, E2 = Sb)	**3** (E1 = E2 = Sb)
C1–E1–C2	96.8(1)	100.2(2)	93.7(1)
C1–E1–C3	97.2(1)	100.6(2)	94.6(1)
C2–E1–C3	96.8(1)	99.4(2)	94.0(1)
C4–E2–C5	96.8(1)	90.0(2)	94.1(1)
C4–E2–C6	97.2(1)	90.0(2)	93.6(1)
C5–E2–C6	96.8(1)	90.8(2)	95.2(1)

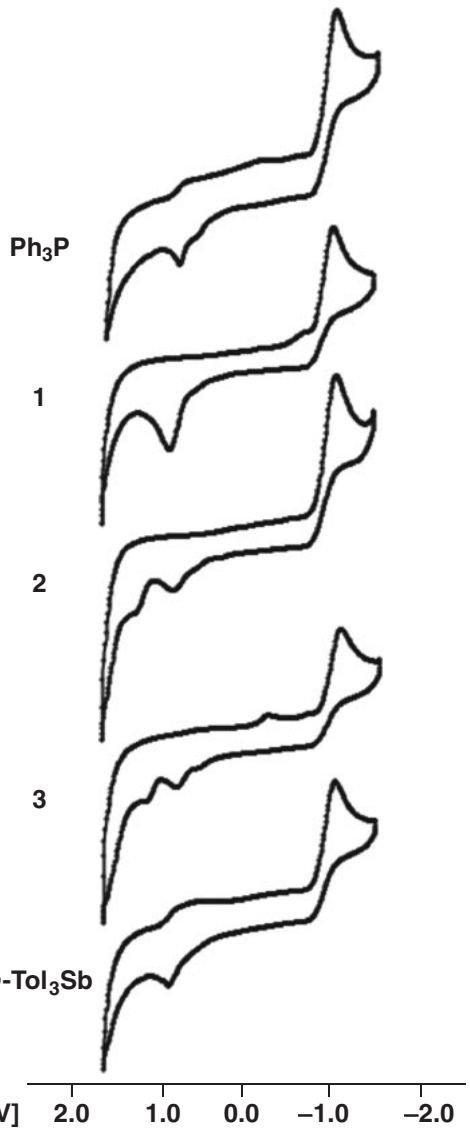


Figure 2. The cyclic voltammograms of Ph_3P, **1**, **2**, **3**, and $(p\text{-Tol})_3Sb$. The data are reported vs. Fc/Fc^+. Conditions: 1.0 mM solutions in 0.1 M $[n\text{-}Bu_4N\cdot ClO_4^-]/CH_2Cl_2$ as supporting electrolyte, 100 mV s^{-1}.

second irreversible oxidation wave appeared at 1.3 V was a slightly higher than the second oxidation wave of compound **3** (1.1 V). These oxidation properties on phosphorus and antimony atoms would depend on structural features, that is, inner angles of C_{ipso}–P–C_{ipso} and C_{ipso}–Sb–C_{ipso} rather than the electrolytic nature of these compounds, judging from consideration of the following situations. As the angles of C_{ipso}–P–C_{ipso} became smaller in the order of Ph_3P (102.8°), 9-phospha-

Table 3. Comparison of CV Data for Ph_3P, Compounds **1**, **2**, **3**, and $(p\text{-Tol})_3Sb$

	Ph_3P	**1**	**2**	**3**	$(p\text{-Tol})_3Sb$
$E_{1/2}(1)$/V	0.66	0.75	0.72	0.68	0.79
$E_{1/2}(2)$/V	—	—	1.3	1.1	—

10-stibatriptycene **2** (100.1°), and 9,10-diphosphatriptycene **1** (96.9°), the first oxidation potentials of these became larger, 0.66, 0.72, and 0.75 V. In the antimony portion, the oxidation potentials, 0.79, 1.1, and 1.3 V, except for the first one of 9,10-distibatriptycene **3** became larger in the order $(p\text{-Tol})_3Sb$ (96.3°), **3** (94.2°), and **2** (90.3°).

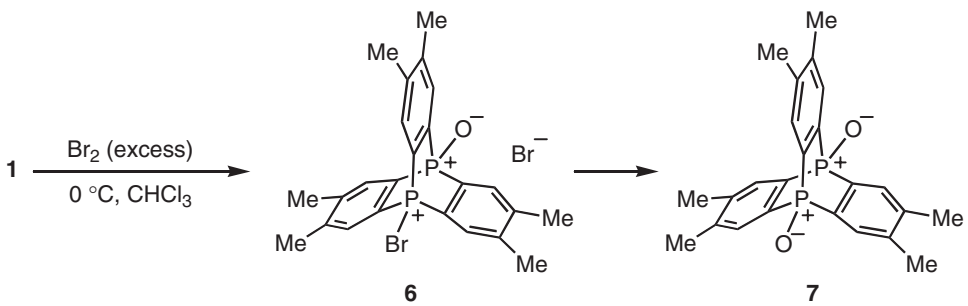
Reaction with Bromine and Structures of the Adducts. The reaction of 9,10-diphosphatriptycene **1** with bromine in $CHCl_3$ was complicated because of the instability of the possible initial product, the bis(bromophosphonium) salt. However, the isolated product was guessed to be the mono-(bromophosphonium) *P*-oxide salt **6** on the basis of a MS peak of m/z 470 as well as ^1H and ^{31}P NMR data (Scheme 2). Compound **6** was presumably formed upon hydrolysis of the initial product with a trace of water in the reaction mixture. The compound **6** was easily hydrolyzed by atmospheric moisture to give quantitatively the *P*,*P*′-dioxide **7**, which was a very stable compound (Scheme 2). This change was also followed by ^{31}P NMR: a mixture of **1** and bromine in $CDCl_3$ initially gave two signals at δ −4.05 and 22.8 assignable to **6**, but after 10 h only one signal at δ −3.77 ascribed to **7**. The *P*,*P*′-dioxide of the parent 9,10-diphosphatriptycene was shown to have a highly symmetric structure by X-ray crystallographic analysis.[3c]

