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Review

New aspects in the chemistry of low-coordinated inter-element compounds of heavier Group 15 elements

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Abstract

Recent results obtained in the studies of the author and co-workers on the synthesis and properties of doubly bonded systems between heavier Group 15 elements are described together with a brief historical survey on the chemistry of low-coordinated heavier Group 15 elements. The first stable distibene and dibismuthene were successfully synthesized by taking an advantage of kinetic stabilization using new bulky substituents and the spectroscopic studies and crystallographic analysis of them led to the systematic comparison of structural parameters and physical properties for all doubly bonded systems between heavier Group 15 elements from phosphorus to bismuth. In addition to these experimental data, theoretical calculations also revealed the intrinsic character of low-coordinated inter-element compounds containing heavier Group 15 elements, especially that of dibismuthene, i.e. the heaviest double-bond compounds of non-radioactive elements. Furthermore, a unique intermolecular crystalline-state reaction was observed in the oxidation of the overcrowded distibene and dibismuthene, the reaction process of which was successfully monitored by repeated measurements of the cell dimensions using an imaging-plate X-ray diffraction technique. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Doubly bonded systems; Heavier Group 15 elements; Distibene; Dibismuthene; Intermolecular crystalline-state reaction

1. Introduction

The chemistry of compounds featuring multiple bonds between the heavier main Group elements has attracted attention in recent years. According to the so-called ‘classical double-bond rule’ [1], only elements in the second-row in the periodic table should be able to form stable compounds with double-bonds, and such bonding in heavier elements would be impossible since the long distance between the elements would not allow sufficient overlapping of the p orbitals. This ‘classical double-bond rule’ was supported by a number of unsuccessful attempts to synthesize such compounds. For example, Köller and Michaelis reported that the condensation reaction of $PhPCl_2$ and $PhPH_2$ resulted in the formation of diphenyldiphosphene (Ph–P=P–Ph; called ‘phosphobenzene’ in the original paper) [2] but later it was shown, first by molecular weight measurements and subsequently by X-ray structure analyses, that this product was a mixture of oligomers of ‘phosphobenzene’ (i.e. $(PhP)_5$ and $(PhP)_6$) [3]. A similar mistake was made in determining the structure of the chemotherapeutic drug ‘Salvarsan’ which was first described as a monomeric diarsene structure by Ehrlich [4] but once again, X-ray crystallographic work revealed that compound of empirical formula is, in fact, oligomeric [5]. From these failures, it was realized that the introduction of sufficiently large substituents is necessary to avoid the oligomerization of these reactive species. This idea of kinetic stabilization of reactive multiple bonds by bulky ligands led to the first syntheses of disilene **1** [6] and diphosphene **2** [7] in 1981 (Chart 1).

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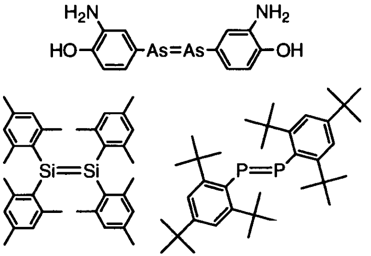


1 **2**

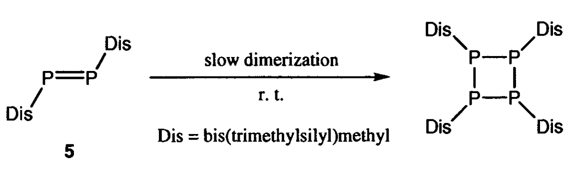
Chart 1.

2. Historical survey of double-bond species of heavier Group 15 elements

2.1. Diphosphenes

Since the first isolation of diphosphene **2**, intensive works on the chemistry of this new class of compounds have been performed. Yoshifuji obtained diphosphene **2** by the reduction of (2,4,6-tri-*tert*-butylphenyl)dichlorophosphine with elemental magnesium [7], and it has been demonstrated that various other reducing agents can be employed in the synthesis of diphosphene **2** [8]. When the sodium naphthalenide reduction was carried out with a mixture of Mes*PCl_2 (Mes* = 2,4,6-tri-*tert*-butylphenyl) and TsiPCl_2 (Tsi = tris(trimethylsilyl)methyl [$C(SiMe_3)_3$]), unsymmetrical diphosphene **3** was formed, apart from the symmetrical diphosphenes **2** and **4** (Scheme 1) [9]. Another approach to the syntheses of symmetrical and unsymmetrical diphosphenes was provided by the condensation reaction of dichlorophosphines and primary phosphines using DBU (Scheme 2) [8,10].

The importance of sufficient protection by the substituents is clearly demonstrated by the oligomerization of some transient diphosphenes (Scheme 3) [11]. Diphosphene **5** bearing bis(trimethylsilyl)methyl (Dis) groups, which is isolable but less hindered than **2**, **3**, or **4**, undergoes very slow self-dimerization at room temperature (Scheme 4) [12]. The half-life time of this process was estimated to be one week, and this diphosphene **5** is probably at the borderline of kinetic stability.



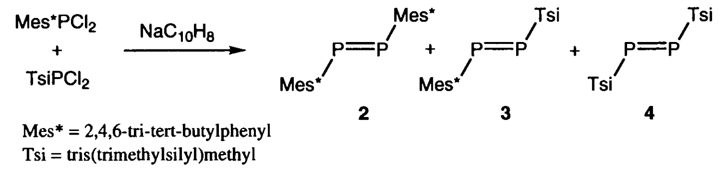
Scheme 4.

Several diphosphenes have been structurally characterized by X-ray crystallographic analyses [8]. The bond lengths of the phosphorus–phosphorus double bond (2.001–2.034 Å) are much shorter than those in diphosphines (~ 2.21 Å), and are also in good agreement with the theoretical calculations on P_2H_2 (2.005 Å) [13]. In the symmetrical diphosphenes, the bond angle, which is expected to be 96.1° in P_2H_2 by the theoretical calculations, varies from 102.2 to 108.9°. This trend can be explained by the steric demands of the bulky substituents.

