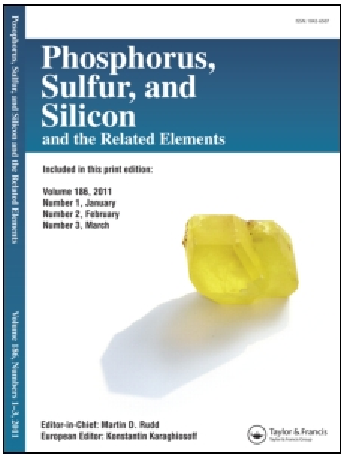

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Selenization and Tellurization Reactions of Kinetically Stabilized Dipnictenes

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The kinetically stabilized heavier dipnictenes, diphosphene, distibene, and dibismuthene, bearing 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)]-methylphenyl (Bbt groups were found to undergo selenization and tellurization reactions leading to the formation of the corresponding three-membered ring hetercycles, chalcogenadipnictiranes. The structural parameters and spectroscopic data of the isolated chalcogenadipnictiranes will be described.

Keywords Diphosphene; distibene; dibismuthene; selenadipnictirane; telluradipnictirane

INTRODUCTION

In recent years, there has been much interest in compounds with a double bond containing heavier group 15 elements from the viewpoints of their unusual chemical and physical properties. Up to now, several examples of stable diphosphenes and diarsenes (RAs=AsR) have been synthesized as stable compounds by taking advantage of steric protection with bulky substituents. We have also succeeded in the synthesis and characterization of the first stable distibene (ArSb=SbAr) and dibismuthene (ArBi=BiAr) by taking advantage of efficient steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group.[1] Here, we will present the selenization and tellurization reactions of

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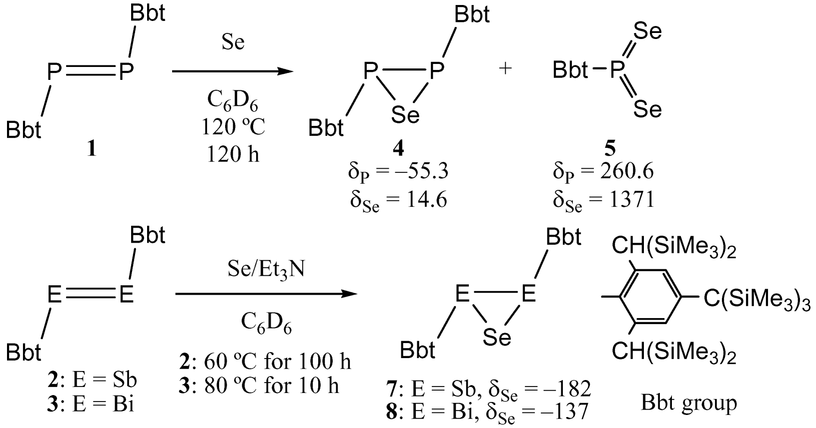
a series of stable dipnictenes, BbtP=PBbt (**1**), BbtSb=SbBbt (**2**), and BbtBi=BiBbt (**3**), leading to the formation of the corresponding selena- and tellura-dipnictiranes.

RESULTS AND DISCUSSION

Selenization and Tellurization Reactions of Dipnictenes 1-3

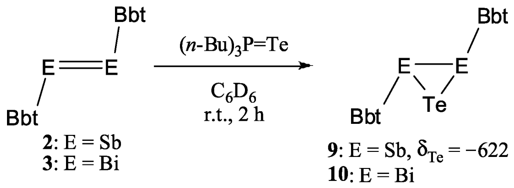
When diphosphene **1** was treated with an excess amount (10 eq.) of elemental selenium in C_6D_6 at 120°C (sealed tube) for 120 h, selenadiphosphirane **4** and diselenoxophosphorane **5** were obtained in 57% and 12% yield, respectively.[1d] Since the previously reported diphosphene, Mes*P=PMes* (**6**), was reported to undergo selenization reaction leading to the formation of the corresponding selenadiphosphirane and diselenoxophosphorane derivatives,[2] the reactivities of the diphosphenes, **1** and **6**, were found to be similar to each other.

On the other hand, heating of the C_6D_6 solution of distibene **2** with elemental selenium (3 eq.) in the presence of Et_3N (3 eq.) at 60°C for 100 h afforded selenadistibirane **7** in 50% yield. In addition, the selenization reaction of dibismuthene **3** under the similar conditions (2.6 eq. of Se, 3.1 eq. of Et_3N, C_6D_6 in a sealed tube, at 80°C for 10 h) afforded the corresponding selenadibismirane (**8**) in 58% yield.