The reaction of compounds **2** and **3** with molecular bromine in CH_2Cl_2 or $CHCl_3$ at 0 °C gave bromine adducts **8** and **9** with the composition **2**·2Br_2 and **3**·2Br_2, respectively, as yellow solids with sufficient solubility in common organic solvents and high stability toward air and moisture (Scheme 3).

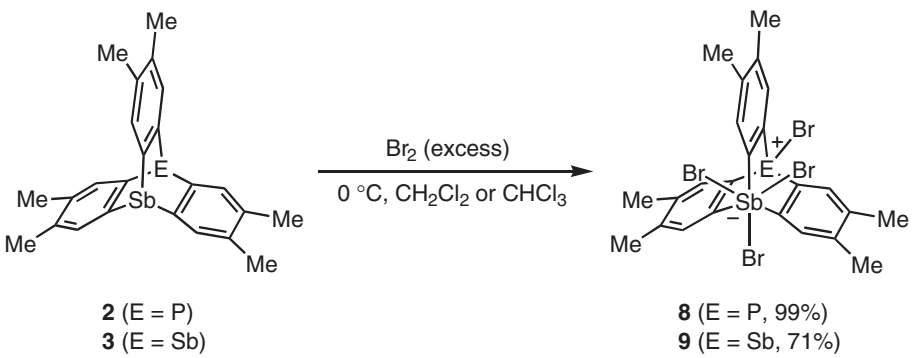
The molecular structures of the bromine adducts **8** and **9** obtained by X-ray crystallography are shown in Figure 3, and selected bond lengths and angles are compiled in Tables 4 and 5. In the bromine adduct **8**, one bromine atom bonds to the phosphorus atom and three bromine atoms bond to the antimony atom. The average angles of Br–P–C and C–P–C are 110.8 and 108.1°, respectively, indicating the tetrahedral geometry around the phosphorus atom. On the other hand, the averaged *trans*-Br–Sb–C angle is 176.8°, indicating the octahedral geometry around the antimony atom. The bond lengths of the P–Br bond and the P–C bonds on average are 2.137 and 1.795 Å, the latter being ca. 0.05 Å shorter than that of **2**, while the average length of the Sb–Br and Sb–C bonds are 2.624 and 2.181 Å, respectively, the latter being ca. 0.03 Å longer than that of **2**. These results suggest that the bromine adduct **8** is an intramolecular salt with a zwitterionic structure composed of a tetracoordinate triarylbromophosphonium cation and a hexacoordinate triaryltribromostiborate anion.

The C–P–C angles of **8** (108.1° on average) are typical for the tetrahedral geometry, though significantly wider than those of **2** (100.1° on average). The C–Sb–C angles in **8** (91.3° on average) are also typical for the octahedral geometry, though slightly larger than those of **2** (90.3° on average). The smaller Sb···P non-bonded distance in **8** (3.267 Å) than in **2** (3.482 Å) will mainly be ascribed to these changes rather than the electrostatic attraction between the opposite charges in **8**.

In the adduct **9**, one antimony atom, Sb1, bonds to one Br atom and is almost tetrahedral. The C–Sb1–C and C–Sb1–Br angles are 103.7 and 114.5°, respectively, on average. The other antimony atom, Sb2, bonds to three Br atoms constituting hexacoordination. The C–Sb2–C and *trans*-C–Sb2–Br angles



Scheme 2.



Scheme 3.

