

Headline Articles

Syntheses, Structures and Properties of Kinetically Stabilized Distibenes and Dibismuthenes, Novel Doubly Bonded Systems between Heavier Group 15 Elements.

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The first stable distibene ($\text{RSb}=\text{SbR}$) and dibismuthene ($\text{RBi}=\text{BiR}$) were successfully synthesized by taking advantage of steric protection using an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). Since it is quite difficult to investigate the reactivities of the distibene ($\text{TbtSb}=\text{SbTbt}$) and dibismuthene ($\text{TbtBi}=\text{BiTbt}$) in solution due to their extremely low solubility values, similarly overcrowded distibene and dibismuthene, $\text{BbtE}=\text{EBbt}$ ($\text{E} = \text{Sb, Bi}$), with sufficiently high solubility were also synthesized using another bulky substituent, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl group (Bbt). The crystallographic analysis and spectroscopic studies of these stable dipnictenes led to the systematic comparison of structural parameters and physical properties for all homonuclear doubly bonded systems between heavier group 15 elements. In addition to these experimentally obtained results, theoretical calculations for these doubly bonded systems also revealed the intrinsic character of dipnictenes.

The syntheses of stable compounds containing multiple bonds between heavier main group elements have been among the frontiers of great interest in chemical research.¹ The history of heavier congeners of azo-compounds dates back to 1877, when Köller and Michaelis reported that condensation reaction of PhPCl_2 and PhPH_2 resulted in the formation of a compound formulated as “ $\text{C}_6\text{H}_5\text{P}=\text{PC}_6\text{H}_5$ ”, which they dubbed “phosphobenzene”.² However, subsequent X-ray diffraction studies have revealed that this product has a pentameric or hexameric structure in the solid state.³ A similar mistake arose in the case of arsenic. The structure of the chemotherapeutic drug “Salvarsan” was first formulated as a monomeric diarsene structure by Ehrlich,⁴ but here again, X-ray crystallographic work on the compound of the empirical composition $\text{C}_6\text{H}_5\text{As}$ revealed their

oligomeric character.⁵ These failures developed a concept that compounds featuring double bonds between the heavier main group elements would not be isolable, which has been sometimes referred to as “the classical double-bond rule”.⁶ The pioneering syntheses and isolation of reactive doubly bonded systems stemmed from a realization that the steric bulk of sufficiently large ligands makes it possible to avoid the oligomerization of these reactive multiple bonds. Namely, the first disilene ($\text{Mes}_2\text{Si}=\text{SiMes}_2$; $\text{Mes} = \text{mesityl}$)⁷ and the first diphosphene ($\text{Mes}^*\text{P}=\text{PMes}^*$; $\text{Mes}^* = 2,4,6\text{-tri-}i\text{-butylphenyl}$)⁸ were successfully synthesized by the kinetic stabilization of reactive double-bonds using bulky ligands in 1981. The synthesis of these compounds is a significant landmark in the chemistry of doubly bonded systems between the heavier main group elements. Nowadays, as for the heavier dipnictene series, numerous examples of kinetically stabilized diphosphenes ($\text{RP}=\text{PR}$),⁹ diarsenes ($\text{RAs}=\text{AsR}$),¹⁰ and phospharsenes ($\text{RP}=\text{AsR}$)¹¹ have been isolated and fully characterized, and their various chemical properties have been revealed.

Although distibene ($\text{RSb}=\text{SbR}$) and dibismuthene ($\text{RBi}=\text{BiR}$) should be the key compounds of great importance

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in the systematic elucidation of the intrinsic nature of low-coordinated compounds of heavier group 15 elements, no stable doubly bonded compound between two antimony atoms or two bismuth atoms had been reported so far except for a few transition-metal complexes,¹² in which the multiple bond was supported by metal bridging, until our successful syntheses and isolation of the first stable distibene¹³ and dibismuthene¹⁴ utilizing a very effective and bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group (denoted as Tbt hereafter),¹⁵ which we developed during the course of our investigation on the kinetic stabilization of low-coordinated highly reactive species. The synthetic route of these Tbt-substituted distibene and dibismuthene was based on an indirect way, that is, the deselenation reaction of the six-membered precursors, (TbtESe)₃ (E = Sb and Bi). At this stage, however, we could not sufficiently elucidate the reactivities of these new dipnictenes in solution due to their extremely low solubility in organic solvents. Later on, Power and co-workers also synthesized another type of stable distibenes and dibismuthenes substituted by bulky 2,6-Ar₂C₆H₃ groups (Ar = mesityl or 2,4,6-triisopropylphenyl) via simple reductive coupling reaction of the corresponding dihalide precursors, which is the traditional method for the synthesis of homonuclear double-bond compounds between the heavier group 15 elements.¹⁶ On the other hand, we have developed another bulky aromatic substituent, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt group),¹⁷ which is expected to be a potentially more useful steric protection group than Tbt group. Indeed, the first stable stibabismuthene (BbtSb=BiBbt), a novel heteronuclear double-bond compound between antimony and bismuth, has been synthesized by taking advantage of the Bbt group.¹⁸ The syntheses of a Bbt-substituted distibene and dibismuthene were examined in the hope of obtaining a stable distibene and dibismuthene which would have different solubility from the Tbt-substituted ones. The Bbt-substituted distibene and dibismuthene were successfully synthesized via simple and direct reductive coupling reaction of the corresponding dibromide precursors.¹⁹ In this paper, we present the details of the syntheses of these distibenes and dibismuthenes, which are kinetically stabilized by Tbt or Bbt groups, together with their chemical and physical properties.

Results and Discussion

As described above, the first stable diphosphene having a P=P double bond was synthesized and isolated utilizing steric protection afforded by bulky Mes* groups.⁸ Using a similar synthetic approach, diarsenes (RAs=AsR) have also been successfully synthesized and isolated.¹⁰ These compounds bear considerable structural similarity to azo compounds, i. e., their lighter congeners. For example, their P-P and As-As double bonds are shorter than the corresponding single bonds (by about 7–10%), and they have an almost planar trans geometry. As for the counterparts of group 14 elements, i. e., Si and Ge analogues of ethylene, disilenes (R₂Si=SiR₂)²⁰ and digermenes (R₂Ge=GeR₂),²¹ can be isolated by taking advantage of kinetic stabilization like diphosphenes and diarsenes. By contrast, the heavier Sn and Pb atoms are reluctant to form doubly bonded systems, distannenes (R₂Sn=SnR₂)^{20–22} and diplumbenes (R₂Pb=PbR₂),^{20–23} because of the high tendency to dissociate

into the corresponding divalent analogues in solution. On the other hand, ab initio calculations have suggested that the heavier group 15 elements, Sb or Bi, can form a compound with rather high double-bond character and RE=ER (E = Sb or Bi) should be stable enough to be isolated if the reactive E=E double bond is kinetically protected from dimerization by sufficiently large substituents.²⁴

The natural and simple approach to the synthesis of a distibene may be that based on the methods used in the syntheses of diphosphenes and diarsenes, that is, the coupling reactions of dihalostibines. However, unsuccessful attempts to synthesize distibenes with some bulky substituents,^{12,25} which were used in the synthesis of diphosphenes and diarsenes, prompted us to choose other types of bulky substituents as steric protection groups. We chose first Tbt as a steric protection group, since we have already succeeded in the synthesis of stable disilene,²⁶ sila-aromatic compounds (2-silanaphthalene,²⁷ silabenzene,²⁸ and 9-silaanthracene²⁹), and a variety of compounds having a double bond between the heavier group 14 and 16 elements (heavy ketones)³⁰ by taking advantage of kinetic stabilization using a Tbt group (Chart 1). These examples clearly show that the Tbt group is a very effective steric protection group to stabilize these highly reactive compounds, in particular, compounds with a multiple bond containing fifth row elements or sixth row elements such as Sn, Te, and Pb. From these points of view, we expected that Tbt-substituted distibene and dibismuthene would be isolated as stable doubly bonded systems protected by two Tbt groups effectively.

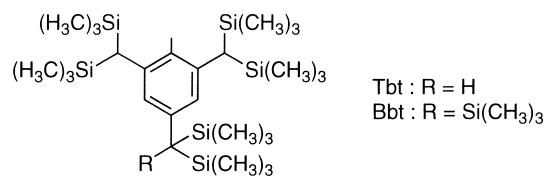
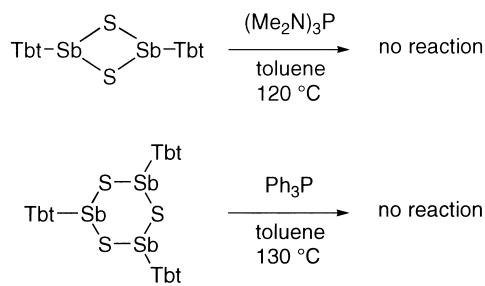


Chart 1.

Synthesis of Tbt-Substituted Distibene and Dibismuthene. Dichlorostibine **1a** and dichlorobismuthine **2a** bearing a Tbt group TbtECl₂ (**1a**; E = Sb, **2a**; E = Bi) were readily synthesized by the reaction of TbtLi with SbCl₃ or BiCl₃, respectively, where neither Tbt₂ECl nor Tbt₃E was obtained, probably due to the bulkiness of the Tbt group. In the initial stage of the investigation, the simplest approach to distibenes, i. e., the attempted coupling reactions of dichlorostibine **1a** using various reducing reagents such as magnesium, lithium, lithium

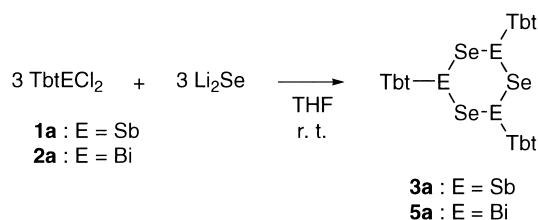


Scheme 1.

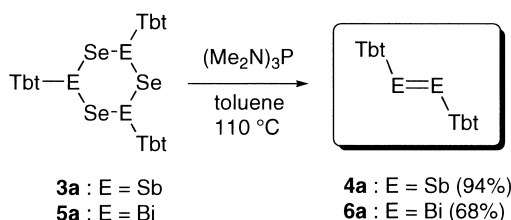
naphthalenide, and so on resulted in the recovery of a small amount of starting materials together with the formation of a small amount of TbtH. The reason why distibene could not be isolated via this simple reductive coupling method will be explained later.