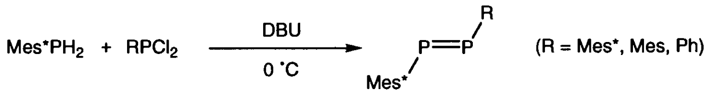
Since to date several reviews and accounts have already been described for stable and transient diphosphenes [8], detailed description and discussion on their structures and properties are not made in this article.

2.2. Phosphaarsenes, diarsenes, and phosphastibenes

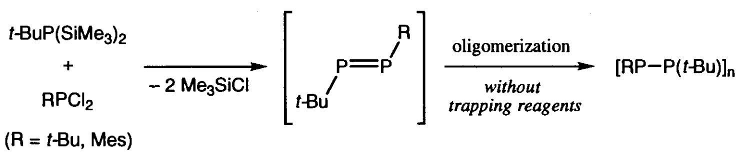
The strategies used in the syntheses of diphosphenes can be applied for the species containing even heavier Group 15 elements, i.e. arsenic and antimony. Symmet-



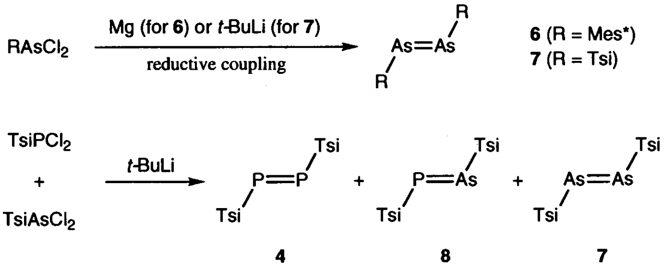
Scheme 1.



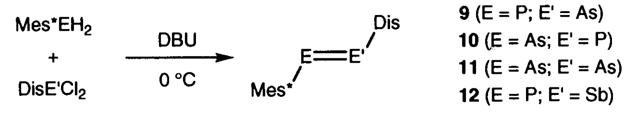
Scheme 2.



Scheme 3.



Scheme 5.

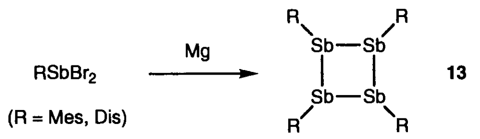


Scheme 6.

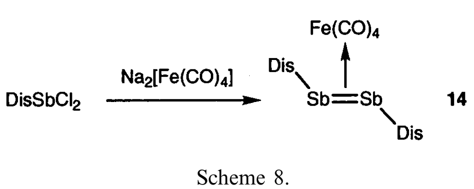
rically substituted diaryl- and dialkyldiarsenes **6** [14] and **7** [15] were synthesized as stable compounds by the reductive coupling reactions of the corresponding dichloroarsines (Scheme 5). When *tert*-butyllithium was added to a mixture of $TsiPCl_2$ and $TsiAsCl_2$, phosphaarsene **8**, diarsene **7**, and diphosphene **4** were formed (Scheme 5) [16]. The DBU reaction proved to be effective in the syntheses of phosphaarsenes **9** and **10**, diarsene **11**, and phosphastibene **12** (Scheme 6) [17]. Phosphaarsene **9** and diarsene **11** were structurally characterized by X-ray crystallographic analyses and the shortening of the phosphorus–arsenic and the arsenic–arsenic bonds compared to the single bond indisputably showed the double bond character in these compounds. Phosphastibene **12** was characterized by high-resolution mass spectrum and ^{31}P-NMR ($\delta = 620.0$), but it was unstable in solution and decomposed within two hours to yield the symmetrical diphosphene **2**. Attempts to prepare a phosphorus-bismuth double bond by this method have been unsuccessful so far.

2.3. Distibene and dibismuthene

The successful synthesis and isolation of diphosphenes and diarsenes have naturally provoked chemists to try to prepare their heavier analogues, i.e. distibenes (RSb=SbR) and dibismuthenes (RBi=BiR), but all attempts have been unsuccessful until the authors have reported the synthesis of the first stable distibene and dibismuthene by taking advantage of a new steric protection group.



Scheme 7.



Scheme 8.

The ab initio calculations of the parent compounds, HSb=SbH and HBi=BiH, have suggested that these compounds are thermally stable, unlike the double bond species of heavier Group 14 elements, $H_2Pb{=}PbH_2$ [13]. The coupling reactions of dibromostibines bearing a bulky substituent such as mesityl or bis(trimethylsilyl)methyl group by magnesium have resulted in the formation of four-membered rings **13**, i.e. the dimers of expected distibenes, showing that these ligands are not large enough to avoid the dimerization of the corresponding distibene (Scheme 7) [18]. Although several transition-metal-coordinated distibene complexes have been synthesized as in the case of compound **14** (Scheme 8) [19], the double-bond character of the Sb–Sb bond is lost in these complexes because of side-on η^2 coordination.

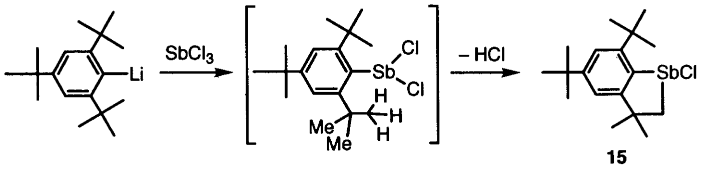
2.4. Choice of the steric protection group

In the following sections, the noticeable recent progress in the chemistry of double-bond species containing antimony and bismuth, i.e. distibene (RSb=SbR), dibismuthene (RBi=BiR), and related compounds. Since these low-coordinated heavier Group 15 element species are expected to be highly reactive, it will require either thermodynamic or kinetic stabilization for their synthesis and isolation as stable compounds.