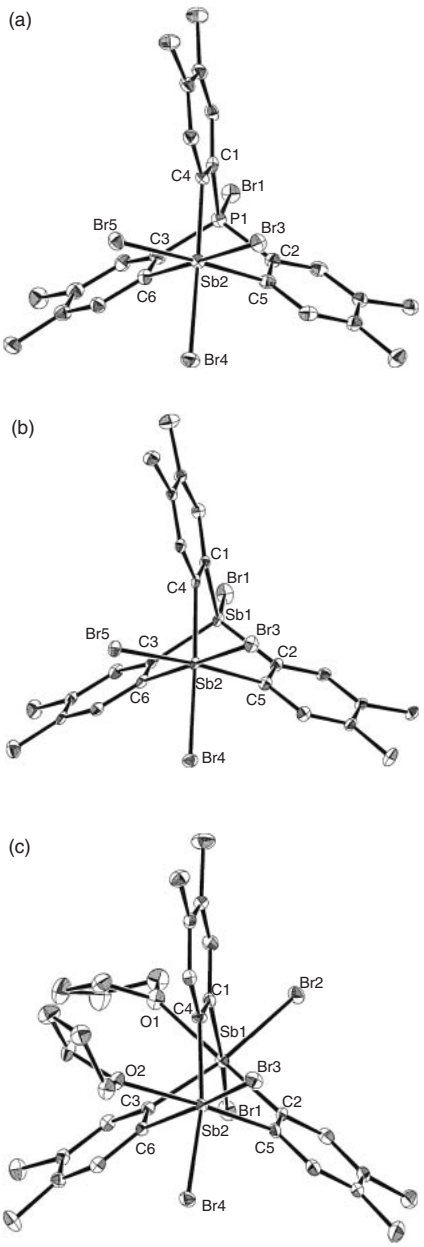


Figure 3. Molecular structures of (a) bromine adduct **8**, (b) bromine adduct **9**, and (c) the THF complex **10** drawn with 50% probability.

are 94.9 and 173.4° on average, respectively, indicating that Sb2 has a slightly distorted octahedral geometry. The Sb1–Br bond (2.407 Å) is considerably shorter than the Sb2–Br bonds (2.647 Å in average), suggesting the cationic nature of the tetracoordinate moiety. These data strongly indicate that the adduct **9** is a zwitterion composed of a triarylbromostibonium cation and a triaryltribromostiborate anion. The Sb2–Br bond lengths are comparable with those in dibromotriphenylstiborane (2.63–2.64 Å), where the bromine atoms are in the apical positions of a trigonal bipyramid (TBP) structure.[21] The smaller Sb···Sb distance in **9** (3.426 Å) than in **3** (3.692 Å) will again be ascribed to these geometric features.

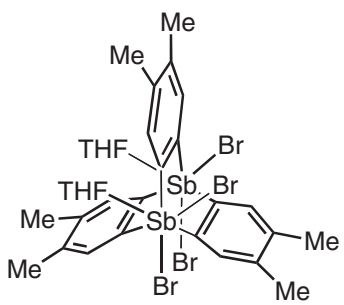
Recrystallization of compound **9** from THF–mesitylene gave crystals **10** with the composition of **3**·2Br_2·2THF (Chart 3).

Table 4. Selected Bond Lengths (Å) of Compounds **8**, **9**, and **10**

	8 (E = P)	**9** (E = Sb1)	**10** (E = Sb1)
E–C1	1.794(5)	2.086(3)	2.151(3)
E–C2	1.790(5)	2.080(3)	2.133(3)
E–C3	1.801(5)	2.096(3)	2.166(3)
Sb2–C4	2.192(5)	2.213(3)	2.159(3)
Sb2–C5	2.176(5)	2.200(3)	2.137(3)
S2b–C6	2.174(5)	2.190(3)	2.160(3)
E–Br1	2.137(2)	2.407(1)	2.604(1)
E–Br2	—	—	2.615(1)
E–O1	—	—	2.478(2)
Sb2–Br3	2.637(1)	2.639(1)	2.640(1)
Sb2–Br4	2.621(1)	2.669(1)	2.582(1)
Sb2–Br5	2.615(1)	2.634(1)	—
Sb2–O2	—	—	2.458(2)
E···Sb2	3.267	3.426	3.534

Table 5. Selected Bond Angles (deg) of Compounds **8**, **9**, and **10**

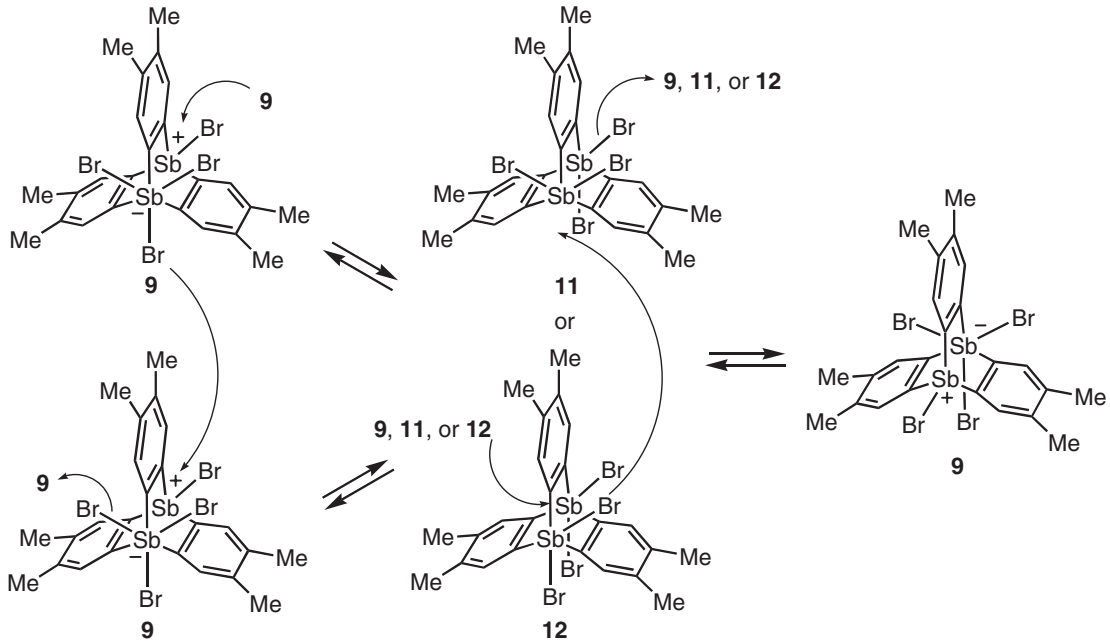
	8 (E = P)	**9** (E = Sb1)	**10** (E = Sb1)
C1–E–C2	108.4(2)	105.7(1)	100.6(1)
C1–E–C3	109.4(2)	100.5(1)	94.2(1)
C2–E–C3	106.6(2)	105.0(1)	97.2(1)
C4–Sb2–C5	92.3(2)	96.3(1)	100.8(1)
C4–Sb2–C6	90.2(2)	92.9(1)	94.7(1)
C5–Sb2–C6	91.5(2)	95.6(1)	96.4(1)
C1–E–Br1	111.0(2)	116.8(1)	163.2(1)
C2–E–Br1	111.5(2)	118.4(1)	—
C3–E–Br1	109.8(2)	108.4(1)	—
C2–E–O1	—	—	177.2(1)
C3–E–Br2	—	—	165.8(1)
C4–Sb2–Br4	176.6(1)	173.6(1)	161.8(1)
C5–Sb2–Br5	176.4(1)	172.0(1)	—
C6–Sb2–Br3	177.4(1)	174.6(1)	166.2(1)
C5–Sb2–O2	—	—	177.1(1)