SCHEME 1

The successful synthesis of the stable selenadipnictiranes, **4**, **7**, and **8**, prompted us to examine tellurization reaction of dipnictenes **1–3** in the expectation of obtaining telluradipnictiranes since there is no report on isolation of telluradipnictiranes except for only one report on the spectroscopic observation of a telluradiphosphirane derivative.[3]



SCHEME 2

In contrast to the case of selenization reactions of the dipnictiranes, however, diphosphene **1** was found to be inert toward elemental tellurium and $(n\text{-Bu})_3P = Te$ even on heating at 120–150°C in a sealed tube of C_6D_6. On the other hand, reactions of the distibene **2** and dibismuthene **3** with $(n\text{-Bu})_3P = Te$ at r.t. for 2 h resulted in the formation of telluradistibirane **9** and telluradibismirane **10** as stable crystalline compounds.[4]

Structures of the Obtained Chalcogenadipnictiranes

The obtained selena- and tellura-dipnictiranes, **4**, **7**, **8**, **9**, and **10**, showed isomorphous structures with the isosceles triangles of the E–Ch–E atoms (E=P, Sb, Bi, Ch=Se, Te). The X-ray crystallographic analyses revealed their structural parameters as shown in Table I. The E–E bond lengths in the chalcogenadipnictiranes were within the range of the corresponding single bond lengths, and slightly longer than the sum of the corresponding covalent radii (P, 1.10; Sb, 1.41; Bi, 1.52; Se,

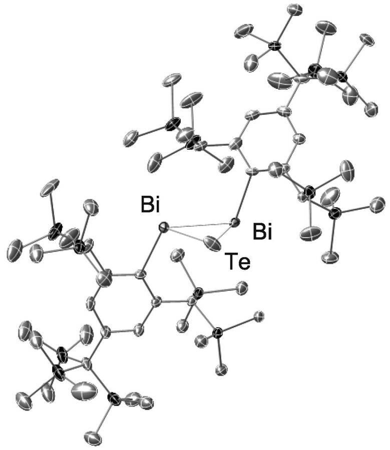
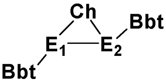


FIGURE 1 Ortep drawing (50% probability) of telluradibismirane 10.

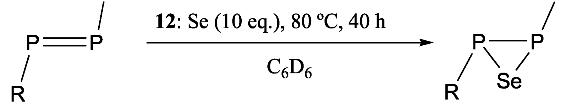
TABLE I Structural Parameters for the Chalcogenadipnictiranes

	Bond lengths Å			Bond angles (°)		
	E_1-E_2	E_1-Ch	Ch-E_2	Ch-E_1-E_2	Ch-E_2-E_1	E_1-Ch—E_2
4: E = **P**, Ch = **Se**	2.250 (3)	2.250 (3)	2.270 (3)	60.59 (9)	59.71 (9)	59.70 (8)
7: E = **Sb**, Ch = **Se**	2.852 (2)	2.562 (2)	2.565 (1)	56.25 (4)	56.15 (4)	67.60 (5)
9: E = **Sb**, Ch = **Te**	2.8833 (6)	2.7607 (7)	2.7719 (6)	58.781 (16)	58.402 (17)	62.817 (16)
8: E = **Bi**, Ch = **Se**	3.0105 (4)	2.6492 (9)	2.6649 (8)	55.741 (19)	55.25 (2)	69.01 (2)
10: E = **Bi**, Ch = **Te**	3.0388 (3)	2.8546 (4)	2.8648 (4)	58.068 (9)	57.742 (9)	64.190 (9)

1.17; Te, 1.37). In the ^{31}P, ^{77}Se, and ^{125}Te NMR spectra, these chalcogenadipnictiranes showed characteristic up-fielded signals (the observed chemical shifts were shown in Schemes 1 and 2). Unfortunately, no signal was observed in the ^{125}Te NMR spectrum of **10** probably due to the considerable broadened peak caused by the adjacent two bismuth atoms (I = 9/2).

Selenization and Tellurization of Unsymmetrically Substituted Diphosphenes

As described above, the selenization reaction of diphosphene **1** was found to proceed under severe conditions probably due to the extreme bulkiness of the two Bbt groups around the central P = P moiety. On the other hand, we have reported the synthesis of unique diphosphenes, which have a Tbt group as a steric protection group and a functional group on the other side, i.e., TbtP=P(Fc) (**11**) and TbtP=P(9-Anth) (**12**) (Fc = ferrocenyl, 9-Anth = 9-anthryl).[5] Diphosphenes **11** and **12** were found to undergo selenization reactions using elemental selenium leading to the formation of the corresponding selenadiphosphiranes, **13** and **14**, respectively (Scheme 3). In addition, heating of ferrocenyl diphosphene **11** at 60°C for 3 days in the presence of (n-Bu)$_3$P = Te (5 eq.) afforded compound **X**, which may be the corresponding telluradiphosphirane taking the characteristic up-fielded chemical shifts of



11: R = Fc
12: R = 9-Anth

13: R = Fc $\delta_P = -69.7, -84.1$ $\delta_{Se} = -58.3$
$^1J_{PP} = 217$ Hz, $^1J_{PSe} = 149, 86$ Hz

14: R = 9-Anth $\delta_P = -64.7, -72.8$ $\delta_{Se} = 67.8$
$^1J_{PP} = 237$ Hz, $^1J_{PSe} = 120, 128$ Hz

SCHEME 3

$\delta_P = -86.7$, -98.3 with $^1J_{PP} = 203$ Hz into consideration.[3,6] Further identification of compound **X** and investigation of the chalcogenation reactions of **11** and **12** are currently in progress.

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[6] In the ^{31}P and ^{125}Te NMR spectra, 2,3-di-*t*-butyltelluradiphosphirane, which is the only one example of a telluraphosphirane, show the characteristic signals at $\delta_P = -70$ and $\delta_{Te} = -696$ ($^1J_{PTe} = 229$ Hz), see du Mont and Severengiz.[3]