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Synthesis and reactions of new diphosphenes bearing extremely bulky substituents†

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epoc ABSTRACT: In this paper, we present the synthesis of new diphosphenes TbtP═PTbt and BbtP═PBbt having extremely bulky substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)-methyl]-4-[tris(trimethylsilyl)methyl]phenyl groups (Bbt). Their x-ray crystallographic analysis revealed their unique structures in the solid state. Furthermore, the configurations of these extremely overcrowded diphosphenes, TbtP═PTbt and BbtP═PBbt, are twisted in different ways in spite of the close structural similarity between Tbt and Bbt groups. DFT calculations were performed to estimate the energy difference between the two configurations of diphosphenes. In addition, their structures and physical properties were compared with those of their heavier congeners, distibenes (ArSb═SbAr, Ar = Tbt and Bbt) and dibismuthenes (ArBi═BiAr, Ar = Tbt and Bbt) having the same substituents. Although the reactivities of the extremely hindered diphosphenes might be considerably suppressed owing to the severe steric congestion, it was found that they can react with elemental sulfur and selenium to give the corresponding thia- and selenadiphosphirane derivatives, respectively, in addition to the previously reported diphosphenes. Copyright © 2003 John Wiley & Sons, Ltd.
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KEYWORDS: diphosphenes; steric protection; kinetic stabilization; group 15 elements; distibene; dibismuthene; multiple bond; chalcogenadiphosphirane

INTRODUCTION

Multiple-bond compounds between heavier group 15 elements have fascinated chemists for a long time.[1–3] Since the first isolation of the diphosphene Mes*P═PMes*,[4] intensive studies have been performed using several steric protection groups on the chemistry of a variety of diphosphenes (RP═PR),[1] diarsenes (RAs═AsR)[2] and phosphaarsenes (RP═AsR).[3]

Although the conventional steric protection groups could not be applied to the synthesis of distibene and dibismuthene, we have recently succeeded in the syntheses and isolation of the first stable distibenes and dibismuthenes, RE═ER (E = Sb or Bi, R = Tbt ot Bbt), by taking advantage of the more effective steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) groups.[5,6] Now, all the doubly bonded compounds between heavier group 15 elements are no longer imaginary species but actually exist.[7]

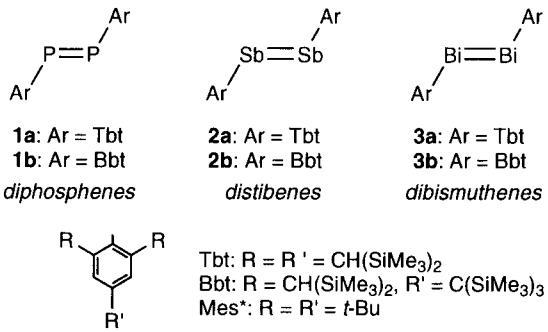

Chart 1

Here, it was considered worth comparing the features of Tbt- and Bbt-substituted diphosphenes **1a,b** with those of the distibenes **2a,b** and the dibismuthenes **3a,b** (Chart 1) to make a systematic comparison among a series of heavier dipnictenes under the same effects of substituents. There is a question of whether extremely bulky substituents such as Tbt or Bbt groups could be applicable to kinetic stabilization of the lighter analogue, diphosphene, regardless of severe steric repulsion. In this paper, we present the details of the syntheses of new diphosphenes having extremely bulky substituents, Tbt

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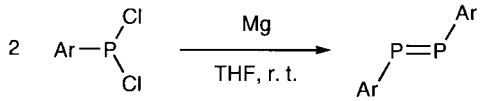

4a: Ar = Tbt
4b: Ar = Bbt

1a: Ar = Tbt
1b: Ar = Bbt

Scheme 1

and Bbt groups, together with their physical and chemical properties.

RESULTS AND DISCUSSION

Synthesis of TbtP═PTbt and BbtP═PBbt

We examined the synthesis of new diphosphenes having Tbt and Bbt groups via the most traditional method, i.e. the simple reductive coupling reaction of the corresponding dichlorophosphines. When $ArPCl_2$ (**4a**, Ar = Tbt; **4b**, Ar = Bbt) prepared by the reaction of ArLi with PCl_3 were treated with metallic magnesium in THF at room temperature, stable red crystals of diphosphenes ArP═PAr (**1a**, Ar = Tbt; **1b**, Ar = Bbt) were obtained in more than 90% yield (Scheme 1). The characteristic low-field chemical shifts of 531.8 ppm for **1a** and 529.1 ppm for **1b** in the ^{31}P NMR spectra in C_6D_6 strongly indicated their P═P double-bond character. Thus, the Tbt and Bbt groups were found to be effective protection groups to stabilize not only the heavier Sb═Sb and Bi═Bi double bonds but also the lighter P═P double bond.