Thermodynamic stabilization, for example by introducing heteroatoms in the substituents, lowers the ground state energy of the reactive species and has proved very effective in the isolation of many compounds containing multiple bonds between heavier main group elements. But, in many of these cases, the character of the multiple bond itself is changed enormously. This undesirable effect can be avoided by taking advantage of bulky steric protection groups, i.e. by kinetic stabilization. Here, the bulky substituents prevent the self-oligomerizations of these reactive species; in other words, by increasing the transition state energy. But one must be careful that over-protection around the reactive bond prevents the reactions with other molecules and would make it difficult to examine the nature of the multiple bond.

One of the most widely used steric protection groups is 2,4,6-tri-*tert*-butylphenyl (Mes*), but the attempt to prepare dichlorostibine bearing Mes* group resulted in the formation of the cyclic compound **15** (Scheme 9) [19].

Dichlorostibine bearing another bulky substituent, $(Me_3Si)_3C$ group, is reported to be extremely sensitive



Scheme 9.

to light [19], hence it is difficult to use this substrate in further transformations.

In order to synthesize stable distibene and dibismuthene, the author and his co-workers chose 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Chart 2; denoted as Tbt hereafter [20]) as the steric protection group on antimony since it has proved to be very effective in the kinetic stabilization of many reactive low-coordinated species of main group elements such as metallylenes and dimetallenes of heavier Group 14 elements, double-bond compounds between heavier Group 14 and 16 elements (we call these species 'heavy ketones'), and silaaromatic compounds [21]. After the successful isolation of the first stable distibene and dibismuthene bearing Tbt groups, Power et al. also reported the synthesis of stable doubly bonded systems containing antimony and bismuth using their original bulky *m*-terphenyl ligands (Chart 2) [22], the detail of which will be delineated in the final section.

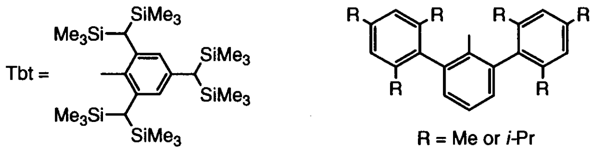


Chart 2.

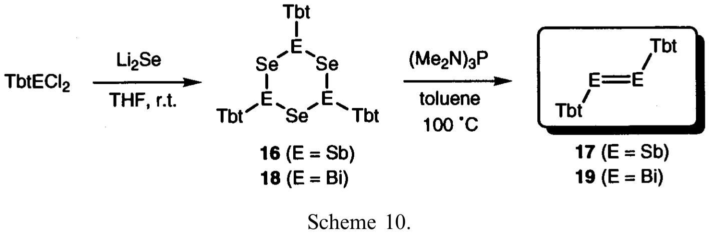
3. Synthesis and properties of the first stable distibene and dibismuthene

3.1. Synthesis of stable distibene and dibismuthene bearing Tbt groups [23,24]

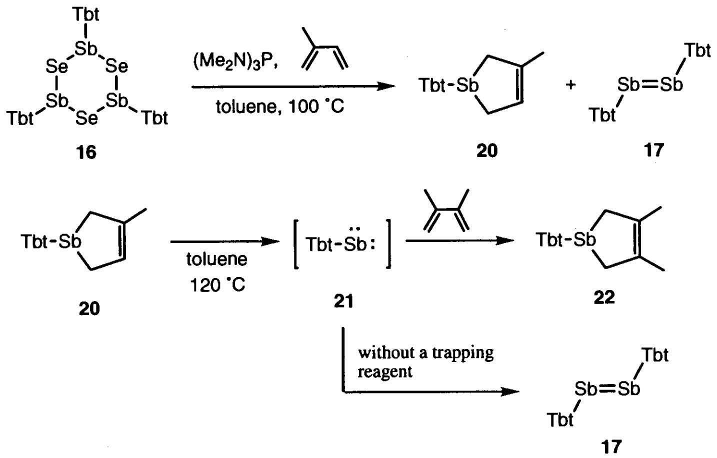
By taking advantage of an efficient steric protection group (Tbt), the long-sought doubly bonded compound consisting of antimony and bismuth, i.e. distibene and dibismuthene, were successfully synthesized and isolated as stable compounds. Since the conventional synthetic methods for stable diphosphenes and diarsenes were found to be not applicable or sometimes not effective for the synthesis and isolation of TbtSb=SbTbt (**17**), a new synthetic method, i.e. deselenation reaction of 1,3,5,2,4,6-triselenatristibane **16** (E = Sb) with a phosphine reagent, has been developed. As shown in Scheme 10, the precursor **16** was readily synthesized by treatment of $TbtSbCl_2$ with Li_2Se in THF. Triselenatristibane **16** thus isolated as a stable crystalline compound was then treated with an excess amount of hexamethylphosphorous triamide in toluene at 100°C in a sealed tube. After heating for 12 h the solution turned green and the expected distibene **17**, which precipitated from the mixture on cooling, was isolated by filtration in a glovebox filled with argon as deep green single crystals in 94% yield (Scheme 10) [23]. The distibene **17** has a very low solubility in common organic solvents probably due to its high symmetry in the molecular structure, thus making its isolation quite simple.

The heaviest congeners of azo-compounds, i.e. dibismuthene, was also successfully isolated as a stable compound by the use of Tbt groups as steric protection groups. Thus, TbtBi=BiTbt (**19**), the first stable Bi=Bi double-bond compound, was synthesized by the same method as in the case of distibene **17**, i.e. deselenation reaction of the 1,3,5,2,4,6-triselenatribismane **18** (E = Bi) [24]. Treatment of **18**, prepared by the reaction of $TbtBiCl_2$ with Li_2Se in THF, with excess amount of hexamethylphosphorous triamide in toluene at 100°C in a sealed tube resulted in a formation of a purple solution. On gradual cooling to room temperature (r.t.), dibismuthene **19** precipitated from the mixture as purple single crystals (68%) (Scheme 10) [24].