Desulfurization reaction of novel sulfur-containing antimony compounds synthesized by the reaction of TbtSbH₂ with elemental sulfur (Scheme 1)³¹ was also examined as another synthetic approach to a distibene. However, no distibene was observed in the reaction of 1,3,2,4-dithiadistibetane with hexamethylphosphorous triamide (HMPT) in toluene-*d*₈ at 120 °C. Also, the desulfurization of 1,3,5,2,4,6-trithiatristibane (TbtSbS)₃ with triphenylphosphine did not proceed even under severe reaction conditions (130 °C for 30 h in toluene). These unsuccessful results of desulfurization reactions of cyclic antimony-sulfur compounds turned our attention to the possible deselenation reaction of an appropriate selenium-containing compound, because selenium is known to be removed more easily than sulfur in the case of chalcogenadiphosphirane derivatives.³²

A six-membered ring precursor, 1,3,5,2,4,6-triselenatristibane **3a**, was synthesized by the reaction of TbtSbCl₂ **1a** with Li₂Se in THF at room temperature (Scheme 2). The structure of **3a** was supported by ¹H and ⁷⁷Se NMR, elemental analysis, and molecular weight measurement. When a toluene solution of **3a** and excess amount of HMPT was heated at 110 °C in a sealed tube, distibene TbtSb=SbTbt (**4a**) was precipitated from the mixture on cooling and was isolated as deep green single crystals in 94% yield by filtration in a glovebox filled with argon (Scheme 3). This roundabout deselenation synthetic route to distibene **4a** was expected to be also applicable to the synthesis of the first stable dibismuthene. Indeed, treatment of TbtBiCl₂ (**2a**) with Li₂Se in THF afforded a bismuth- and selenium-containing six-membered ring compound, (TbtBiSe)₃ (**5a**). The first example of the heaviest congener of azo-compounds, i. e., dibismuthene **6a**, was also successfully synthesized by a similar method, namely, the deselenation reaction of 1,3,5,2,4,6-triselenatristibismane **5a** with an excess amount of HMPT in toluene at 110 °C in a sealed tube. After heating for



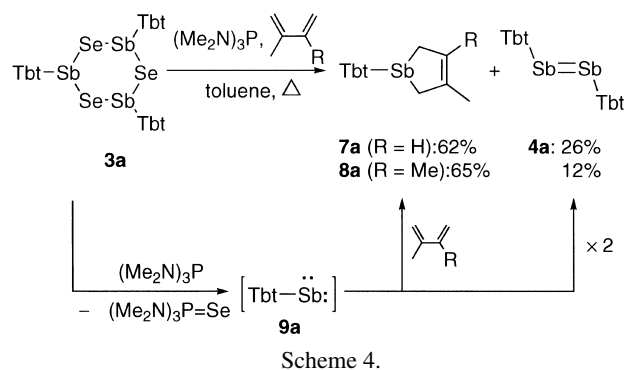
Scheme 2.



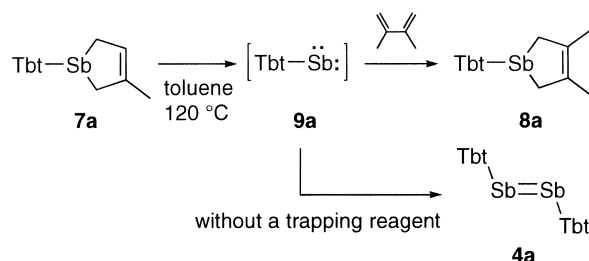
Scheme 3.

12 h, the solution turned purple, and then the expected dibismuthene **6a** was precipitated on cooling and isolated in 68% yield as deep-purple single crystals by filtration as in the case of **4a**. Thus, the first stable distibene and dibismuthene, i. e., the long-sought doubly bonded compounds consisting of antimony and bismuth, were synthesized and isolated as stable compounds. Fortunately, the extremely low solubility of **4a** and **6a** in common organic solvents made their isolation quite simple.

In the final step in the synthesis of distibene **4a**, that is, the deselenation reaction of **3a**, it is reasonable to postulate the initial formation of stibinidene **9a**, i. e., a monovalent species of antimony, as an intermediate.³³ We tried the trapping reaction of the intermediate in this deselenation reaction. When **3a** was treated with HMPT in the presence of isoprene in toluene at 110 °C in a sealed tube for 22 h, Tbt-substituted stibolene derivative **7a** was obtained as a main product (62%) together with a small amount of green crystals of distibene **1** (26%). Stibolene **8a** was also obtained (65%) in a similar deselenation reaction of **3a** using 2,3-dimethyl-1,3-butadiene instead of isoprene (Scheme 4). On the other hand, thermolysis of the isolated distibene **4a** in the presence of 2,3-dimethyl-1,3-butadiene (in toluene, at 150 °C) did not give such [1 + 4]cycloadduct of stibinidene **8a** but resulted in an almost quantitative recovery of **4a**. These results suggest that distibene **4a** is not thermally dissociated into stibinidenes **9a**, because **9a** should be trapped as stibolene derivative **8a** if generated. Taking account of the above-mentioned results, we can reasonably explain the formation of **7a** and **8a** as a main product in the deselenation reactions of **3a** by the initial formation of an intermediary stibinidene **9a** and its subsequent [1 + 4]cycloaddition reactions with butadienes. Furthermore, thermolysis of a toluene-*d*₈ solution of the isolated stibolene **7a** in the presence of excess amount of 2,3-dimethyl-1,3-butadiene at 120 °C in a



Scheme 4.



Scheme 5.

sealed tube resulted in the formation of the diene-exchange adduct **8a** in 74% yield. Thermolysis of **8a** in toluene- d_8 in the presence of an excess amount of isoprene also afforded the corresponding diene-exchanged product **7a** in 78% yield. These results indicate that the stibinidene **9a** was regenerated by the thermal retrocycloaddition of both stibolenes **7a** and **8a**. In addition, thermolysis of **7a** in the absence of any trapping reagents afforded distibene **4a** in 55% yield, suggesting the dimerization of the thermally generated stibinidene intermediate **9a** (Scheme 5). These facts indicate that this reaction can be used as another synthetic method for distibene **4a**.

In the case of deselenation of $(\text{TbtBiSe})_3$ (**5a**) in the presence of either isoprene or 2,3-dimethyl-1,3-butadiene, no diene-adduct of the corresponding bismuthinidene intermediate was obtained, probably due to the weakness of the Bi–C bonds in the diene-adducts and/or the extremely high reactivity of the bismuthinidene intermediate toward dimerization.

Molecular Structures of Tbt-Substituted Distibene and Dibismuthene. The molecular geometries and the definitive structural parameters for Sb=Sb and Bi=Bi bonds of distibene **4a** and dibismuthene **6a** are of great interest. In particular, it is a very interesting question to be answered whether **6a** has a “true” double bond between bismuth atoms because **6a** is the first compound containing a bismuth-bismuth double bond, the heaviest doubly bonded system among those which consist of non-radioactive elements in the periodic table. The definitive structures of **4a** and **6a** were determined by X-ray crystallographic analysis. These molecules have trans configuration with the Tbt groups perpendicular to the C–E–E–C plane. The X-ray crystallographic structural analyses of distibene **4a** and dibismuthene **6a** revealed important parameters of E=E distances and C–E–E angles, which are shown in Fig. 1. The Sb–Sb bond length [2.642(1) Å] in **4a** is 7% shorter than the reported Sb–Sb single bond length for $\text{Ph}_2\text{Sb–SbPh}_2$ (2.837 Å).³⁴ As in the case of antimony, obvious bond shortening (7%) of the Bi–Bi bond length [2.8206(8) Å] of **6a** as compared with that of $\text{Ph}_2\text{Bi–BiPh}_2$ (2.990 Å)³⁵ agrees with the calculated bond-shortening of 6–8% from $\text{H}_2\text{Bi–BiH}_2$ to HBi=BiH obtained at the MP2, B3LYP, and QCISD levels. It is interesting that the observed bond-shortenings of the Sb=Sb and Bi=Bi bonds are comparable with those reported for diphosphenes; the experimentally observed bond-shortening is 8% from the P–P single bond in $(\text{PhP})_5$ [2.217(6) Å]³ to the P=P double bond in $\text{Mes}^*\text{P=PMes}^*$ [2.034(2) Å].⁸ The calculated bond

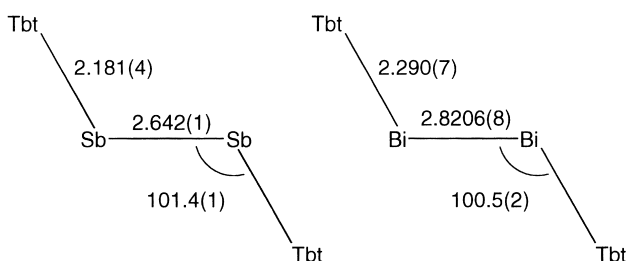


Fig. 1. Selected bond lengths (Å) and bond angles (°) for distibene **4a** and dibismuthene **6a**.

lengths for HE=EH and $\text{H}_2\text{E–EH}_2$ (E = group 15 elements) are summarized in Table 1.³⁶

The observed Sb–Sb–C bond angle of 101.4(1)° in **4a** and the Bi–Bi–C bond angle of 100.5(2)° in **6a** deviate greatly from the ideal sp^2 hybridized bond angle (120°). These experimental results indicate that the heavy atoms like antimony and bismuth atoms have a lower tendency to form a hybridized orbital and prefer to maintain the $(\text{ns})^2(\text{np})^3$ valence electron configuration. The size-difference and energy-gap between the valence *s* and *p* orbitals are known to increase upon going from N to Bi atoms (the significant 6*s* orbital contraction originates mostly from the relativistic effect).³⁷ Theoretical calculations for HE=EH (Table 1) also show the E–E–H angles get closer to 90° as the center element “E” goes from N to Bi, because the use of these three orthogonal 6*p* orbitals without significant hybridization leads to a bond angle of approximately 90° at bismuth. Although the experimental values of C–Sb–Sb angle in **4a** and C–Bi–Bi angle in **6a** which are larger than 90° are not consistent with those obtained by the theoretical calculations for HE=EH models, the results of DFT calculations for sterically congested systems of RE=ER lead us to a reasonable understanding. The optimized structural parameters of PhE=EPh and PhE=EH models are summarized in Table 2.³⁶ In any pnictogen systems (E = P, As, Sb, Bi), all the optimized structures for HE=EH , PhE=EPh , and PhE=EH systems show very similar E=E bond lengths to each other, and they are comparable to the experimentally obtained values of the corresponding double-bond compounds. By contrast, the bond angles at the pnictogen atom are sensitive to the substituents on the central pnictogen atoms. As for PhE=EPh systems, the bond angles at the pnictogen atoms reasonably become smaller with increasing the atomic number [from P (99.7°) to Bi

Table 1. The Calculated Values of the Bond Lengths and Angles for HE=EH and $\text{H}_2\text{E–EH}_2$ [Basis Sets: TZ(2d) (DZ(p) for H)]

Compounds	E–E bond lengths/Å			H–E–E bond angles/°		
	MP2	B3LYP	QCISD	MP2	B3LYP	QCISD
HP=PH	2.048	2.045	2.047	94.1	94.2	94.6
HAs=AsH	2.279	2.270	2.278	92.1	92.6	92.7
HSb=SbH	2.674	2.656	2.676	90.5	91.2	91.3
HBi=BiH	2.794	2.767	2.795	89.1	90.4	90.2
$\text{H}_2\text{P–PH}_2$	2.227	2.255	2.241			
$\text{H}_2\text{As–AsH}_2$	2.496	2.500	2.488			
$\text{H}_2\text{Sb–SbH}_2$	2.867	2.895	2.887			
$\text{H}_2\text{Bi–BiH}_2$	2.984	3.007	3.009			

Table 2. The Calculated Values of the Bond Lengths and Angles for PhE=EPh and PhE=EH

Compounds	E–E bond lengths/Å	bond angles/°	
		C–E–E	H–E–E
PhP=PPh	2.049	99.7	
PhAs=AsPh	2.271	97.4	
PhSb=SbPh	2.659	95.4	
PhBi=BiPh	2.770	94.5	
PhP=PH	2.046	100.3	93.4
PhAs=AsH	2.270	97.7	92.1
PhSb=SbH	2.657	95.9	90.7
PhBi=BiH	2.768	94.9	90.2

B3LYP/TZ(2d) (6-31G(d) for C and H).