X-ray crystallographic analysis of Tbt- and Bbt-substituted diphosphenes

The molecular geometries and selected bond lengths and angles of **1a,b** revealed by x-ray crystallographic analysis are shown in Figs 1 and 2. In the all cases of distibenes **2a,b** and dibismuthenes **3a,b**, their molecular structures have a center of symmetry in the middle of their E═E (E = Sb, Bi) double bonds and have *trans* configurations with the plane of the aryl rings of the Tbt or Bbt groups perpendicular to their C—E—E—C (E = Sb, Bi) planes.[6a] Also, the diphosphene Mes*P═PMes* (**5**) has been reported to have similar features in its structure.[4] The molecular structures of the newly obtained, extremely hindered diphosphenes **1a** and **1b** also have *trans* configurations with their aryl substituents (Tbt or Bbt, respectively), in addition to the distibenes and dibismuthenes. However, in sharp contrast to **2a,b** and **3a,b**, the diphosphenes **1a** and **1b** do not have an intramolecular center of symmetry, and the two Tbt and Bbt groups in **1a** and **1b** are intertwined with each other.

The bond lengths of the P═P double bonds in **1a**

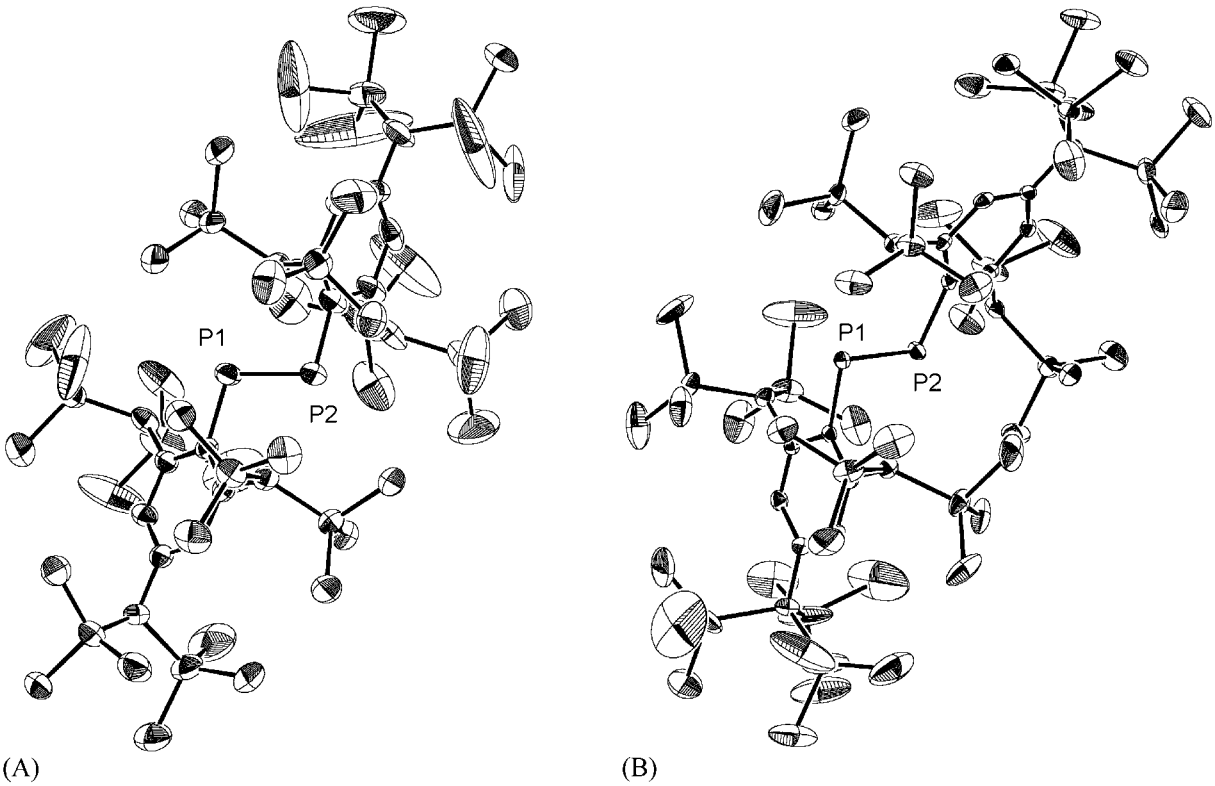

Figure 1. ORTEP drawings of (A) TbtP═PTbt (**1a**) and (B) BbtP═PBbt (**1b**) with thermal ellipsoid plot (50% probability). The fragment of the solvated hexane was omitted for clarity