When the deselenation of triselenatristibane **16** with $(Me_2N)_3P$ in the presence of an excess amount of isoprene, Tbt-substituted stibolene **20** was obtained as a main product (62%) together with a small amount of distibene **17** (26%) as shown in Scheme 11 [25]. The formation of **20** strongly suggests that the initial formation of a stibinidene intermediate **21** in the deselenation of **16** and the subsequent [1 + 4]cycloaddition reaction of **21** with isoprene. Interestingly, the thermolysis of the



Scheme 10.



Scheme 11.

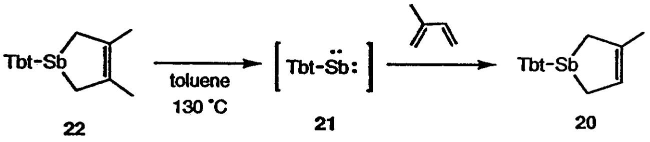
toluene solution of the isolated cycloadduct **20** in the presence of 2,3-dimethyl-1,3-butadiene (10 equivalents) at 120°C in a sealed tube resulted in a formation of the diene-exchanged cycloadduct **22** in 74% yield, while thermolysis of **20** in the absence of 2,3-dimethyl-1,3-butadiene afforded distibene **17** in 55% yield (Scheme 11) [26].

These results indicate that it is possible to regenerate the stibinidene intermediate **21** by the thermal retrocycloaddition of stibolene **20** and this reaction can be used as another synthetic method for distibene **17**. The diene-exchange reaction via retrocycloaddition of **20** is rationalized by an equilibrium between the cycloadducts and the intermediary stibinidene **21**, since the reverse exchange reaction was observed in the thermolysis of stibolane **22** in the presence of excess isoprene (10 equivalents) at 130°C under similar conditions leading to the formation of **20** in 78% yield (Scheme 12) [26]. The predominant dimerization of **21** leading to the formation of distibene **17** in the absence of an excess amount of dienes might be interpreted in terms of the extremely low solubility of **17** in toluene.

In the case of deselenation of triselenatribismane **18** in the presence of either isoprene or 2,3-dimethyl-1,3-butadiene, no diene adduct was obtained probably due to the instability and high reactivity of the corresponding bismuthinidene intermediate [25,26].

3.2. Physical properties of stable distibene and dibismuthene bearing Tbt groups

Distibene **17** is the first example of a stable antimony–antimony double bond, and the green solution of **17** in hexane showed two absorption maxima at $\lambda_1 = 599$ (ε 170) and $\lambda_2 = 466$ nm (ε 5200), which correspond to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the Sb=Sb chromophore, respectively [23]. Dibismuthene **19** is purple in hexane and the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the Bi=Bi chromophore appeared as absorption maxima at $\lambda_1 = 660$ (sh, ε 100) and $\lambda_2 = 525$ nm (ε 4000), respectively [24a]. In Table 1 are shown the typical examples of absorption maxima reported for the double-bond compounds between heavier Group 15 elements [8] together with those of **17** and **19**. The experimentally observed red-shifts of **17** and **19** relative to the values reported for diphosphenes[7,10,17] and diarsenes[17] agree with the changes in the n, π, and π* orbital levels calculated for HE=EH (E = P, As, Sb, and Bi) [13].



Scheme 12.

In the FT-Raman spectrum distibene **17** showed a strong Raman line at 207 cm^{-1} (solid; excitation, He–Ne laser 632.8 nm) which is much higher than the frequencies observed for distibines (e. g. Ph_2Sb–$SbPh_2$ 141 cm^{-1}) [27]. Meanwhile, a strong band attributable to the Bi–Bi stretching was observed at 134 cm^{-1} for the dibismuthene **19** (solid; excitation, He–Ne laser 632.8 nm) [24]. This is 31 cm^{-1} higher than the Bi–Bi

Table 1
UV–vis data for double-bond systems of heavier Group 15 elements

Compound	λ_1 (nm) (ε)	λ_2 (nm) (ε)
Mes*P=PMes* (2)	460 (1360)	340 (7690)
TsiP=Ptsi (**4**)	484 (62.8)	353 (9474)
Mes*P=PDis	427 (370)	325 (13 000)
Mes*P=PMes	456 (220)	326 (2500)
TsiP=AsTsi (**8**)	497 (20)	361 (7900)
Mes*As=PDis (**10**)	431 (220)	354 (8400)
Mes*As=AsDis (**11**)	449 (180)	368 (6960)
TsiAs=AsTsi (**7**)	505 (10)	380 (5000)
TbtSb=SbTbt (**17**)	599 (170)	466 (5200)
TbtBi=BiTbt (**19**)	660 (100)	525 (4000)

stretching frequency of $Ph_2Bi–BiPh_2$ (103 cm^{-1}) [28], agreeing with the frequency shift of 34 cm^{-1} calculated for HBi=BiH (153 cm^{-1}) and $H_2Bi–BiH_2$ (119 cm^{-1}) [24a]. Thus, the spectroscopic data here obtained indicate that both distibene **17** and dibismuthene **19** feature Sb=Sb and Bi=Bi double bonds even in solution.

The diaryldiphosphene (**2**; Mes*P=PMes*) is known to show the vibrational frequency for its P=P double bond at 610 cm^{-1} in the Raman spectra [29], and the assignment was confirmed by the theoretically calculated value (617 cm^{-1}) at MP2 level [30].