The phenyl groups are fixed perpendicularly to the C–E–E plane.

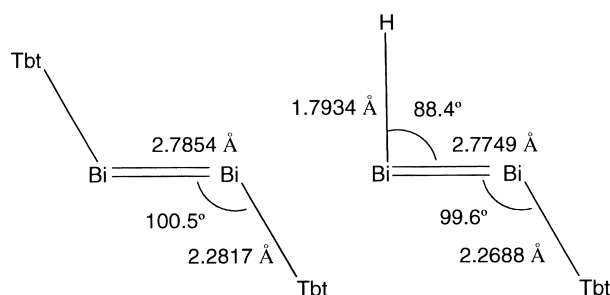


Fig. 2. The theoretically optimized structural parameters of dibismuthenes.

(94.5°)] as in the case of HE=EH systems. However, they are clearly wider than those of HE=EH models. On the other hand, the optimized structures of PhE=EH systems, which have a relatively bulky phenyl group on the only one side, show that the C–E–E angles for all heavier pnictogen atoms (E = P, As, Sb, Bi) are widened like PhE=EPh, and that the H–E–E angles are similar to those of HE=EH systems. Furthermore, the optimized structural parameters for TbtBi=BiTbt (Fig. 2), which was calculated as a representative of the sterically congested systems (TbtE=ETbt; E = P, As, Sb, Bi), was found to have almost the same structural parameters (Bi=Bi: 2.7854 Å, C–Bi–Bi: 100.5°) as experimentally obtained values [Bi=Bi: 2.806(8) Å, C–Bi–Bi: 100.5(2)°]. In addition, the C–Bi–Bi angle of HBi=BiTbt model (Fig. 2.), which has only one bulky Tbt group on the bismuth atom, was also found to be widened to ca. 100°. Taking these results of theoretical calculations into account, it can be concluded that the wider angles at the antimony and bismuth atoms observed in the X-ray crystallographic analysis of **4a** and **6a** are probably not due to the packing force or steric repulsion between the two bulky substituents but are due to the steric repulsion between the bulky Tbt group and the central E=E moiety.

Physical Properties of Tbt-Substituted Distibene and Dibismuthene. Generally, the heavier congeners of azo-compounds are intensely colored. Their color arises from the E=E double-bond chromophore, which appears as the two absorption maxima at wavelengths longer than 300 nm. These absorption maxima can reasonably be assigned as the symmetry allowed $\pi \rightarrow \pi^*$ and symmetry forbidden $n \rightarrow \pi^*$ electron

Table 3. UV/Vis Spectral Data for the Double-Bond Compounds between Heavier Group 15 Elements

Compounds	λ_1/nm (ϵ) $n \rightarrow \pi^*$	λ_2/nm (ϵ) $\pi \rightarrow \pi^*$
Mes*P=PMes*	460(1360)	340(7690)
TsiP=PTsi	484(62.8)	353(9474)
Mes*P=PDis	427(370)	325(13000)
Mes*P=PMes	456(220)	326(2500)
TsiP=AsTsi	497(20)	361(7900)
DisP=AsMes*	431(220)	354(8400)
Mes*As=AsDis	449(180)	368(6960)
TsiAs=AsTsi	505(10)	380(5000)
TbtSb=SbTbt	559(170)	466(5200)
TbtBi=BiTbt	660(100)	525(4000)

Mes* = 2,4,6-Tri-*t*-butylphenyl, Tsi = C(SiMe₃)₃,
Dis = CH(SiMe₃)₂.

transitions. The absorption of $\pi \rightarrow \pi^*$ transition is much more intense than that of $n \rightarrow \pi^*$ transition. Distibene **4a** is the first example of a stable antimony-antimony doubly bonded system, and the green solution of **4a** in hexane showed two absorption maxima at 466 (ϵ 5200) and 599 nm (ϵ 170), which correspond to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the Sb=Sb chromophore respectively. Dibismuthene **6a** is also a new member of the doubly bonded systems between group 15 elements and **6a** is purple in hexane. The $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the Bi=Bi chromophore of **6a** appeared as absorption maxima at 525 (ϵ 4000) and 660 nm (sh, ϵ 100), respectively. The typical examples of absorption maxima reported for the double-bond compounds between group 15 elements^{9–11} are shown in Table 3, together with those of **4a** and **6a**. The experimentally observed red-shifts of **4a** and **6a** relative to the values reported for diphosphenes and diarsenes agree with the decreasing trend in the calculated values [HF/DZ(d,p)] of the frontier orbital energy gaps of HE=EH (E = P, As, Sb, and Bi).²⁴ Power and co-workers also reported the synthesis of ArSb=SbAr and ArBi=BiAr with bulky *m*-terphenyl ligands (Ar = 2,6-Mes₂C₆H₃ or 2,6-Tip₂C₆H₃; Tip = 2,4,6-triisopropylphenyl).¹⁶ Their ArE=EAR systems also show absorption at longer wavelengths for the $\pi \rightarrow \pi^*$ transition; 451 nm (ϵ 5450; E = Sb, Ar = 2,6-Mes₂C₆H₃), 470 nm (ϵ 6570; E = Sb, Ar = 2,6-Tip₂C₆H₃), 505 nm (ϵ 5010; E = Bi, Ar = 2,6-

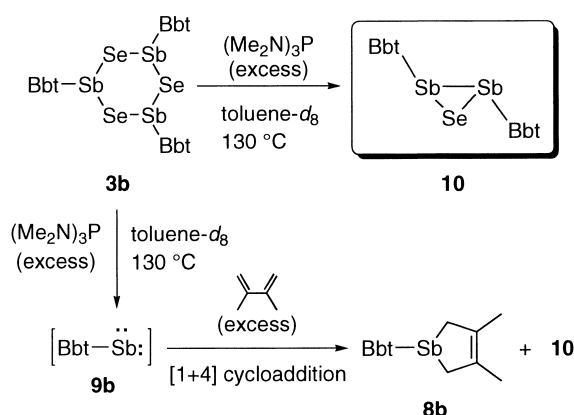
Table 4. The Calculated Values of the Harmonic Vibrational Frequencies (cm^{-1}) of $\text{HE}=\text{EH}$ and $\text{H}_2\text{E}-\text{EH}_2$ [Basis Sets: TZ(2d) (DZ(p) for H)]

Compounds	MP2	B3LYP	QCISD
$\text{HP}=\text{PH}$	606.4	615.2	626.4
$\text{HAs}=\text{AsH}$	331.4	343.6	337.6
$\text{HSb}=\text{SbH}$	213.7	223.8	216.7
$\text{HBi}=\text{BiH}$	150.8	159.9	152.9
$\text{H}_2\text{P}-\text{PH}_2$	448.1	418.8	436.4
$\text{H}_2\text{As}-\text{AsH}_2$	254.3	239.9	244.9
$\text{H}_2\text{Sb}-\text{SbH}_2$	172.7	163.0	167.4
$\text{H}_2\text{Bi}-\text{BiH}_2$	125.3	118.6	119.5

$\text{Mes}_2\text{C}_6\text{H}_3$), and 518 nm (ϵ 6920; $\text{E} = \text{Bi}$, $\text{Ar} = 2,6\text{-Tip}_2\text{C}_6\text{H}_3$). These UV-vis spectral data indicate that **4a** and **6a** feature $\text{Sb}=\text{Sb}$ and $\text{Bi}=\text{Bi}$ double bonds, respectively, even in solution, as in the case of diphosphenes, diarsenes, and phospharsenes.

In order to identify the double-bond characters of the central $\text{E}=\text{E}$ bonds in distibene **4a** and dibismuthene **6a**, the frequencies of the $\text{Sb}=\text{Sb}$ and $\text{Bi}=\text{Bi}$ stretching vibrations were measured by resonance Raman spectroscopy. Distibene **4a** showed a characteristic strong Raman shift at 207 cm^{-1} (solid; excitation, He-Ne laser 632.8 nm) which is higher than the frequencies observed for distibanes (e.g. $\text{Ph}_2\text{Sb}-\text{SbPh}_2$ 141 cm^{-1}).³⁴ The calculated values of the harmonic vibrational frequency of $\text{HSb}=\text{SbH}$ obtained at MP2, B3LYP, and QCISD/TZ(2d) (DZ(p) for H) levels are shown in Table 4, and these values agree with the experimentally observed value for **4a**. The diphosphene ($\text{Mes}^*\text{P}=\text{PMes}^*$) is known to show the vibrational frequency for its $\text{P}=\text{P}$ double bond at 610 cm^{-1} in the Raman spectra,³⁸ and the assignment was confirmed by the theoretically calculated values shown in Table 4. Meanwhile, a strong band attributable to the $\text{Bi}=\text{Bi}$ stretching was observed at 134 cm^{-1} for **6a** (solid; excitation, He-Ne laser 632.8 nm). This is higher by 31 cm^{-1} than the $\text{Bi}-\text{Bi}$ stretching frequency of $\text{Ph}_2\text{Bi}-\text{BiPh}_2$ (103 cm^{-1}),³⁹ agreeing with the frequency shift of 34 cm^{-1} calculated for $\text{HBi}=\text{BiH}$ (153 cm^{-1}) and $\text{H}_2\text{Bi}-\text{BiH}_2$ (119 cm^{-1}) at the QCISD level. These results in Raman spectra suggest that **4a** and **6a** feature stronger $\text{E}=\text{E}$ bonds as compared with the corresponding $\text{E}-\text{E}$ single bonds ($\text{E} = \text{Sb}, \text{Bi}$), indicating that **4a** and **6a** has considerable double bond character in the solid state.