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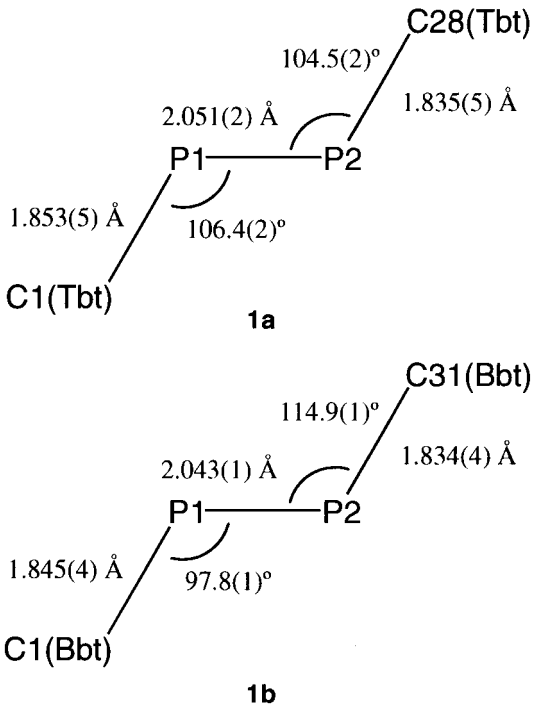

Figure 2. Selected bond lengths and bond angles of diphosphenes **1a** and **1b**

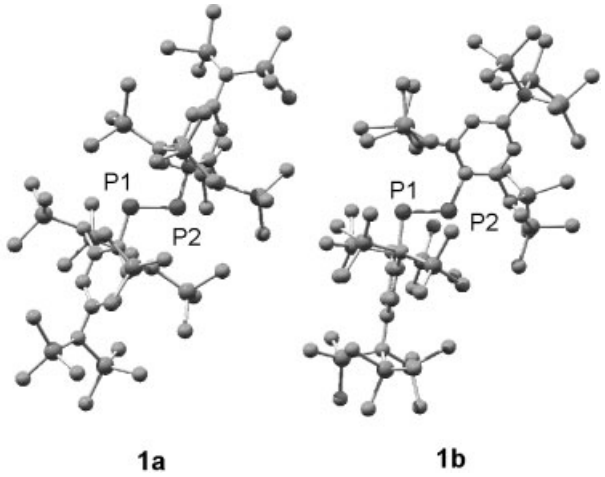

Figure 3. Side views of the diphosphenes **1a** and **1b**

[2.051(2) Å] and **1b** [2.043(1) Å] are very close to that in Mes*P=PMes* (**5**; 2.034 Å)[4] and they are considerably shorter by ca **8**% than the typical P—P single-bond length [$(PhP)_5$, 2.217 Å;[8] $(PhP)_6$, 2.237 Å[9]]. Thus, it was found that the difference in geometries between diphosphenes and their heavier analogues do not affect the double-bond character of the central P=P bond in the solid state. It appears that the bulkiness of the two Tbt or Bbt groups does not allow them to be parallel owing to the steric repulsion between the bulky $CH(SiMe_3)_2$ groups at the *ortho* positions accompanied by the shorter bond length of P=P double bonds than those of Sb=Sb [**2a**, 2.6422(7) Å;[5a] **2b**, 2.7037(6) Å[6a]] and Bi=Bi [**3a**, 2.8206(8) Å;[5b] **3b**, 2.8699(6) Å[6a]] double bonds. Here, it was found that the P—C bonds between the phosphorus and the *ipso*-carbon atoms of the extremely bulky Tbt or Bbt group were rotated to release the severe steric repulsion without elongating the central P=P bond in the solid state.