3.3. Molecular structure of distibene and dibismuthene bearing Tbt groups

Since dibismuthene **19** is the first compound containing a bismuth–bismuth double bond which is the heaviest among those which consist of non-radioactive elements in the periodic table, it should be very important to know its molecular geometry and get the definitive structural parameters for the Bi=Bi double bond. The X-ray crystallographic structural analysis of dibismuthene **19** (Fig. 1) revealed two important parameters, i.e. the Bi–Bi bond length (2.8206(8) Å) and the Bi–Bi–C angle (100.5(2)°) [24]. The Bi–Bi bond in **19** is 6% (0.169 Å) shorter than the Bi–Bi single bond length of 2.990(2) Å in $Ph_2Bi–BiPh_2$ [31]. This agrees reasonably well with the calculated bond shortening of 7% (0.214 Å) from $H_2Bi–BiH_2$ (3.009 Å) to HBi=BiH (2.795 Å) [24]. In addition, it is interesting that the bond shortenings are comparable with those reported for diphosphenes; the experimental value is 8% (0.183 Å) from $(PhP)_5$ (2.217(6) Å) [3c] to Mes*P=PMes* (**2**) (2.034(2) Å) [7], while the calculated value is 9% (0.200 Å) from $H_2P–PH_2$ (2.247 Å) to HP=PH (2.047 Å) [24]. The observed Bi–Bi–C angle of 100.5° deviates greatly from the ideal sp^2 hybridized bond angle (120°). This is due to the fact that the heavy Bi atom has the lowest tendency to form a hybrid orbital because the size-difference of the valence s and p orbitals increases upon going from N to Bi (the significant 6s orbital contraction originates mostly from the relativistic effect) and prefers to maintain the $(6s)^2(6p)^3$ valence electron configuration. The use of these three orthogonal 6p orbitals without significant hybridization leads to a bond angle of approximately 90° at Bi [13,24]. The Bi–Bi–C bond angle in **19**, being close to 90°, is exactly the experimental evidence for the core-like nature of the 6s electrons, i.e. so called 'inert s-pair effect' or 'non-hybridization effect' [32].

X-ray crystallographic analysis of the green crystal of distibene **17** was also performed to reveal its molecular geometry as shown in Fig. 2, which was found to be completely isomorphous with the dibismuthene **19** [23]. Considerable bond shortening (7%) of the Sb–Sb bond length (2.642(1) Å) in **17** as compared with that reported for $Ph_2Sb–SbPh_2$ (2.837 Å) [27] clearly indicates its double-bond character, while the observed Sb–Sb–C bond angle of 101.4(1)°, which deviates greatly from the ideal sp^2 hybridized bond angle (120°) and approaches to 90°, suggests that **17** has a non-hybridized Sb–Sb double bond due to the core-like nature of Sb atom as in the case of dibismuthene **19**.

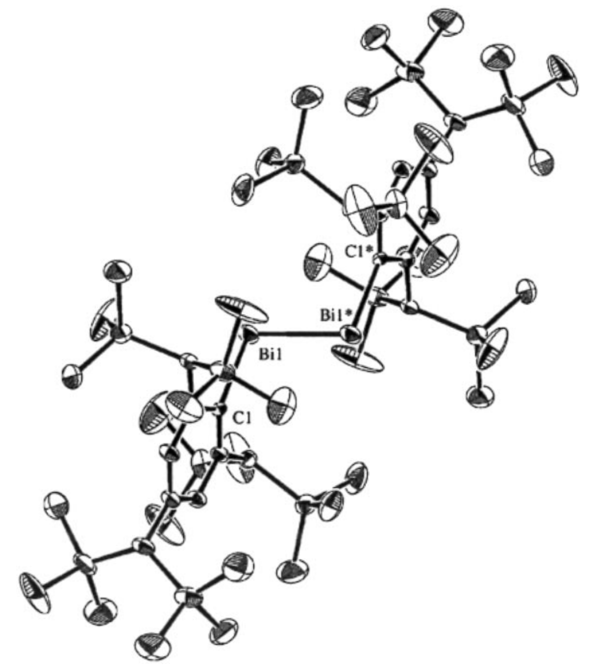


Fig. 1. ORTEP drawing of TbtBi=BiTbt (**19**) with thermal ellipsoid plot (30% probability).

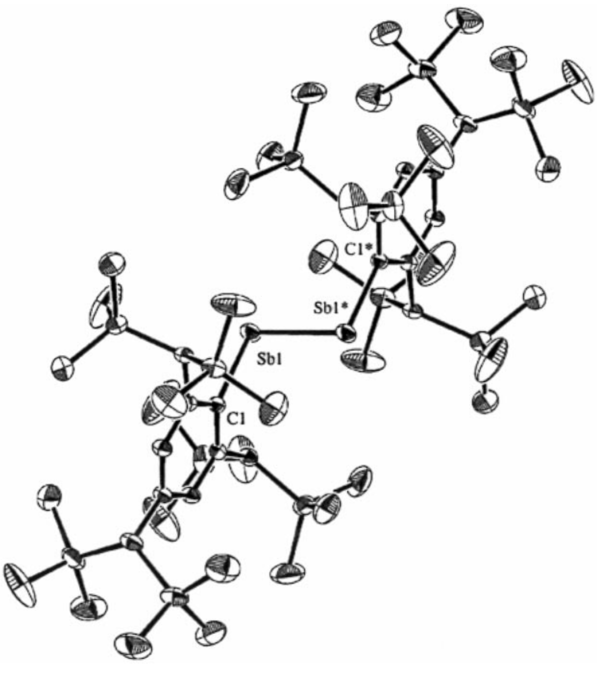
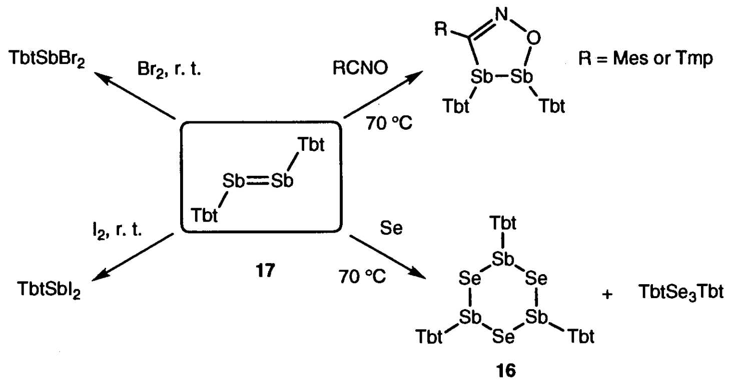


Fig. 2. ORTEP drawing of TbtSb=SbTbt (**17**) with thermal ellipsoid plot (30% probability).