Introduction of Bbt-groups to Distibene. Synthesis of the First Stable Selenadistibirane. Although the first stable distibene **4a** and dibismuthene **6a** have been synthesized and isolated by taking advantage of the kinetic stabilization using Tbt groups, the extremely low solubility of **4a** and **6a** in common organic solvents (e.g., hexane, benzene, toluene, CHCl_3 , CH_2Cl_2 , THF, Et_2O , etc.) prevented further studies on their chemical properties in solution. On the other hand, we have developed a new bulky aromatic substituent, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt) group,^{17,18} which is expected to be a potentially more useful steric protection group than Tbt group. Taking account of the empirical fact that TbtH has very low solubility while BbtH is comparatively more soluble than TbtH, the synthesis of a Bbt-substituted distibene **4b** was examined in the

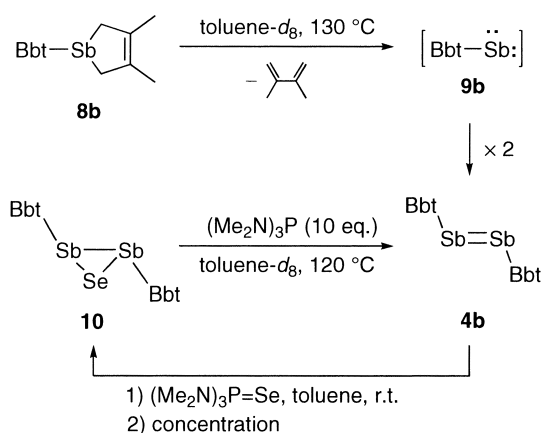


Scheme 6.

hope of obtaining a new distibene which has higher solubility than **4a**.

When a 1,3,5,2,4,6-triselenatristibane derivative **3b** bearing three Bbt groups on the antimony atoms, prepared by the reaction of BbtSbBr_2 **1b** with Li_2Se in THF, was treated with HMPT (excess) in toluene at $130\text{ }^\circ\text{C}$ in a sealed tube in a manner similar to that used for the transformation of the Tbt analogue **3a** into distibene **4a**, the color of the reaction mixture turned deep red. The UV-vis spectrum of this reaction mixture showed two characteristic absorption maxima at 490 and 594 nm, attributable to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, of the expected distibene **4b** ($\text{BbtSb}=\text{SbBbt}$) as in the case of distibene **4a**. Strangely, no distibene **4b** was observed on concentration of the reaction mixture, but a new antimony-containing three-membered ring compound, selenadistibirane derivative **10**, was isolated as air-stable orange crystals in 85% yield. Selenadistibirane **10** showed satisfactory spectral data and the molecular geometry of **10** was definitively determined by X-ray structural analysis.⁴⁰ The selenadistibirane ring skeleton of **10** is an almost isosceles triangle with the normal $\text{Sb}-\text{Sb}$ bond length [$2.852(2)\text{ \AA}$] and the two Bbt groups are oriented in trans configuration with regard to the central selenadistibirane ring.

On the other hand, the deselenation reaction of **3b** with an excess amount of HMPT in the presence of 2,3-dimethyl-1,3-butadiene afforded the stibolene derivative **8b** (70%) together with **10** (30%) (Scheme 6). The formation of **8b** as a major product strongly suggests the initial generation of intermediary stibinidene **9b** in the deselenation reaction of **3b**, as in the case of the deselenation reaction of Tbt derivative **3a**, since **10** is almost inert toward 2,3-dimethyl-1,3-butadiene even at $130\text{ }^\circ\text{C}$ in toluene- d_8 for a long time. Taking into consideration the previously mentioned results in the thermolysis of Tbt-substituted stibolene derivative **7a** and **8a**, the stibolene **8b** is expected to be a good precursor of Bbt-substituted distibene **4b**. Indeed, the diene adduct **8b** was found to readily undergo thermal retrocycloaddition in toluene- d_8 at $130\text{ }^\circ\text{C}$ for 64 h in a sealed tube to give the deep red solution of expected distibene **4b**, which has indubitably higher solubility than **4a**, probably via dimerization of intermediary stibinidene **9b**. The UV-vis spectrum of **4b** thus obtained was identical with that obtained from the direct deselenation of **3b** with HMPT; the two characteristic absorption maxima of $\text{Sb}=\text{Sb}$ moiety of **4b** were ob-



Scheme 7.

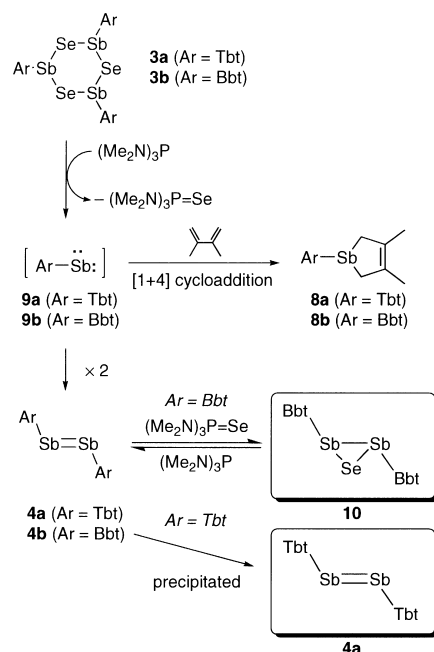
served at 490 (ϵ 6000) and 594 nm (ϵ 200).

In order to elucidate the formation mechanism of the selenadistibirane **10**, the reaction of distibene **4b**, prepared from **8b**, with an excess of phosphine selenide (Me₂N)₃P=Se in toluene at room temperature was examined. Removal of the solvent and (Me₂N)₃P generated in the reaction from the reaction mixture resulted in the almost quantitative formation of selenadistibirane **10**, while the reaction of isolated **10** with an excess of HMPT in toluene-*d*₈ at 120 °C for 2 h gave a solution of 4:1 mixture of **4b** and **10** as judged by ¹H NMR (Scheme 7). These results are important as experimental evidence for the equilibrium between **4b** plus (Me₂N)₃P=Se and **10** plus (Me₂N)₃P, which may be a key factor in the final step for the formation of **10** in the deselenation reaction of **3b**.

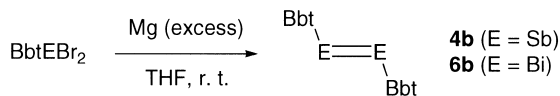
As mentioned above, the deselenation reactions of overcrowded 1,3,5,2,4,6-triselenatristibanes, (TbtSbSe)₃ (**3a**) and (BbtSbSe)₃ (**3b**), which are very similar to each other, afforded quite different types of reaction products, i. e., distibene (**4a**) and selenadistibirane (**10**), respectively. These facts are very interesting since the initial formation of the stibinidene intermediates **9a** and **9b** has been confirmed by the trapping experiments with dienes in both reactions. The unexpected great difference in the deselenation between **3a** and **3b** is most likely interpreted in terms of the remarkable insolubility of **4a** in common organic solvents, which may prevent **4a** from undergoing further transformation into its selenadistibirane derivative via redistribution of a selenium atom between the initially formed distibene and (Me₂N)₃P=Se on concentration (Scheme 8).

Thus, it was found that Bbt-substituted distibene **4b** cannot be isolated by the deselenation reaction of **3b** but can be prepared and isolated as a stable compound by the stepwise transformation via stibolene derivative **8b**. As for its bismuth analogue, 1,3,5,2,4,6-triselenatirbismane (BbtBiSe)₃ is not stable enough to be isolated, unfortunately. It is necessary to investigate other synthetic methods for the soluble dibismuthene.

Synthesis of Bbt-Substituted Distibene and Dibismuthene. Since Bbt-substituted distibene **4b** was found to be soluble in hexane, the direct reductive coupling reaction was examined for the synthesis of **4b**. Bbt-substituted dibromostibine **1b** was treated with Mg metal in THF at room temperature for 30 min and then the reaction mixture was extracted with



Scheme 8.



Scheme 9.

hexane. Removal of inorganic salts and subsequent evaporation of hexane gave the expected distibene **4b** almost quantitatively. This efficient synthetic method is also applicable to Bbt-substituted dibismuthene **6b** (Scheme 9). Treatment of BbtBiBr₂ **2b** with Mg in THF at room temperature afforded purple powder of **6b**, which has the desired solubility in common organic solvents, in almost quantitative yields. The formation of **6b** was readily confirmed by its two characteristic absorption maxima at 537 (ϵ 6000) and 670 nm (sh, ϵ 20) in hexane, which are similar to those of Tbt-substituted dibismuthene **6a**. Thus, it was found that the traditional synthetic method for heavier dipnictenes, i. e., reductive coupling reaction of the corresponding dihalide precursor, is also applicable even to antimony and bismuth analogues. These results also reveal a reason why we could isolate Tbt-substituted distibene and dibismuthene not via simple direct reduction of their halide precursors but via a more roundabout route. In our initial experiments where TbtSbCl₂ or TbtSbBr₂ was treated with metallic Mg as reducing reagents, the green powder generated, i. e., distibene **4a** had been removed together with inorganic salts by filtration. Unfortunately, we could not realize at first that the green powder is distibene **4a**, which has extremely low solubility.

In addition to the solubility, Tbt-substituted distibene **4a** and Bbt-substituted distibene **4b** are also different in color; **4a** is green crystals while **4b** is a deep red solid. In UV-vis spectra of these distibenes and dibismuthenes, the characteristic absorption maxima corresponding to the $\pi \rightarrow \pi^*$ electron transitions of Bbt-substituted compounds are observed at longer

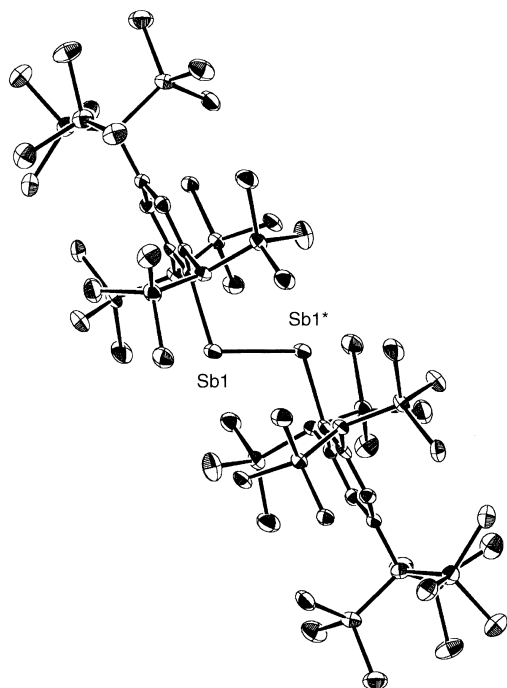


Fig. 3. ORTEP drawing of BbtSb=SbBbt (**4b**) with thermal ellipsoid plot (50% probability).