The two planes of the aryl rings of Tbt or Bbt groups are nearly perpendicular in both **1a** and **1b**, but the nature of the distortion between the substituents and the C—P—P—C plane is different in **1a** and **1b**. The difference is clearly indicated by Fig. 3, in which the side views of **1a** and **1b** are shown. As for the case of Tbt-substituted diphosphene **1a**, both of the two Tbt groups are twisted from the C—P—P—C plane by 50° and 57°. By contrast, in the case of **1b** the plane of the aryl ring of one Bbt group [Bbt group attached to P1 in Figs 1(B) and 2] is almost perpendicular (83°) and that of the other [Bbt group on P2 in Figs 1(B) and 2] is nearly parallel (23°) to the C—P—P—C plane (see Table 1). Therefore, the C—P—P angle at P2 atom [114.9(1)°] is wider than that at the other phosphorus atom (P1) [97.8(1)°] in **1b** owing to the steric repulsion between the P=P double bond and one of the $CH(SiMe_3)_2$ groups at the *ortho*-position of the Bbt group. A diphosphene and a diarsene having bulky *m*-terphenyl ligands [2,6-$Mes_2C_6H_3$ or 2,6-$Tip_2C_6H_3$ (Tip = 2,4,6-triisopropylphenyl)] have been recently reported to have a twisted configuration similar to diphosphene **1b**.[7c,10] Although it was found that the bulkiness of the substituents on the central atoms of the diphosphenes causes the twisted structure, the reason for the difference in configurations between **1a** and **1b** is not clear. The crystals of **1a** and **1b** contain different solvents (**1a**,

Table 1. Theoretically optimized and experimentally obtained structural parameters for diphosphenes

Compound	*d* (P=P) (Å)	∠ P—P—C (°)	Dihedral angles[a] (°)
1a (TbtP=PTbt)[b]	2.088	110.9	39
		103.0	65
1b (BbtP=PBbt)[b]	2.068	101.7	85
		114.4	23
1a′ (ArP=PAr)[b]	2.055	105.9	56
		105.9	56
1b′ (ArP=PAr)[b]	2.065	98.4	81
		114.7	13
1a (TbtP=PTbt)[c]	2.051(2)	106.4(2)	50
		104.5(2)	57
1b (BbtP=PBbt)[c]	2.043(1)	97.8(1)	83
		114.9(1)	23

[a] The dihedral angles between aryl group and the C—P—P—C plane.
[b] Ar = 2,6-$[CH(SiMe_3)_2]_2C_6H_3$. Structural parameters were obtained by the theoretical calculations at the B3LYP/[TZ(2d) for P, 6–31G(d) for Si and 3–21G for C and H] level as the local minimum point because it was difficult to find the global minimum point owing to the immense number of atoms.
[c] Structural parameters were obtained by x-ray crystallographic analysis (see Figs 1 and 2).

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benzene; **1b**, hexane), but they are not thought to affect the molecular geometries of the diphosphenes.

In order to estimate the energy gap between the two types of conformations observed for **1a** and **1b**, DFT calculations were performed. When experimentally obtained structures of **1a** and **1b** were used as initial structures, the local minima of TbtP=PTbt and BbtP=PBbt were found, respectively. Next, the structural optimization were examined for two diphosphenes **1a′** and **1b′** (ArP=PAr, Ar = 2,6-$[CH(SiMe_3)_2]_2$-C_6H_3), whose initial structures were obtained by replacing the alkyl groups at *para* positions of the theoretically optimized structures of **1a** and **1b** with hydrogen atoms, respectively. As shown in Table 1, the optimized structures of **1a, 1b**, **1a′** and **1b′** have twisted conformations similar to the experimentally obtained structures of **1a** and **1b**, respectively. The results of theoretical calculations show that the energy gap between **1a′** and **1b′** is only 0.8 kcal mol^{-1} (1 kcal = 4.184 kJ) and **1a′** is slightly more stable than **1b′**. Thus, the difference between the conformations of **1a** and **1b** may be attributed to the subtle difference of bulkiness between Tbt and Bbt groups.