Scheme 13.

3.4. Reactivity of distibene and dibismuthene bearing Tbt groups

Although both distibene **17** and dibismuthene **19** were isolated as crystalline compounds which are almost insoluble in common organic solvents, some reactions have been examined for distibene **17** (Scheme 13) [23,25,26].

Thus, treatment of **17** with bromine and iodine in carbon tetrachloride at r.t. resulted in the cleavage of the Sb–Sb bond to give the corresponding dihalostibines $TbtSbBr_2$ and $TbtSbI_2$ in quantitative yields, respectively, while the reaction of **17** with elemental selenium in tetrahydrofuran at 70°C gave the precursor **16** (23%) together with a triselenide $TbtSe_3Tbt$ (16%). On the other hand, distibene **17** underwent cycloaddition reactions with bulky aryl-substituted nitrile oxides ArCNO [Ar = 2,4,6-trimethoxyphenyl (Tmp) or 2,4,6-trimethylphenyl (Mes)] to afford the corresponding [2 + 3]-cycloadducts in 58 and 59% yields, respectively.

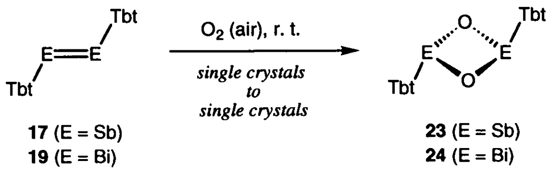
In contrast to the case of distibene **17**, dibismuthene **19** reacted most of the reagent mentioned above to give decomposition products without a bismuth moiety probably due to the instability of the carbon–bismuth and/or heteroatom–bismuth single bonds in the reaction products [26].

3.5. Unique crystalline-state intermolecular reactions of distibene and dibismuthene with aerobic oxygen

During the course of studies on the reactivity of distibene **17** and dibismuthene **19** a unique, interesting reactivity with oxygen was found. Although **17** and **19** react with aerobic oxygen in solution quite rapidly to give the corresponding 1,3,2,4-dioxadistibetane and 1,3,2,4-dioxadibismetane derivatives **23** and **24** quantitatively, both of them are considerably stable in the solid state in the open air. The crystals of **17** remained dark green for several hours, but they slowly reacted with atmospheric oxygen to give **23** quantitatively (Scheme 14) [23]. Similarly, the purple color of the crystals of dibismuthene **19** gradually faded in the open to give **24** as colorless crystals, the structure of which was definitively determined by X-ray crystallographic analysis (Scheme 14) [24b]. Of particular note is that **17** and **19** reacted with molecular oxygen in the crystalline state while retaining their crystallinity. In other words, the reactions proceeded from single crystals to single crystals.

The oxidation process of **17** 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 (Fig. 3), which clearly indicate that the crystal dimensions of **17** abruptly changed to those of **23** within 10 h after an induction period (ca. 30 h) [23]. After completion of the transformation of the unit cell dimensions three dimensional intensity data of **23** were collected using the identical crystal initially used for the structural analysis of **17**.

This unique reactivity in the crystalline-state observed for distibene **17** and dibismuthene **19** 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 consisted of overcrowded molecules bearing very bulky Tbt groups.



Scheme 14.

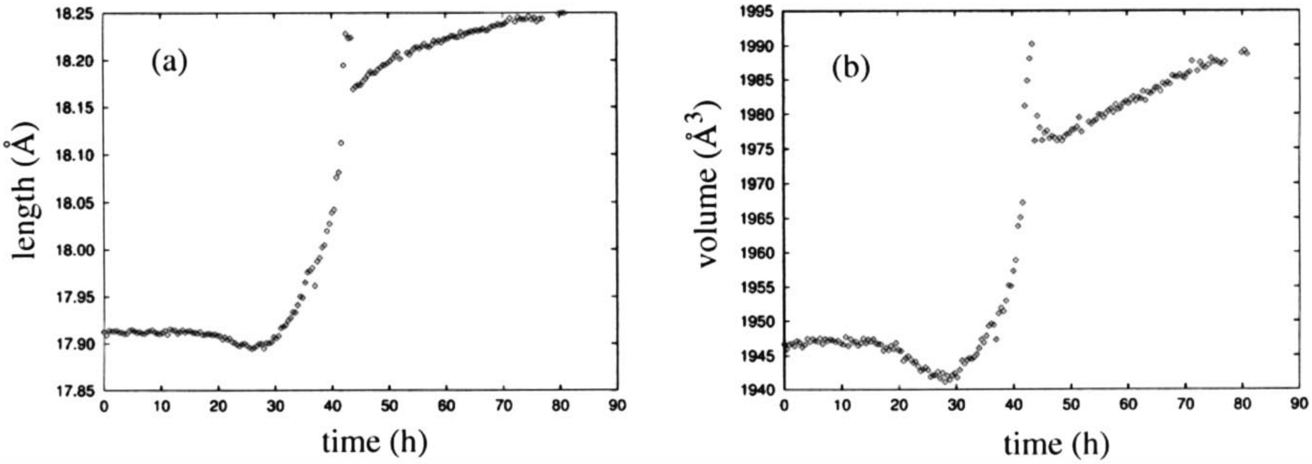


Fig. 3. Monitored changes of the cell parameters from 17 to 23: (a) change of the b-axis length; (b) change of the unit volume.