10

Chart 3. The structue of **10** was obtained by recrystallization of **9** from THF–mesitylene.

X-ray crystallographic analysis of **10** revealed that one THF molecule and two bromine atoms are bonded to each antimony atom, and therefore the compound is regarded as a THF complex of a bis(dibromostiborane) (Figure 3c). Two THF molecules are located in the same notch made of the two benzene rings of the 9,10-distibatriptycene skeleton so that the molecule



Scheme 4.

has a near C_2 (or C_{2v} if conformations of the THF moieties are neglected) symmetry (Figure 3). Selected bond lengths and angles are given in Tables 4 and 5. The *trans*-C–Sb–O and *trans*-C–Sb–Br angles are 177.2 and 164.3° on average, respectively, showing a distorted octahedral geometry around the antimony atoms. The Sb1–C2 and Sb2–C5 bonds (2.133 and 2.137 Å) are shorter than the other Sb–C bonds (2.16 Å in average) presumably because of the trans effect of THF oxygen atoms locating against C2 and C5. The non-bonded Sb···Sb distance in **10** (3.534 Å) lies in between those in **3** and **9**.

Highly coordinate compounds have been known to become increasingly stable by increasing presence of electron-withdrawing groups and elements because the Lewis acidity of the center atom is increased.[1c,22,23] According to a general rule of the stabilization of hypervalent compounds, the THF complex **10** was constructed by antimony atom with two bromine atoms and three aryl groups as Lewis acid and a THF molecule as Lewis base. Hexacoordinate stiborate anions of **8** and **9** with three bromine atoms and three aryl groups were also formed because dibromotriarylstiborane and bromide ion behaved as Lewis acid and base, respectively. Additionally, bromine adducts **8** and **9** had phosphonium or stibonium cation as counter ion toward antimony ate complex to be isolated as intramolecular salts.

NMR Studies of the Bromine Adducts. The ^{1}H NMR spectrum of compound **8** in CD_2Cl_2 at room temperature showed two methyl singlets at δ 2.29 and 2.37 and two aromatic doublets at δ 7.44 ($J_{PH} = 18.5$ Hz) and 8.44 ($J_{PH} = 8.9$ Hz). The signal at δ 8.44 was assigned to the *peri*-protons close to the antimony atom based on the smaller coupling with the phosphorus and the deshielding effect of the nearby antimony atom. ^{31}P NMR spectrum of **8** showed the signal at δ 37.4 at a significantly lower field than that of 9-phospha-10-stibatriptycene **2** (δ −10.1) because of the cationic nature of the P atom and the bromine substitution.

On the other hand, the ^{1}H NMR spectrum of compound **9** in CD_2Cl_2 at 27 °C showed only two singlets at δ 2.34 and 7.87 with an intensity ratio of 3:1 due to the methyl and the aromatic protons, respectively, which are contradictory to the structure obtained in the crystalline state. Upon lowering the temperature, however, each singlet broadened and split into two equally intense singlets. The aromatic signal decoalesced at ca. −20 °C and gave two sharp singlets at δ 7.20 and 8.35 at −90 °C. The methyl protons appeared as two singlets at δ 2.20 and 2.29 at −90 °C. The temperature dependence of the line shape could be explained in terms of the interchange between the two topomeric structures as shown in Scheme 4. This process takes place fast at room temperature and the averaged spectrum is observed in ^{1}H NMR spectroscopy. At −90 °C, the interchange is sufficiently slow on the NMR timescale. The lower-field aromatic signal at δ 8.35 is ascribed to the *peri*-protons close to the stiborate moiety as in the case of compound **8**.