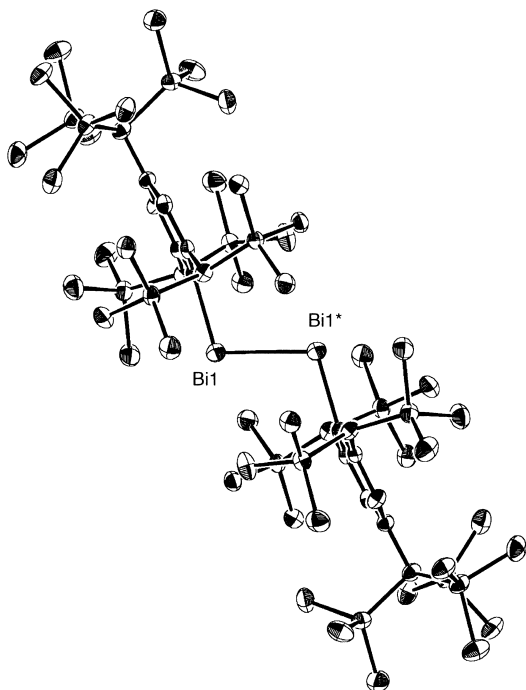


Fig. 4. ORTEP drawing of BbtBi=BiBbt (**6b**) with thermal ellipsoid plot (50% probability).

wavelengths than those of Tbt-substituted ones by 24 nm for distibenes and 12 nm for dibismuthene. These bathochromic shifts, which mean lower degree of interaction between *p* orbitals, may be indicative of the longer E–E bond lengths of **4b** and **6b** than of **4a** and **6a**, respectively, in solution.

Molecular Structures of Bbt-Substituted Distibene and

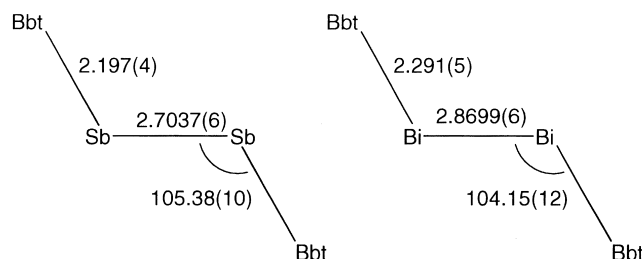
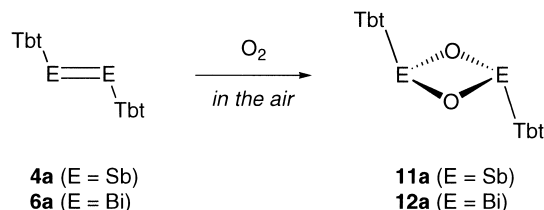


Fig. 5. Selected bond lengths (Å) and bond angles (°) for distibene **4b** and dibismuthene **6b**.



Scheme 10.

Dibismuthene. The definitive structural parameters of **4b** and **6b** in the solid state were determined by the X-ray crystallographic structural analysis. These molecular geometries and selected bond lengths and angles are shown in Figs. 3, 4, and 5, which reveal that **4b** and **6b** have quite similar structures to those of **4a** and **6a**, respectively. The Sb=Sb [2.7037(6) Å] and Bi=Bi [2.8699(6) Å] double bond lengths of **4b** and **6b** are considerably shorter than the typical Sb–Sb and Bi–Bi single bond lengths (Ph₂Sb–SbPh₂; 2.837 Å³⁴ and Ph₂Bi–BiPh₂; 2.990 Å³⁵), respectively. The previous discussion for TbtE=ETbt suggests that the C–E–E angles of **4b** [105.38(10)°] and **6b** [104.15(12)°] may be widened due to the steric repulsion between the Bbt group and the central E=E moiety, as in the case of **4a** and **6a**, respectively. The structural optimization at B3LYP level of HBi=BiBbt model shows the C–Bi–Bi angle (104.8°) to be very close to that of **6b** (104.1°) and shows the reasonable Bi=Bi bond length of 2.777 Å. A small difference between structures of Tbt-substituted and Bbt-substituted distibenes is found in the Sb–Sb bond length and the C–Sb–Sb angle. Distibene **4b** has a longer Sb–Sb bond length by 0.07 Å and a larger C–Sb–Sb angle by 3° than **4a**. In the case of Bi analogues, **6b** also has a longer Bi–Bi bond by 0.05 Å and a larger C–Bi–Bi angle by 4° than **6a**. This tendency might indicate that the Bbt group is bulkier than Tbt group due to the difference of the substituents at *p*-position. The greater steric repulsion of Bbt group slightly elongates the E=E bonds and enlarges the C–E–E angles.

Chemical Properties of the Distibenes and the Dibismuthenes. Distibenes **4a,b** and dibismuthenes **6a,b** are quite stable compounds at room temperature in the absence of air in the solid state and are inert to photolysis (100 W medium pressure Hg lamp/ Pyrex filter/ in a sealed tube) in C₆D₆ solution. Furthermore, **4b** and **6b** are surprisingly inert to deoxygenated water and MeOH even at 100 °C for a long time in a sealed tube in C₆D₆ solution. On the other hand, the distibenes **4a,b** and dibismuthenes **6a,b** lose their color upon exposure to air. Furthermore, during the course of our studies on the reactivity

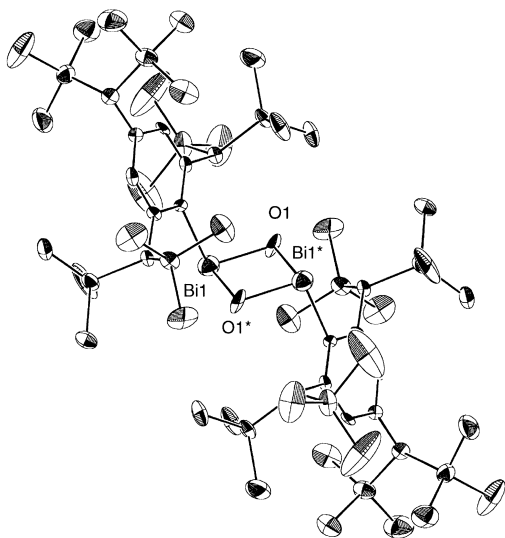


Fig. 6. ORTEP drawing of **12a** with thermal ellipsoid plot (30% probability).

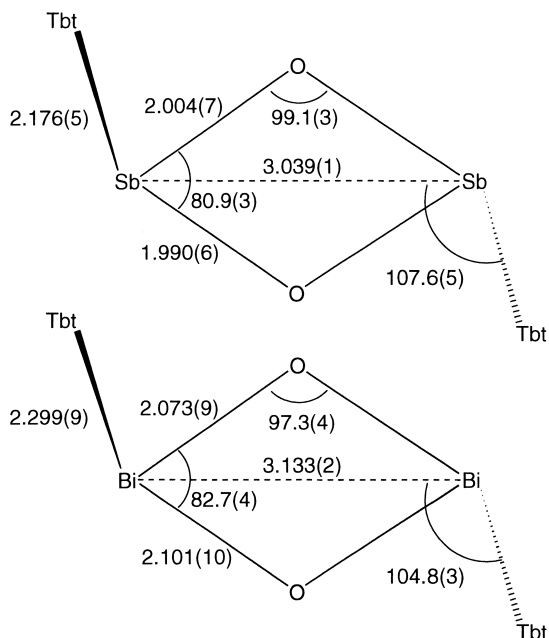


Fig. 7. Selected bond lengths (Å) and bond angles (°) for **11a** and **12a**.

with oxygen of distibenes and dibismuthene, a unique and interesting reactivity of **4a** and **6a** with oxygen was found. Crystalline dipnictenes **4a** and **6a** reacted with atmospheric oxygen to give the corresponding 1,3,2,4-dioxadistibetane and 1,3,2,4-dioxadibismetane derivatives **11a** and **12a**, which are rather stable in the solid state in open air (Scheme 10). Thus, the crystals of **4a** remained dark green for several hours, but they slowly reacted with atmospheric oxygen to give **11a** quantitatively. Similarly, the purple color of the crystals of **6a** gradually faded in open air to give **12a** as colorless crystals. Single crystals of these compounds suitable for X-ray crystallographic analysis were obtained by a unique method of leaving the single crystals of **4a** and **6a** in air for a few days, and the struc-

ture was finally confirmed to be 1,3,2,4-dioxadistibetane **11a** and 1,3,2,4-dioxadibismetane **12a**, respectively. We have already reported in detail that the oxidation process of **4a** in the crystalline phase was successfully monitored by repeated measurements of the cell dimensions using an X-ray diffraction technique with an imaging plate Weissenberg diffractometer.¹³ Although the oxidation process of **6a** was not monitored by this method, dibismuthene **6a** might also undergo the crystalline-state oxidation reaction to give 1,3,2,4-dioxadibismetane **12a**. Figures 6 and 7 show the ORTEP drawing of **12a** and selected bond lengths and angles of **11a** and **12a**, respectively. The geometries of **11a** and **12a** are very similar to each other; they have a completely flat four-membered ring of 1,3,2,4-dioxadistibetane and 1,3,2,4-dioxadibismetane, respectively. The intramolecular distance between the two antimony atoms of **11a** was found to be increased by about 0.4 Å, and the C-Sb-Sb angle was widened by 6° compared to distibene **4a**. 1,3,2,4-Dioxadibismetane **12a** also has similar features; **12a** has an elongated intramolecular distance between the two bismuth atoms [3.133(2) Å] and widened C-Bi-Bi angle [104.8(3)°] compared to dibismuthene **6a**. Such unique reactivity in the crystalline-state as observed for **4a** and **6a** is most likely interpreted in terms of the combination of the high reactivity of the Sb=Sb and Bi=Bi double bond moieties toward oxygen with the loose packing structure of the crystals, consisting of overcrowded molecules bearing very bulky Tbt group. On the other hand, **4b** and **6b** also reacted with atmospheric oxygen in the crystalline state to give colorless crystals. In contrast to the case of **4a** and **6a**, however, the oxidation reactions gave only very complicated mixtures containing BbtH. In solution, **4b** and **6b** reacted with atmospheric oxygen very rapidly to give again complex mixtures containing BbtH. Although the corresponding 1,3,2,4-dioxadistibetane and 1,3,2,4-dioxadibismetane derivatives **11b** and **12b** may be generated in these oxidation reactions, we have not succeeded in clarifying the fate of the oxidized products. They may easily undergo over-oxidation and decomposition in solution due to their high solubility, in contrast to **11a** and **12a** which are almost insoluble.