4. Current progress in the chemistry of distibene and dibismuthene

4.1. Synthesis of the first stable selenadistibirane and its transformation into a distibene

Although the first stable distibene **17** and dibismuthene **19** have been synthesized as stable crystals by taking advantage of the kinetic stabilization using Tbt groups [23,24] (vide supra), the extremely low solubility of **17** and **19** in common organic solvent prevented further studies on their chemical reactivity in solution. On the other hand, in the course of studies on the synthesis of sterically congested molecules the author and coworkers have developed another bulky aromatic substituent, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl group (denoted as Bbt group; Chart 3) [33], which is expected to be a potentially more useful steric protection group than Tbt group. Therefore, the synthesis of a Bbt-substituted distibene was examined in the hope of obtaining a stable distibene having higher solubility than **17**.

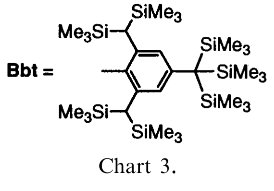
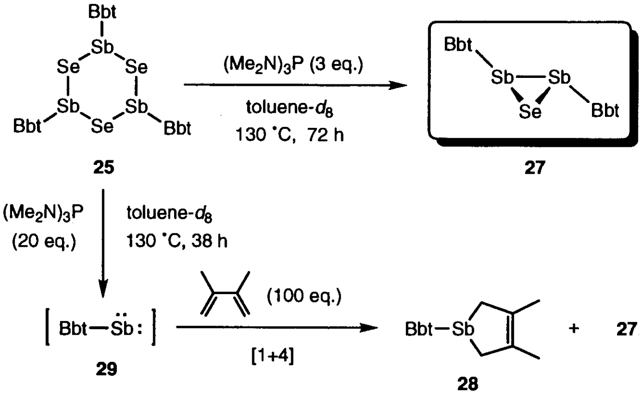


Chart 3.

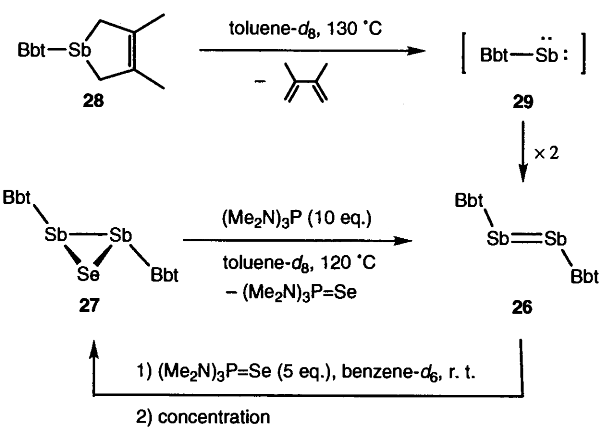
When an extremely hindered 1,3,5,2,4,6-triselenatristibane **25** bearing three Bbt groups on the antimony atoms was treated with hexamethylphosphorous triamide (HMPT; three equivalents) in toluene-d_8 at 130°C as well as in the transformation of the Tbt analogue **16** into distibene **17** [23], the color of the reaction mixture turned deep red. Although the UV–vis spectrum of this reaction mixture showed two characteristic absorption maxima at 490 (ε, ca. 4000) and 600 (ε, ca. 200) nm attributable to the π–π* and n–π* transitions of the expected distibene **26** (Bbt–Sb=Sb–Bbt), concentration of the reaction mixture afforded a new antimony-containing three-membered ring system, selenadistibirane **27**, as air-stable orange crystals in 70% yield (Scheme 15) [34].

On the other hand, treatment of **25** with an excess amount of HMPT (20 equivalents) in the presence of 2,3-dimethyl-1,3-butadiene (100 equivalents) gave the stibolene derivative **28** (70%) as a major product together with **27** (30%) (Scheme 15). The formation of **28** strongly suggests the involvement of the stibinidene intermediate **29** in the deselenation of **25**, since selenadistibirane **27** is almost inert toward 2,3-dimethyl-1,3-butadiene even at 130°C in toluene-d_8 for a long time.

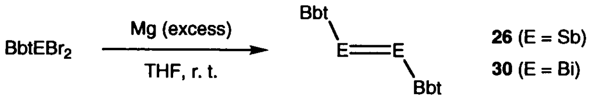
The diene adduct **28** here obtained was found to undergo ready thermal retrocycloaddition in toluene-d_8 at 130°C for 64 h to give the deep-red solution of distibene **26**, the electronic spectrum of which was identical with that obtained from the direct deselenation of **27** with HMPT (Scheme 16). The reaction of distibene **26**, prepared from **28**, with an excess amount of $(Me_2N)_3P{=}Se$ in benzene-d_6 at r.t. followed by concentration resulted in the almost quantitative formation



Scheme 15.



Scheme 16.



Scheme 17.

of **27**, while the reaction of isolated **27** with HMPT (ca. 10 equivalents) in toluene-d_8 at 120°C gave only the deselenated distibene **26** in solution as judged by ^{1}H-NMR (Scheme 16) [34].

The above-mentioned selenation reaction of the isolated distibene **26** with (Me$_2$N)$_3$P=Se under high concentration giving selenadistibirane **27** is important not only as a new reaction for a distibene but also as the experimental evidence of the final step for the formation of **27** in the deselenation of **25**. The big difference between the reaction products in the deselenation of Tbt- and Bbt-substituted triselenatristibanes **16** and **25** is most likely interpreted in terms of the remarkable insolubility of **17** in common organic solvents, which may prevent further transformation of **17** into its selenadistibirane derivative via redistribution of a selenium atom between the initially formed distibene and the phosphine selenide on concentration.

Thus, it was found that Bbt-substituted distibene **26** cannot be isolated by the direct deselenation of triselenatristibane **25** but can be prepared and isolated as a stable compound by the stepwise transformation via stibolene **28**.