Although the detailed mechanism of the topomerization is still uncertain, it seems to occur intermolecularly, because the topomerization rate was shown to be dependent on the concentration of **9**. The rate constants, which were obtained by line shape analysis using DNMR3,[24] in CD_2Cl_2 at −83 °C, are 52, 83, and 113 s^{-1} for the 2.63, 5.72, and 10.8 M solutions, respectively, which correspond to the free energies of activation of 39.6, 38.9, and 38.4 kJ mol^{-1}.[16] This notion is further supported by the finding that addition of tetrabutylammonium bromide in the sample increased the rate so that the signal splitting could not be observed even at −90 °C. It is speculated that two bromide ions move from the stiborate site to the stibonium site stepwise by way of a bis(dibromostiborane) intermediate **11**, which would be unstable under the isolation conditions but could be significantly stabilized in the presence of Lewis bases such as THF to give compound **10**.

^{1}H NMR spectrum of the THF complex **10** in CD_2Cl_2 gives signals ascribed to **9** and THF, indicating that **10** dissociates in

solution to give the bis(dibromostiborane) **12** and THF, and the former immediately isomerizes to **9** because the intramolecular salts **9** is the most stable species thermodynamically in these equilibrium systems.

Studies of the reactions of 9,10-diheteratriptycenes **1**–**3** with other halogens, F_2, Cl_2, and I_2, and also with organic electrophiles such as alkyl halides are in progress.

Experimental

General Procedure. All reactions were carried out under argon atmosphere except for bromination reactions. Preparative gel permeation chromatography (GPC) was performed on LC-908, LC-918, or LC-9201 with JAIGEL 1H column (Japan Analytical Industry) with chloroform as the eluent. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker ARX300 (300/75/121 MHz) or a Bruker Avance 600 spectrometer (600/151/243 MHz). Chemical shifts are reported in δ using the residual proton signal of the deuterated solvents [CD_2Cl_2 (δ_H 5.32)] or the signal of tetramethylsilane [TMS (δ_H 0.00)] as internal standards for ^{1}H NMR spectra, the central peak of the solvent signal [$CDCl_3$ (δ_C 77.0)] for ^{13}C NMR spectra, and the signal of phosphoric acid [85% H_3PO_4 (δ_P 0.00) in a sealed tube] as external standard for ^{31}P NMR spectra, respectively. Letters p, s, t, and q given with the ^{13}C chemical shifts denote primary, secondary, tertiary, and quaternary, respectively. MS spectra were taken on a Hitachi-2500 mass spectrometer. Melting points were determined by differential scanning calorimetry using a DSC-50 differential scanning calorimeter. Elemental analysis was performed on a Perkin-Elmer CHN/S 2400II analyzer. Cyclic voltammetry measurements were carried out with a Hokuto Denko Corporation HZ-5000 analyzer.

Tris(2-bromo-4,5-dimethylphenyl)phosphine (4). To a solution of 4,5-dibromo-*o*-xylene (16.0 g, 60.6 mmol) in THF–Et_2O (9:8, 170 mL) at −110 °C was added 1.54 M (1 M = 1 mol dm^{-3}) *n*-BuLi in hexane (39.0 mL, 60.1 mmol), and the reaction mixture was stirred for 1 h at −110 °C. To the mixture was added a solution of PCl_3 (1.3 mL, 14.9 mmol) in Et_2O (20 mL) at −110 °C, and the mixture was stirred for 1.5 h at −110 °C and gradually warmed to rt. The mixture was quenched with H_2O (200 mL) and was extracted with $CHCl_3$ (200 mL × 3). The organic extracts were washed with aq NaCl (200 mL), dried over $MgSO_4$, and evaporated to give **4** as a white solid (3.32 g, 5.69 mmol, 38%), mp 249–250 °C (dec.) (from CH_2Cl_2/hexane). Found: C, 49.63; H, 4.17%. Calcd for $C_{24}H_{24}Br_3P$: C, 49.43; H, 4.15%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.07 (9H, s), 2.25 (9H, s), 6.48 (3H, s), 7.39 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.4 (p), 19.5 (p), 127.0 (q, J = 57.4 Hz), 133.5 (q, J = 10.5 Hz), 133.8 (t, J = 2.9 Hz), 135.8 (t), 136.1 (q), 139.6 (q). ^{31}P NMR (121 MHz, $CDCl_3$): δ −4.75 (s). MS (70 eV) m/z 580 (M^+, 100%).

Tris(2-bromo-4,5-dimethylphenyl)stibine (5). To a solution of 4,5-dibromo-*o*-xylene (2.60 g, 9.85 mmol) in THF–Et_2O (1:1, 100 mL) at −110 °C was added 1.54 M *n*-BuLi in hexane (6.2 mL, 9.55 mmol), and the reaction mixture was stirred for 30 min at −110 °C. To the mixture was added a solution of $SbCl_3$ (758 mg, 3.3 mmol) in THF–Et_2O (1:1, 50 mL) at −110 °C, and the mixture was stirred for 12 h at −110 °C. The mixture was quenched with aq NH_4Cl (200 mL) and was extracted with $CHCl_3$ (200 mL × 3). The organic extracts were washed with aq NaCl (200 mL), dried over $MgSO_4$, and evaporated to give **5** as a white solid (1.32 g, 1.96 mmol, 59%), mp 251–252 °C (dec.) (from EtOAc). Found: C, 42.74; H, 3.80%. Calcd for $C_{24}H_{24}Br_3Sb$: C, 42.77; H, 3.59%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05 (9H, s), 2.23 (9H, s), 6.77 (3H, s), 7.36 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.4 (p), 19.5 (p), 129.4 (q), 132.8 (q), 136.5 (t), 138.2 (t), 139.8 (q), 139.9 (q). MS (70 eV) m/z 670 (M^+, 100%).