Conclusion

Following the pioneering work on stable diphosphenes and diarsenes, the first stable distibenes and dibismuthenes were successfully synthesized by taking advantage of kinetic stabilization using bulky Tbt and Bbt groups. Thus, the doubly bonded compounds between heavier group 15 elements are no more imaginary species but are those with real existence which are stable, even in the heaviest non-radioactive element of bismuth, when they are appropriately protected by bulky substituents. The construction of a series of doubly bonded systems between group 15 elements in the present work revealed the feature of the core-like nature of the ns electron, namely, the so-called "inert s-pair effect" or "non-hybridization effect" of the heavier group 15 elements. Although it is difficult to investigate the reactivities of **4a** and **6a** in solution due to their extremely low solubility values, the syntheses of soluble distibene **4b** and dibismuthene **6b** have made it possible for us to elucidate their reactivity in solution, which will be described elsewhere in the near future. Furthermore, theoretical calcula-

tions showed that the bond angles of C–E–E of these doubly bonded systems between heavier group 15 elements were considerably widened by bulky substituents, which are indispensable to isolate these compounds, while the E=E bond lengths were not so influenced by the steric congestion.

The concept of kinetic stabilization should certainly be of great use for the construction of these unprecedented chemical bondings. Also, matching of theoretical calculations with experiments has been shown to be very important to elucidate the intrinsic nature of new inter-element linkages of heavier main group elements. We hope the successful application of the kinetic stabilization to the chemistry of heavier dipnictenes will lead to further progress in the synthesis and properties of a unique class of low-coordinated main group elements in future.

Experimental

Theoretical Calculations. All theoretical calculations were carried out using the Gaussian 98 program.⁴¹ The triple zeta basis set ([3s3p])⁴² augmented by two sets of d polarization functions for P (d exponents 0.537 and 0.153), As (d exponents 0.434 and 0.129), Sb (d exponents 0.277 and 0.088), and Bi (d exponents 0.229 and 0.069) and double zeta basis ([2s2p]) set for Si were used with an effective core potential. The 6-31G(d) basis set (PhE=EPh and HE=EPh) and the 3-21G basis set (the others) were used for C and H. In geometrical optimization of PhE=EPh and HE=EPh, the phenyl groups were fixed perpendicularly to the C–E–E plane.

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. ¹H NMR (500, 300, or 270 MHz) and ¹³C NMR (125, 75, or 68 MHz) spectra were measured in CDCl₃ or C₆D₆ with a Bruker AM-500, Bruker DRX-500, JEOL JNM-A500, JEOL AL-300, or JEOL EX-270 spectrometer. In ¹H NMR signals due to CHCl₃ (7.25 ppm) and C₆D₅H (7.15 ppm) were used as references, and those due to CDCl₃ (77 ppm) and C₆D₆ (128 ppm) were used in ¹³C NMR. Multiplicity of signals in ¹³C NMR spectra was determined by DEPT technique. ⁷⁷Se NMR (95 MHz) spectra were measured in CDCl₃ or C₆D₆ with a JEOL JNM-A500 spectrometer using diphenyl diselenide as an external standard (480 ppm). High- and low-resolution mass spectral data were obtained on a JEOL JMS-SX102 spectrometer. Molecular weights were measured by vapor pressure osmometry in CHCl₃ with HITACHI 117. GPC (gel permeation liquid chromatography) was performed on an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform or toluene). Electronic spectra were recorded on a JASCO V530 UV/VIS or JASCO Ubest-50 UV/VIS spectrometer. Raman spectra were measured at room temperature on a Raman spectrometer consisting of a Spex 1877 Triplemate and an EG & G PARC 1421 intensified photodiode array detector. An NEC GLG 108 He-Ne laser (632.8 nm) was used for Raman excitation. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo or at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. 1-Bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene (TbtBr)¹⁵ and 1-bromo-2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]benzene (BbtBr)¹⁷ were prepared according to the reported proce-

dures.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}dichlorostibine (1a). To a solution of TbtBr (5.05 g, 8.00 mmol) in THF (120 mL) was added *t*-butyllithium (1.6 M pentane solution, 11.0 mL, 17.6 mmol) at –78 °C. After 30 min, a solution of SbCl₃ (2.82 g, 12.3 mmol) in THF (40 mL) was added. The reaction mixture was warmed to room temperature and stirred for 2 h. The solvents were evaporated under reduced pressure and 100 mL of hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. After removal of the solvent from the filtrate, the residue was reprecipitated from CH₂Cl₂/isopropyl alcohol to afford TbtSbCl₂ (**1a**, 4.13 g, 69%). **1a**: pale yellow crystals, mp 128–129 °C (decomp). Found: C, 42.89; H, 7.80; Cl, 9.88%. Calcd for C₂₇H₅₉Cl₂SbSi₆: C, 43.53; H, 7.98; Cl, 9.52%. ¹H NMR (500 MHz, CDCl₃) δ 0.05 (s, 18H), 0.09 (s, 36H), 1.36 (s, 1H), 2.44 (s, 1H), 2.53 (s, 1H), 6.36 (s, 1H), 6.52 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 0.67 (q), 0.75 (q), 0.97 (q), 30.1 (d), 31.36 (d), 31.40 (d), 123.5 (s), 128.2 (d), 145.3 (d), 148.3 (s), 151.8 (s), 152.6 (s). HRMS (FAB) Found: *m/z* 744.1651 ([M]⁺). Calcd for C₂₇H₅₉Cl₂SbSi₆ ([M]⁺): 744.1703.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}dichlorobismuthine (2a). To a solution of TbtBr (3.16 g, 5.00 mmol) in THF (45 mL) was added *t*-butyllithium (1.6 M pentane solution, 6.9 mL, 11.0 mmol) at –78 °C. After 30 min, a solution of BiCl₃ (2.37 g, 7.5 mmol) in THF (15 mL) was added. The reaction mixture was warmed to room temperature and stirred for 12 h. The solvents were evaporated under reduced pressure and 100 mL of hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. The removal of the solvent from the filtrate gave 2.0 g of a lemon yellow solid, which contained TbtBiCl₂ (**2a**, 42%) and TbtH (9%) with the ratio of 9:2 as estimated by ¹H NMR spectrum. This mixture was used for the next reaction without further purification. **2a**: lemon yellow crystals, mp 235–250 °C (decomp). ¹H NMR (500 MHz, CDCl₃) δ 0.05 (s, 18H), 0.10 (s, 36H), 1.34 (s, 1H), 2.27 (s, 1H), 2.31 (s, 1H), 7.05 (s, 1H), 7.25 (s, 1H). HRMS (FAB) Found: *m/z* 832.2487 ([M]⁺). Calcd for C₂₇H₅₉BiCl₂Si₆ ([M]⁺): 832.2384.

Preparation of 2,4,6-Tris{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,5,2,4,6-triselenatristibane (3a). To a suspension of selenium (23.8 mg, 0.30 mmol) in THF (1 mL) was added a THF solution (0.67 mL) of LiB(C₂H₅)₃H (1.0 M, 0.67 mmol) at room temperature. After 15 min, a solution of TbtSbCl₂ **1a** (224 mg, 0.30 mmol) in THF (5 mL) was added and the reaction mixture was stirred for 1 h. The solvent was evaporated under reduced pressure and 30 mL of hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. After removal of the solvent from the filtrate, the residue was purified by GPC and reprecipitation from CH₂Cl₂/EtOH to afford (TbtSbSe)₃ (**3a**, 154 mg, 68%) **3a**: yellow crystals, mp 284–286 °C. Found: C, 42.77; H, 7.62; Se, 10.33%. Calcd for C₈₁H₁₇₇Sb₃Se₃Si₁₈: C, 43.06; H, 7.89; Se, 10.48%. ¹H NMR (500 MHz, CDCl₃) δ 0.03 (s, 54H), 0.06 (s, 54H), 0.08 (s, 54H), 1.30 (s, 3H), 2.69 (s, 6H), 6.30 (s, 3H), 6.42 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 0.72 (q), 0.87 (q), 1.13 (q), 30.38 (d), 32.32 (d), 32.71 (d), 122.8 (d), 127.6 (d), 139.6 (s), 144.8 (s), 150.9 (s), 151.1 (s). ⁷⁷Se NMR (95 MHz, CDCl₃) δ 179. Molecular weight (osmometry in CHCl₃) Found: 2146. Calcd for C₈₁H₁₇₇Sb₃Se₃Si₁₈: 2259.

Synthesis and Isolation of Bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}distibene (4a). To a toluene solution (5 mL) of **3a** (338 mg, 0.15 mmol) was added 0.29 mL of P(NMe₂)₃ (1.5

mmol), and the reaction mixture was heated at 110 °C in a sealed tube for 12 h. Green crystals, which were precipitated by cooling the mixture to room temperature, were filtered in a glovebox filled with argon to afford Tb_2Sb_2 **4a** (284 mg, 94%). **4a**: green crystals, mp > 300 °C. Found: C, 47.50; H, 8.70%. Calcd for $\text{C}_{54}\text{H}_{118}\text{Sb}_2\text{Si}_{12}$: C, 48.11; H, 8.82%. ^1H NMR (500 MHz, CDCl_3) δ 0.128 (s, 36H), 0.132 (s, 36H), 0.15 (s, 36H), 1.44 (s, 2H), 2.75 (s, 2H), 2.94 (s, 2H), 6.54 (s, 2H), 6.64 (s, 2H). UV-vis (hexane) 599 (ϵ 170), 466 nm (ϵ 5200). FT-Raman (solid, excitation; He-Ne laser 632.8 nm) 207 cm^{-1} ($\nu_{\text{Sb-Sb}}$).

Preparation of 2,4,6-Tris[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-1,3,5,2,4,6-triselenatribismane (5a). To a suspension of selenium (31.6 mg, 0.40 mmol) in THF (1 mL) was added a THF solution (0.84 mL) of $\text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$ (1.0 M, 0.84 mmol) at room temperature. After 15 min, a solution of TbBiCl_2 **2a** (332 mg, 0.4 mmol) in THF (5 mL) was added and the reaction mixture was stirred for 1 h. After removal of the solvent from the filtrate, the residue was purified by GLPC to afford $(\text{TbTbSe})_3$ (**5a**, 94.5 mg, 28%) **5a**: orange crystals, mp 262–265 °C. HRMS (FAB) Found: m/z 1967.3241 ($[\text{M}-\text{Tb}]^+$), 1890.4158 ($[\text{M} + \text{H}-\text{Tb}]^+$). Calcd for $\text{C}_{54}\text{H}_{118}\text{Bi}_3^{78}\text{Se}^{80}\text{Se}_2\text{Si}_{12}$ ($[\text{M}-\text{Tb}]^+$): 1967.338, $\text{C}_{54}\text{H}_{119}\text{Si}_{12}\text{Bi}_3^{80}\text{Se}_2$ ($[\text{M} + \text{H}-\text{Tb}]^+$): 1890.4286. ^1H NMR (500 MHz, CDCl_3) δ 0.03 (s, 54H), 0.07 (s, 118H), 1.28 (s, 3H), 2.42 (s, 2H), 2.44 (s, 2H), 2.51 (s, 2H), 6.65 (s, 2H), 6.68 (s, 2H), 6.75 (s, 2H).