4.2. Synthesis of new distibene and dibismuthene bearing Bbt groups

Since much improved solubility was confirmed for the new distibene **26** bearing Bbt groups, the author and coworkers have examined the synthesis of distibene **26** and its bismuth analogue **30** (Bbt-Bi=Bi-Bbt) by the conventional reductive coupling reaction. Treatment of the corresponding dibromostibine and dibromobismuthine with magnesium metal in THF at r.t. afforded the expected distibene **26** and dibismuthene **30** in almost quantitative yield (Scheme 17) [26].

The formation of **26** and **30** were readily confirmed by their characteristic absorption maxima (490 (ε, 6000) and 594 (ε, 200) for **26** and 537 (ε, 6000) and 670 (ε, sh, 20) for **30**, respectively [26].

4.3. Steric protection of doubly bonded systems of heavier Group 15 elements with bulky terphenyl ligands.

As mentioned in the previous sections, double-bond species between heavier Group 15 elements, i.e. all of the homonuclear double-bonds from P through Bi and some heteronuclear double-bonds such as P=As and P=Sb, have now been synthesized and isolated as stable compounds by taking advantage of kinetic stabilization with bulky substituents such as Dis, Tsi, Mes*, Tbt and Bbt.

Recently, much attention has been focused on a new family of bulky aromatic substituents, i.e. overcrowded *m*-terphenyl ligands, and they have been successfully applied to the kinetic stabilization of a number of low-coordinated compounds of heavier main group elements. For example, the following doubly bonded systems of heavier Group 15 elements have been synthesized utilizing bulky *m*-terphenyl ligands as steric protection groups (Chart 4).

Yoshifuji and co-workers reported the synthesis of a phosphaarsene **31** bearing 2,6-dimesityl-4-methylphenyl groups and the EPR study of its radical anion [35]. Protasiewicz and co-workers also described the synthesis of several diphosphenes **32**–**34** bearing 2,6-dimesitylphenyl, 2,6-dimesityl-4-methylphenyl or 2,6-di(*m*-xylyl)phenyl groups and their electrochemical and EPR investigations [36]. Power and co-workers have shown that 2,6-dimesitylphenyl group is effective in the kinetic stabilization of not only diphosphene **32** but also its heavier congeners, diarsene **35**, distibene **36**, and dibismuthene **37** [22b]. Furthermore, they developed a much bulkier *m*-terphenyl ligand, 2,6-bis(2,4,6-triisopropylphenyl)phenyl, which was also applicable to the synthesis of a series of diphosphene **38**, diarsene **39**, distibene **40**, and dibismuthene **41** [22b]. Also, they have succeeded in the synthesis of stable phosphaarsene **42** and phosphastibene **43** using this bulky ligand on the arsenic and antimony atoms in combination with a mesityl group on the phosphorus atom [22a]. Most of these doubly bonded systems were readily prepared by the simple reductive coupling reactions of the corresponding halide precursors or dehydrohalogenative condensation reactions between appropriate combination of dihalo- and dihydro-precursors in the presence of a base such as DBU, and in most cases the geometrical parameters of their double-bonds have been successfully determined by X-ray crystallographic analysis [22].

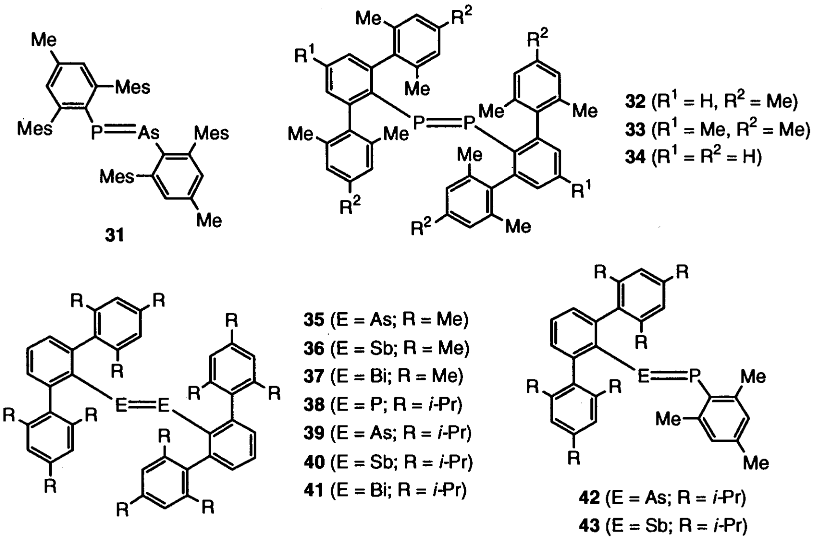


Chart 4.

5. Concluding remarks

As can be seen in this article the doubly bonded systems between heavier Group 15 elements are no more imaginary species but have a real existence as stable compounds even in the heaviest case of bismuth when they are kinetically well stabilized. The pioneering works described in this article will stimulate the chemists in this field, and in near future much more progress will be described the synthesis and properties of this unique class of low-coordinated main group element compounds [37]. For example, the synthesis of heteronuclear double bonds between bismuth and the other Group 15 elements (P=Bi, As=Bi and Sb=Bi) still remained as the next target molecules. Although the double-bonds of antimony and bismuth to heavier Group 14 elements have also been unknown systems so far, the concept of kinetic stabilization should certainly be of great use for the construction of these unprecedented chemical bondings.

The recent remarkable progress in the field of theoretical calculations makes it possible to predict the molecular geometry, physical properties, and some reactivities for not only the parent molecules but also the real molecules bearing complicated substituents even in the case of heavier main group element compounds [21f,21g,24,32]. Therefore, cooperative theoretical verification of the experimental outcome will be much more important to elucidate the intrinsic nature of new inter-element linkages of heavier main group elements.

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