2,3,6,7,14,15-Hexamethyl-9,10-diphosphatriptycene (1). To a solution of tris(2-bromo-4,5-dimethylphenyl)phosphine (**4**) (3.42 g, 5.87 mmol) in THF–Et_2O (7:5, 100 mL) was added 1.54 M *t*-BuLi in pentane (8.0 mL, 12.3 mmol) at −78 °C, and then the reaction mixture was stirred for 1 h at −78 °C. To the mixture was added PCl_3 (0.60 mL, 6.88 mmol) at −78 °C, and the mixture was stirred for 1.5 h at −78 °C. To the reaction mixture was added water (100 mL) and the mixture was extracted with $CHCl_3$ (100 mL × 4). The organic extracts were washed with aq NaCl (50 mL), dried over $MgSO_4$, and evaporated to give crude material. Column chromatography (silica gel, $CHCl_3$) of the residue gave the 9,10-diphosphatriptycene **1** (148 mg, 0.39 mmol, 7%) as white solid, mp >300 °C (dec.) (from hexane). Found: C, 77.37; H, 6.73%. Calcd for $C_{24}H_{24}P_2$: C, 76.99; H, 6.46%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.18 (18H, s), 7.68 (6H, m). ^{13}C NMR (151 MHz, $CDCl_3$): δ 19.5 (p), 135.6 (t), 136.6 (q, J = 5.6 Hz), 142.9 (q, J = 4.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ −46.1 (m). MS (70 eV) m/z 374 (M^+, 100%).

2,3,6,7,14,15-Hexamethyl-9-phospha-10-stibatriptycene (2): With Phosphine Compound 4. To a solution of tris(2-bromo-4,5-dimethylphenyl)phosphine (**4**) (583 mg, 1.00 mmol) in THF (20 mL) was added 1.59 M *t*-BuLi in pentane (3.8 mL, 6.04 mmol) at −78 °C, and then the reaction mixture was stirred for 20 min at −78 °C. To the mixture was added $SbCl_3$ (280 mg, 1.23 mmol) at −78 °C, and the mixture was stirred for 12 h at −78 °C. To the reaction mixture was added aq NH_4Cl (20 mL) and the mixture was extracted with $CHCl_3$ (20 mL × 4). The organic extracts were washed with aq NaCl (20 mL), dried over $MgSO_4$, and evaporated to give 9-phospha-10-stibatriptycene **2** (62 mg, 0.13 mmol, 13%) as white solid.

2,3,6,7,14,15-Hexamethyl-9-phospha-10-stibatriptycene (2): With Stibine Compound 5. To a solution of tris(2-bromo-4,5-dimethylphenyl)stibine (**5**) (2.09 g, 3.10 mmol) in THF (100 mL) was added 1.54 M *t*-BuLi in pentane (13.4 mL, 20.6 mmol) at −78 °C, and then the reaction mixture was stirred for 30 min at −78 °C. To the mixture was added $AlCl_3$ (620 mg, 4.65 mmol), TMEDA (4.0 mL, 3.13 mmol), and PCl_3 (0.19 mL, 2.18 mmol) at −78 °C, and the mixture was stirred for 12 h at −78 °C. To the reaction mixture was added aq NH_4Cl (100 mL) and the mixture was extracted with $CHCl_3$ (100 mL × 4). The organic extracts were washed with aq NaCl (50 mL), dried over $MgSO_4$, and evaporated to give white material. Soxhlet extraction with hexane gave the 9-phospha-10-stibatriptycene **2** (144 mg, 0.31 mmol, 10%) as white solid, mp 257–258 °C (dec.) [from CH_2Cl_2–hexane (1:1)]. Found: C, 61.99; H, 5.37%. Calcd for $C_{24}H_{24}PSb$: C, 61.97; H, 5.20%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14 (9H, s, 3/6/15-Me), 2.18 (9H, s, 2/7/14-Me), 7.68 (3H, s, 4/5/16-H), 7.90 (3H, d, J_{PH} = 12.1 Hz, 1/8/13-H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 19.3 (p, 3/6/15-Me), 19.5 (p, 2/7/14-Me), 136.4 (t, J = 52.2 Hz, 1/8/13-C), 136.5 (t, J = 1.5 Hz, 4/5/16-C), 137.0 (q, J = 29.1 Hz, 2/7/14-C), 137.7 (q, J = 1.7 Hz, 3/6/15-C), 140.4 (q, J = 5.3 Hz, 4a/10a/11-C), 146.3 (q, J = 3.5 Hz, 8a/9a/12-C). ^{31}P NMR (121 MHz, $CDCl_3$): δ −10.1 (q, $^3J_{HP}$ = 11.4 Hz). MS (70 eV) m/z 464 (M^+, 100%), 239 [$P(Me_2–C_6H_2)_2$, 15%], 225 [$Sb(Me_2–C_6H_2)$, 15%], 135 [$P(Me_2–C_6H_2)$, 3%].