Synthesis and Isolation of Bis[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]dibismuthene (6a). To a toluene solution (0.5 mL) of **5a** (20.8 mg, 0.008 mmol) was added 0.02 mL of $\text{P}(\text{NMe}_2)_3$ (0.1 mmol), and the reaction mixture was heated at 110 °C in a sealed tube for 12 h. Deep-purple crystals, which were precipitated by cooling the mixture to room temperature, were filtered in a glovebox filled with argon to afford Tb_2Bi_2 **6a** (12.8 mg, 68%). **6a**: purple crystals, mp > 300 °C. Found: C, 42.37; H, 7.77%. Calcd for $\text{C}_{54}\text{H}_{118}\text{Bi}_2\text{Si}_{12}$: C, 42.60; H, 7.81%. UV-vis (hexane) 660 (sh, ϵ 100), 525 nm (ϵ 4000). FT-Raman (solid, excitation; He-Ne laser 632.8 nm) 134 cm^{-1} ($\nu_{\text{Bi-Bi}}$).

Deselenation Reaction of $(\text{TbTbSe})_3$ (3a**) with $\text{P}(\text{NMe}_2)_3$ in the Presence of Isoprene.** To a toluene solution (4 mL) of **3a** (217 mg, 0.10 mmol) were added 0.18 mL of $\text{P}(\text{NMe}_2)_3$ (1.0 mmol) and 1.0 mL of isoprene (10.0 mmol), and the reaction mixture was heated at 110 °C in a sealed tube for 12 h. Green crystals, which were precipitated by cooling the mixture to room temperature, were filtered in a glovebox filled with argon to afford Tb_2Sb_2 **4a** (16 mg, 26%). The filtrate was separated by GLPC to give the stibolene **7a** (133 mg, 62%). **7a**: colorless powder, mp 123–125 °C (decomp). Found: C, 50.61; H, 8.72%. Calcd for $\text{C}_{32}\text{H}_{67}\text{SbSi}_6\cdot\text{H}_2\text{O}$: C, 50.56; H, 9.14%. ^1H NMR (500 MHz, CDCl_3) δ 0.31 (s, 54H), 1.27 (s, 1H), 1.81 (s, 3H), 1.97 (s, 1H), 2.03 (s, 1H), 2.34–1.47 (m, 2H), 3.05–3.10 (m, 2H), 5.89 (br s, 1H), 6.26 (s, 1H), 6.40 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 0.74 (q), 1.02 (q), 21.4 (d), 23.6 (t), 28.6 (t), 29.9 (q), 30.8 (d), 31.0 (d), 121.8 (d), 126.7 (d), 127.4 (d), 133.3 (s), 142.0 (s), 142.7 (s), 150.5 (s), 150.7 (s).

Deselenation Reaction of $(\text{TbTbSe})_3$ (3a**) with $\text{P}(\text{NMe}_2)_3$ in the Presence of 2,3-Dimethyl-1,3-butadiene.** To a toluene solution (3 mL) of **3a** (136 mg, 0.06 mmol) were added 0.10 mL of $\text{P}(\text{NMe}_2)_3$ (0.6 mmol) and 0.7 mL of 2,3-dimethyl-1,3-butadiene (6.0 mmol), and the reaction mixture was heated at 120 °C in a sealed tube for 15 h. Green crystals, which were precipitated by cooling the mixture to room temperature, were filtered in a glovebox filled with argon to afford Tb_2Sb_2 **4a** (14.5 mg, 12%). The filtrate was separated by GLPC to give the stibolene **8a** (88.3 mg,

65%). **8a**: colorless powder, mp 141–143 °C (decomp). Found: C, 51.64; H, 8.99%. Calcd for $\text{C}_{33}\text{H}_{69}\text{SbSi}_6\cdot\text{H}_2\text{O}$: C, 51.20; H, 9.24%. ^1H NMR (500 MHz, CDCl_3) δ 0.00 (s, 54H), 1.26 (s, 1H), 1.66 (s, 6H), 1.93 (s, 1H), 1.99 (s, 1H), 2.43 (d, $^2J_{\text{HH}} = 14.4$ Hz, 2H), 3.18 (d, $^2J_{\text{HH}} = 14.4$ Hz, 2H), 6.24 (s, 1H), 6.38 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 0.73 (q), 1.03 (q), 20.3 (d), 29.9 (q), 30.7 (t), 30.8 (d), 31.1 (d), 121.8 (d), 126.7 (d), 132.1 (s), 132.2 (s), 142.5 (s), 150.4 (s), 150.5 (s).

Thermolysis of Stibolene 7a in the Presence of 2,3-Dimethyl-1,3-butadiene. **7a** (22.3 mg, 0.03 mmol) and 2,3-dimethyl-1,3-butadiene (34 μL , 0.30 mmol) were dissolved in toluene- d_8 (0.7 mL), and the solution was degassed and sealed in an NMR tube. After the reaction mixture was heated at 90 °C for 4.5 h, no change was observed by ^1H NMR. Furthermore, after the solution was heated at 120 °C for 20 h, the signals of **7a** disappeared and the signals assignable to **8a** were observed by ^1H NMR. The reaction mixture was separated by GLPC to give **8a** (16.7 mg, 74%).

Thermolysis of Stibolene 8a in the Presence of Isoprene. **8a** (22.8 mg, 0.03 mmol) and isoprene (30 μL , 0.30 mmol) were dissolved in toluene- d_8 (0.7 mL), and the solution was degassed and sealed in an NMR tube. After the solution was heated at 120 °C for 23 h and 130 °C for 12 h, the signals of **8a** disappeared and the signals assignable to **7a** were observed by ^1H NMR. The reaction mixture was separated by GLPC to give **7a** (17.4 mg, 78%).

Thermolysis of Stibolene 7a. **7a** (21.0 mg, 0.03 mmol) was dissolved in toluene- d_8 (0.6 mL), and the solution was degassed and sealed in an NMR tube. After the solution was heated at 120 °C for 19 h, the signals of **7a** found by ^1H NMR disappeared. Green crystals, which were precipitated by cooling the mixture to room temperature, were filtered to afford Tb_2Sb_2 **4a** (10.3 mg, 55%).

Preparation of {2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}dibromostibine (1b). To a solution of BbTbBr (3.52 g, 5.00 mmol) in THF (50 mL) was added *t*-butyllithium (1.6 M pentane solution, 7.0 mL, 12.0 mmol) at -78 °C. After 30 min, a solution of SbBr_3 (2.74 g, 7.60 mmol) in THF (15 mL) was added. The reaction mixture was warmed to room temperature and stirred for 12 h. The solvents were evaporated under reduced pressure and 100 mL of hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. After removal of the solvent from the filtrate, the residue was reprecipitated from CH_2Cl_2 /isopropyl alcohol to afford BbTbSbBr_2 (**1b**, 3.05 g, 67%). **1b**: pale yellow crystals, mp 128–130 °C (decomp). ^1H NMR (500 MHz, CDCl_3) δ 0.14 (s, 36H), 0.26 (s, 27H), 2.64 (s, 2H), 6.83 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 1.46 (q), 5.41 (q), 23.16 (s), 32.23 (d), 127.99 (d), 143.13 (s), 149.84 (s), 151.51 (s). HRMS (FAB) Found: m/z 906.1048 ($[\text{M}]^+$). Calcd for $\text{C}_{30}\text{H}_{67}^{79}\text{Br}^{81}\text{BrSi}_7^{123}\text{Sb}$ ($[\text{M}]^+$): 906.1016.

Preparation of 2,4,6-Tris[2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl]-1,3,5,2,4,6-triselenatribismane (3b). To a suspension of selenium (63.4 mg, 0.80 mmol) in THF (2 mL) was added a THF solution (1.7 mL) of $\text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$ (1.0 M, 1.70 mmol) at room temperature. After 10 min, a solution of BbTbSbBr_2 (**1b**) (730 mg, 0.80 mmol) in THF (12 mL) was added and the reaction mixture was stirred for 1.5 h. The solvent was evaporated under reduced pressure and 30 mL of hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. After removal of the solvent from the filtrate, the residue was purified by GLPC and reprecipitation from CHCl_3 /isopropyl alcohol to afford $(\text{BbTbSe})_3$ (**3b**, 484 mg, 73%) **3b**: yellow crystals, mp 293–296 °C (decomp).

Found: C, 43.44; H, 7.89%. Calcd for $C_{90}H_{201}Sb_3Se_3Si_{21}$: C, 43.67; H, 8.18%. 1H NMR (500 MHz, $CDCl_3$) δ 0.13 (s, 108H), 0.26 (s, 81H), 2.75 (brs, 6H), 6.80 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 323 K) δ 1.79 (q), 5.47 (q), 22.48 (s), 34.16 (d), 127.50 (d), 143.38 (s), 146.77 (s), 151.06 (s). Molecular weight (osmometry in $CHCl_3$) Found: 2447. Calcd for $C_{90}H_{201}Sb_3Se_3Si_{21}$: 2475.

Deselenation Reaction of (BbtSbSe)₃ (3b) with P(NMe₂)₃. **3b** (50.2 mg, 0.02 mmol) and P(NMe₂)₃ (0.02 mL, 0.08 mmol) were dissolved in toluene-*d*₈ (0.6 mL), and the solution was degassed and sealed in an NMR tube. After the solution was heated at 130 °C for 33 h, the signals of the selenadistibirane **10** and BbtSb=SeBbt **4b** were observed in the ratio of 6:1 by 1H NMR. Deep red crystals, which were precipitated by cooling the mixture to room temperature, were filtered to afford the selenadistibirane **10** (25.1 mg, 52%). The filtrate was separated by GLPC to give **10** (15.7 mg, 33%) and starting material **3b** (1.9 mg, 4%). **10**: orange crystals, mp 215–220 °C (decomp). Found: C, 46.13; H, 8.37; Se, 4.56%. Calcd for $C_{60}H_{134}Sb_2SeSi_{14}$: C, 45.86; H, 8.60; Se, 5.02%. 1H NMR (500 MHz, $CDCl_3$) δ 0.37 (s, 54H), 0.41 (s, 72H), 3.00 (s, 4H), 6.99 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 323 K) δ 2.01 (q), 2.13 (q), 5.65 (q), 22.30 (s), 36.98 (d), 127.00 (d), 142.19 (s), 146.05 (s), 150.89 (s). ^{77}Se NMR (95 MHz, C_6D_6) δ -182. Molecular weight (osmometry in $CHCl_3$) Found: 1491. Calcd for $C_{60}H_{134}Sb_2SeSi_{14}$: 1571.