2,3,6,7,14,15-Hexamethyl-9,10-distibatriptycene (3). To a solution of tris(2-bromo-4,5-dimethylphenyl)stibine (**5**) (948 mg, 1.71 mmol) in THF (100 mL) was added 1.54 M *t*-BuLi in pentane (5.35 mL, 8.24 mmol) at −78 °C, and the reaction mixture was

Table 6. Crystal Data of Compounds **1**, **2**, and **3**, and Parameters for Data Collection, Structure Determination, and Refinement

	1	**2**	**3**
Formula	$C_{24}H_{24}P_2$	$C_{24}H_{24}PSb$	$C_{24}H_{24}Sb_2 \cdot 0.5C_6F_6$
MW	374.37	465.15	648.96
Crystal system	monoclinic	rhombohedral	monoclinic
Space group	$C2/c$	$R\bar{3}$	$C2/c$
Z	4	18	8
a/Å	16.681(2)	20.086(1)	26.410(1)
b/Å	9.620(1)	20.086(1)	10.113 (1)
c/Å	13.949(1)	26.775(1)	20.503(1)
α/deg	90	90	90
β/deg	108.506(1)	90	116.932(1)
γ/deg	90	120	90
V/Å^3	2122.7(3)	9355.5(5)	4882.1(3)
D_{calcd}/g cm^{-3}	1.171	1.486	1.766
$F(000)$	792	4212	2520
μ(Mo Kα)/Å	0.71070	0.71070	0.71070
Temp/K	103	103	113
$2\theta_{max}$/°	20	20	20
No. of reflections measured			
Total	5663	17749	16932
Unique	2397	4886	5283
No. of refinement variables	122	242	295
$R1$ (all data)	0.0408	0.0583	0.0273
$wR2$ (all data)	0.0909	0.1342	0.0660
GOF	1.048	1.089	1.081

stirred for 30 min at −78 °C. To the mixture was added a solution of $SbBr_3$ (444 mg, 1.23 mmol) in THF (20 mL) at −78 °C, and the mixture was stirred for 12 h at −78 °C. To the reaction mixture was added aq NH_4Cl (50 mL) and the mixture was extracted with Et_2O (100 mL × 3). The organic extracts were washed with aq NaCl (50 mL), dried over $MgSO_4$, and evaporated to give white solid. Column chromatography (silica gel, $CHCl_3$) and subsequent GPC of the residue gave the 9,10-distibatriptycene **3** (67 mg, 0.121 mmol, 9%) as white solid (from benzene), mp 285–290 °C (dec.). Found: C, 52.00; H, 4.46%. Calcd for $C_{24}H_{24}Sb_2$: C, 51.85; H, 4.35%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.18 (18H, s), 7.81 (6H, s). ^{13}C NMR (151 MHz, $CDCl_3$): δ 19.4 (p), 136.9 (q), 137.6 (t), 146.1 (q). MS (70 eV) m/z 554 (M^+, 13%), 226 [Sb(Me$_2$–C$_6$H$_3$), 100%].

Reaction of Compound 1 with Bromine. To a solution of the 9,10-diphosphatriptycene **1** (10 mg, 0.027 mmol) in $CHCl_3$ (3 mL) was added bromine (10 µL, 0.195 mmol) at 0 °C. The reaction mixture was stirred for 0.5 h at 0 °C. The reaction solvent was removed under reduced pressure and the residue was washed with hexane to give the mono(bromophosphonium) *P*-oxide salt **6** quantitatively as an easily hydrolysable compound. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.41 (9H, s), 2.47 (9H, s), 8.02 (3H, m), 8.10 (3H, m). ^{13}C NMR (151 MHz, $CDCl_3$): δ 20.2 (p), 20.4 (p), 124.2 (q), 131.8 (t), 131.9 (t), 134.0 (q), 142.2 (q, J = 14.5 Hz), 144.0 (q, J = 8.8 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ −4.05 (d, J = 55.1 Hz), 22.8 (d, J = 62.4 Hz). SIMS m/z 470 (M^+, 12%), 390 (M − Br, 100%). When the reaction mixture was left standing overnight, the *P,P′*-dioxide **7** was obtained as white solid (10 mg, 0.025 mmol, 93%), mp 270–275 °C (dec.). Found: C, 70.88; H, 6.20%. Calcd for $C_{24}H_{24}P_2O_2$: C, 70.93; H, 5.95%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.29 (18H, s), 7.92 (6H, m). ^{13}C NMR (151 MHz, $CDCl_3$): δ 19.7 (p), 130.2 (t, J = 7.7 Hz), 135.6 (q, J = 52.7 Hz), 139.2 (q, J = 4.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ −3.77 (m). MS (70 eV) m/z 406 (M^+, 100%).

Bromine Adduct 8. To a solution of the 9-phospha-10-stibatriptycene **2** (15 mg, 0.032 mmol) in $CHCl_3$ (3 mL) was added bromine (20 µL, 0.390 mmol) at 0 °C. The reaction mixture was stirred for 0.5 h at 0 °C. The reaction solvent was removed under reduced pressure and the residue was washed with hexane to give the adduct **8** as yellow solid (25 mg, 0.032 mmol, 99%), mp 227–230 °C (dec.). Found: C, 36.49; H, 3.33%. Calcd for $C_{24}H_{24}Br_4PSb$: C, 36.73; H, 3.08%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.29 (9H, s, 3/6/15-Me), 2.37 (9H, s, 2/7/14-Me), 7.44 (3H, d, J_{PH} = 18.5 Hz, 1/8/13-H), 8.44 (3H, d, J_{PH} = 8.9 Hz, 4/5/16-H). ^{13}C NMR (151 MHz, CD_2Cl_2, 27 °C): δ 19.5 (p, CH_3), 20.0 (p, CH_3), 123.4 (q, J = 82.4 Hz), 126.6 (q, J = 9.2 Hz), 137.6 (t, J = 14.0 Hz), 138.0 (t, J = 14.1 Hz), 144.1 (q, J = 3.7 Hz), 158.1 (q, J = 13.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 37.4 (m). SIMS m/z 705 (M − Br + H, 0.2%), 545 (M − 3Br, 20%), 464 (M − 4Br, 0.1%).

Bromine Adduct 9. To a solution of the 9,10-distibatriptycene **3** (64 mg, 0.116 mmol) in CH_2Cl_2 (10 mL) was added bromine (20 µL, 0.390 mmol) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C. The solvent was removed under reduced pressure and the residue was washed with hexane to give the adduct **9** as yellow solid (64 mg, 0.082 mmol, 71%), mp 203–204 °C (dec.). Found: C, 33.20; H, 3.02%. Calcd for $C_{24}H_{24}Br_4Sb_2$: C, 32.92; H, 2.76%. ^{1}H NMR (600 MHz, CD_2Cl_2, 27 °C): δ 2.34 (18H, s), 7.87 (6H, s); ^{13}C NMR (151 MHz, CD_2Cl_2, 27 °C): δ 20.0 (p), 134.5 (q), 138.1 (t), 142.3 (q). SIMS m/z 795 (M − Br + H, 80%), 312 ($(C_6H_2(CH_3)_2)_3$, 100%).

Bis(dibromostiborane)–THF Complex 10. Recrystallization of compound **9** from THF–mesitylene gave yellow solid of **10**, mp 204–205 °C (dec.). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.82 (4H, m, THF), 2.34 (18H, s, **9**), 3.68 (4H, m, THF), 7.87 (6H, s, **9**).

Table 7. Crystal Data of Compounds **8**, **9**, and **10**, and Parameters for Data Collection, Structure Determination, and Refinement

	8	**9**	**10**
Formula	$C_{24}H_{24}Br_4PSb \cdot CHCl_3$	$C_{24}H_{24}Br_4Sb_2 \cdot CHCl_3$	$C_{24}H_{24}Br_4Sb_2 \cdot 2THF$
MW	904.16	994.94	1019.78
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
Z	4	4	8
a/Å	11.092(2)	11.080(1)	21.246(1)
b/Å	18.733(4)	18.922(1)	19.999(1)
c/Å	14.192(3)	14.346(1)	17.183(1)
α/deg	90	90	90
β/deg	98.842(1)	100.184(1)	111.337(1)
γ/deg	90	90	90
V/Å^3	2913.6(11)	2960.2(2)	6800.4(4)
D_{calcd}/g cm^{-3}	2.061	2.232	1.992
$F(000)$	1728	1872	3920
μ(Mo Kα)/Å	0.71070	0.71070	0.71070
Temp/K	113	113	113
$2\theta_{max}$/°	20	20	20
No. of reflections measured			
Total	26063	19685	22747
Unique	8247	5973	6788
No. of refinement variables	313	313	367
$R1$ (all data)	0.0592	0.0271	0.0295
$wR2$ (all data)	0.1231	0.0561	0.0622
GOF	1.029	1.063	1.070

Cyclic Voltammetry. The three-electrode systems consisted of Glass Carbon, a Pt wire as secondary electrode, and an Ag wire as the pseudo-reference electrode. The cyclic voltammograms were recorded 1.0 mM in CH_2Cl_2 solution with 0.1 M [TBAP; n-$Bu_4N^+ \cdot ClO_4^-$] as the supporting electrolyte and data were reported relative to the ferrocene/ferrocenium couple (+0.31 V) with 0.1 M [n-$Bu_4N^+ \cdot ClO_4^-$] in CH_2Cl_2.

X-ray Crystallography. Single crystals of **1**, **2**, **3**, **8**, **9**, and **10** were grown by the slow evaporation of suitable saturated solutions at room temperature. A colorless block crystal for each of **1**, **2**, **3**, **8**, **9**, and **10** having approximate dimensions of 0.20 × 0.20 × 0.20, 0.20 × 0.20 × 0.20, 0.60 × 0.40 × 0.25, 0.20 × 0.20 × 0.15, 0.20 × 0.20 × 0.15, and 0.15 × 0.10 × 0.05 mm^3, respectively, was mounted on a glass fiber. All measurements were made on a Rigaku Mercury-CCD and Bruker AXS Inc. SMART APEXII with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. Crystallographic data are summarized in Tables 6 and 7.

Crystallographic data of **1**–**3** and **8**–**10** have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-725596, -725597, -269390, -725594, -269391, and -725595 for compound Nos. **1**–**3** and **8**–**10**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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