Deselenation Reaction of (BbtSbSe)₃ (3b) with P(NMe₂)₃ in the Presence of 2,3-Dimethyl-1,3-butadiene. To a toluene solution (4 mL) of **3b** (263 mg, 0.11 mmol) were added 0.40 mL of P(NMe₂)₃ (1.6 mmol) and 1.2 mL of 2,3-dimethyl-1,3-butadiene (10.0 mmol), and the reaction mixture was heated at 130 °C in a sealed tube for 38 h. The reaction mixture was separated by GLPC to give the selenadistibirane **10** (80.1 mg, 30%) and the stilbene **8b** (192.7 mg, 70%). **8b**: colorless powder, mp 104–106 °C (decomp). Found: C, 51.42; H, 8.85%. Calcd for $C_{36}H_{77}SbSi_7 \cdot 0.5H_2O$: C, 51.64; H, 9.39%. 1H NMR (500 MHz, $CDCl_3$) δ 0.07 (s, 36H), 0.23 (s, 27H), 1.66 (s, 6H), 1.98 (s, 2H), 2.40 (d, $^2J_{HH}$ = 13.9 Hz, 2H), 3.31 (d, $^2J_{HH}$ = 13.9 Hz, 2H), 6.67 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.50 (q), 5.40 (q), 20.18 (s), 21.40 (q), 31.42 (t), 32.22 (d), 126.31 (d), 131.73 (s), 137.45 (s), 144.03 (s), 149.92 (s).

Thermolysis of Stilbene 8b. **8b** (50.2 mg, 0.06 mmol) was dissolved in toluene-*d*₈ (0.6 mL), and the solution was degassed and sealed in an NMR tube. After the solution was heated at 130 °C for 64 h, the disappearance of the signals of **8b** was confirmed by 1H NMR and only the signals assignable to distibene **4b** and 2,3-dimethyl-1,3-butadiene were observed by 1H NMR. After the solvent and the generated diene were evaporated under reduced pressure in a glovebox filled with argon, the residue (52.5 mg) was found to contain distibene **4b** as the main product (> 90%). **4b**: deep red solid, mp 201–205 °C (decomp). Found: C, 47.88; H, 9.21%. Calcd for $C_{60}H_{134}Sb_2Si_{14}$: C, 48.29; H, 9.05%. 1H NMR (500 MHz, C_6D_6) δ 0.32 (s, 72H), 0.41 (s, 54H), 2.49 (s, 4H), 7.19 (s, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 2.27 (q), 5.77 (q), 22.24 (s), 39.42 (d), 126.97 (d), 146.81 (s), 147.15 (s), 150.37 (s). UV–vis (hexane) 594 (ϵ 200), 490 nm (ϵ 6000).

Reaction of Distibene 4b with Se=P(NMe₂)₃. A toluene solution (1 mL) of **4b** (9.9 mg, 0.01 mmol) and Se=P(NMe₂)₃ (8.2 mg, 0.03 mmol) was concentrated. The reaction mixture was dissolved in C_6D_6 and then the solution was degassed and sealed in an NMR tube. Only the signals for **10** along with those of excess Se=P(NMe₂)₃ were observed in the 1H NMR measurement.

Reaction of Selenadistibirane 10 with P(NMe₂)₃. To a toluene-*d*₈ solution (0.6 mL) of **10** (24.8 mg, 0.02 mmol) was added

0.04 mL of P(NMe₂)₃ (0.16 mmol), and then the solution was degassed and sealed in an NMR tube. The signals of **10** and **4b** were observed in the ratio of 1:1 in the 1H NMR spectrum at room temperature. After the reaction mixture was heated at 120 °C for 2 h, the signals of **10** and **4b** were observed in the ratio of 1:4 by 1H NMR. Even after the solution was further heated at 120 °C for 15 h and at 150 °C for 23 h, no change of the ratio was observed in the 1H NMR spectra.

Synthesis of Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}distibene (4b) via Reductive Coupling Reaction of BbtSbBr₂ (1b) with Mg Metal. To a THF solution (4 mL) of BbtSbBr₂ **1b** (378 mg, 0.09 mmol) was added Mg metal (31.2 mg, 1.28 mmol) at room temperature. After the reaction mixture was stirred for 30 min, the color of the solution changed to deep red. The solvent was evaporated under reduced pressure and 30 mL of hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. The removal of the solvent from the filtrate gave a deep red solid of distibene **4b** (64.0 mg, quant.).

Preparation of {2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}dibromobismuthine (2b). To a solution of BbtBr (2.10 g, 3.00 mmol) in THF (30 mL) was added *t*-butyllithium (1.65 M pentane solution, 4.3 mL, 7.6 mmol) at -78 °C. After 30 min, a solution of BiCl₃ (2.74 g, 7.60 mmol) in THF (15 mL) was added. After the reaction mixture was stirred at -78 °C for 2 h, LiBr (6.75 g, 77.7 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 12 h. The solvents were evaporated under reduced pressure and 100 mL of hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. After removal of the solvent from the filtrate, the residue was recrystallized from hexane to afford BbtBiBr₂ (**2b**, 653 mg, 22%). **2b**: yellow crystals, mp 150–155 °C (decomp). 1H NMR (500 MHz, $CDCl_3$) δ 0.15 (s, 36H), 0.26 (s, 27H), 2.32 (s, 2H), 7.54 (s, 2H). HRMS (FAB) Found: m/z 992.1752 ($[M]^+$). Calcd for $C_{30}H_{67}Bi^{79}Br^{81}BrSi_7$ ($[M]^+$): 992.1778.

Synthesis of Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}dibismuthene (6b) via Reductive Coupling Reaction of BbtBiBr₂ (2b) with Mg Metal. To a THF solution (4 mL) of BbtBiBr₂ (**2b**) (200 mg, 0.20 mmol) was added Mg metal (70.0 mg, 2.88 mmol) at room temperature. After the reaction mixture was stirred for 30 min, the color of the solution changed to violet. The solvent was evaporated under reduced pressure and 30 mL of hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. The removal of the solvent from the filtrate gave dibismuthene **6b** (167 mg, quant.) as a violet solid. **6b**: violet powder, mp 250.5–252.0 °C (decomp). Found: C, 43.34; H, 8.00%. Calcd for $C_{60}H_{134}Bi_2Si_{14}$: C, 43.23; H, 8.10%. 1H NMR (500 MHz, C_6D_6) δ 0.34 (s, 72H), 0.38 (s, 54H), 1.46 (s, 4H), 7.33 (s, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ 3.11 (q), 5.75 (q), 14.29 (s), 46.60 (d), 124.44 (d), 147.40 (s), 154.36 (s), 162.42 (s). UV–vis (hexane) 670 (sh, ϵ 20), 537 nm (ϵ 6000).

X-ray Crystallographic Analyses of 4b and 6b. Crystal data of **4b** and **6b** are shown in Table 5. Single crystals of these compounds suitable for X-ray analysis were obtained by slow recrystallization from hexane in a refrigerator at -40 °C fixed in a glovebox filled with argon. The intensity data were collected on a Rigaku R-Axis RAPID imaging plate detector (for **4b**) and Rigaku/MSM Mercury CCD diffractometer (for **6b**) with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) at -180 °C to $2\theta_{max}$ = 50°. The structures were solved by direct methods

Table 5. Crystal Data for **4b** and **6b**

	4b	6b
Formula	C ₆₀ H ₁₃₄ Sb ₂ Si ₁₄	C ₆₀ H ₁₃₄ Bi ₂ Si ₁₄
Formula weight	1492.44	1666.89
Crystal color, habit	deep red, prismatic	violet, prismatic
Crystal dimensions/mm	0.30×0.20×0.15	0.20×0.10×0.10
Temperature	−180°C	−180°C
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)
Lattice parameters		
<i>a</i> /Å	12.5987(6)	9.2869(18)
<i>b</i> /Å	17.9474(12)	12.5191(13)
<i>c</i> /Å	9.3011(6)	18.122(2)
α /°	93.096(2)	88.841(5)
β /°	98.8541(16)	87.697(4)
γ /°	88.764(3)	81.2683(14)
<i>V</i> /Å ³	2074.8(2)	2080.6(5)
<i>Z</i>	1	1
<i>D</i> _{calc} /g cm ^{−3}	1.194	1.330
Independent reflections	6633	7285
No. of parameters	364	364
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.044	0.040
<i>wR</i> ₂ (all data)	0.132	0.098
Goodness of fit	1.031	1.092

Table 6. Crystal Data for **12a**

Formula	C ₅₄ H ₁₁₈ Bi ₂ O ₂ Si ₁₂
Formula weight	1554.51
Crystal color, habit	pale yellow, prismatic
Crystal dimensions/mm	0.50×0.20×0.10
Temperature	23°C
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$ (#2)
Lattice parameters	
<i>a</i> /Å	12.848(3)
<i>b</i> /Å	18.236(6)
<i>c</i> /Å	9.333(2)
α /°	93.83(2)
β /°	108.43(2)
γ /°	105.84(2)
<i>V</i> /Å ³	1967.5(10)
<i>Z</i>	1
<i>D</i> _{calc} /g cm ^{−3}	1.312
Observed reflections	3108
[<i>I</i> > 3.00σ(<i>I</i>)]	
No. of parameters	316
<i>R</i>	0.069
<i>R</i> _w	0.062
Goodness of fit	2.19

(SIR97⁴³ or SHELXS-97⁴⁴) and refined by full-matrix least-squares procedures on *F*² for all reflections (SHELXL-97⁴⁴). All hydrogens were placed using AFIX instructions.

Oxidation of Dibismuthene 6a. Purple crystals of dibismuthene **6a** were taken out of the glovebox to be exposed to open air. On standing for 20 h, the purple color of **6a** faded to give colorless crystals of Tbt₂Bi₂O₂ **12a** quantitatively. **12a**: colorless crystals, mp 187–191 °C. Found: C, 39.66; H, 7.74%. Calcd for C₅₄H₁₁₈Bi₂O₂Si₁₂: C, 41.72; H, 7.65%. NMR spectral data of **12a**

could not be obtained because of its insolubility in any organic solvent.

X-ray Crystallographic Analysis of 12a. Crystal data of **12a** are shown in Table 6. Single crystals of **12a** suitable for X-ray analysis were obtained by leaving the single crystals of **6a** in open air for a few days. The intensity data were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo *K*α radiation ($\lambda = 0.71069$ Å) at 23 °C to $2\theta_{\max} = 55^\circ$. The structures were solved and refined by using the program package teXsan.⁴⁵

X-ray crystallographic files in CIF format for **4b**, **6b**, and **12a** have been deposited as document No. 75018 at the office of the Editor of Bull. Chem. Soc. Jpn. and also deposited at the CCDC, 12 Union Road, Cambridge CB21EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 177271–177273.

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