Table 2. UV/visble spectroscopic data for homonuclear doubly bonded systems between heavier group 15 elements

Compound[a]	No.	λ_1 (nm) (ε) ($\pi \rightarrow \pi^*$)	λ_2 (nm) (ε) ($n \rightarrow \pi^*$)	Ref.
Mes*P=PMes*	**5**	340 (7690)	460 (1360)	4
TsiP=PTsi	**6**	353 (9474)	484 (62.8)	13
$R^1P=PR^1$	**7**	371 (8000)	455 (501)	10
$R^2P=PR^2$	**8**	393 (7270)	502 (570)	7c
Mes*P=PDis	**9**	325 (13000)	427 (370)	1c
TbtP=PTbt	**1a**	405 (13000)	530 (2000)	This work
BbtP=PBbt	**1b**	418 (12000)	532 (1000)	This work
TsiAs=AsTsi	**10**	380 (5000)	505 (10)	14
Mes*As=AsDis	**11**	368 (6960)	449 (180)	15
$R^1As=AsR^1$	**12**	400 (6970)	462 (650)	7c
$R^2As=AsR^2$	**13**	409 (4060)	504 (120)	7c
TbtSb=SbTbt	**2a**	466 (5200)	599 (170)	5a
BbtSb=SbBbt	**2b**	490 (6000)	594 (200)	6a
$R^1Sb=SbR^1$	**14**	451 (5450)	Not observed	7c
$R^2Sb=SbR^2$	**15**	470 (6570)	Not observed	7c
TbtBi=BiTbt	**3a**	525 (4000)	660 (100)	5b
BbtBi=BiBbt	**3b**	537 (6000)	670 (20)	6a
$R^1Bi=BiR^1$	**16**	505 (5010)	970 (30)	7c
$R^2Bi=BiR^2$	**17**	518 (6920)	913 (200)	7c

[a] Tsi = $C(SiMe_3)_3$; Dis = $CH(SiMe_3)_2$; Mes = mesityl; Tip = 2,4,6-triisopropylphenyl; Mes* = 2,4,6-tri-*tert*-butylphenyl; R^1 = 2,6-Mes_2-C_6H_3; R^2 = 2,6-Tip_2-C_6H_3.

Physical properties of Tbt- and Bbt-substituted diphosphenes

In the Raman spectra (measured in the solid state) of **1a** and **1b**, strong lines attributable to the P=P stretching were observed at 609 and 603 cm^{-1}, respectively. These values observed for the diphosphenes are higher than the frequencies observed for diphosphanes (e.g. Ph_2P-PPh_2, 530 cm^{-1})[11] and very similar to the experimentally observed value for Mes*P=PMes* (**5**, 610 cm^{-1}).[12] In addition, theoretical calculations for the harmonic vibrational frequency of HP=PH obtained at the MP2 (606.4 cm^{-1}), B3LYP (615.2 cm^{-1}) and QCSID (626.4 cm^{-1})/TZ(2d) [DZ(p) for H] levels[6a] also support the assignment of **1a** and **1b**. Thus, the P=P double-bond character in **1a** and **1b** in the solid state is supported by not only their P=P bond lengths but also the vibrational information on their P=P bonds.

The solutions of diphosphenes **1a** and **1b** in common organic solvents (e.g. hexane, benzene, chloroform) are red. Diphosphenes have two absorption maxima reasonably assigned to the symmetry-allowed $\pi \rightarrow \pi^*$ electron transitions and the symmetry-forbidden $n \rightarrow \pi^*$ electron transitions, which appear at wavelengths longer than 300 nm. In Table 2 are shown the absorption maxima and molar extinction coefficients in the UV/visible spectra of diphosphenes **1a** and **1b** together with those for typical examples of the homonuclear double-bond compounds between heavier group 15 elements. The red solutions of **1a** and **1b** in hexane showed two absorption maxima, which correspond to the $\pi \rightarrow \pi^*$ transitions [405 nm (ϵ = 13000) for **1a** and 418 nm (ϵ = 12000) for **1b**] and the $n \rightarrow \pi^*$ transitions [530 nm (ϵ = 2000) for **1a** and 532 nm (ϵ = 1000) for **1b**] of the P=P chromophore, respectively. Although the UV/visible spectral data strongly supported the P=P double-bond character of **1a** and **1b** in solution, the λ_{max} values of these absorption maxima are red shifted compared with those of the previously reported diphosphenes **5** and **6**. The observed red shifts might be due to the extremely bulky Tbt or Bbt group on the phosphorus atoms. As described above, the two Tbt or Bbt groups on the P=P double bonds in **1a** and **1b** are intertwined with each other in the solid state to avoid severe steric repulsion without elongation of the P=P double-bond length. In solution, however, the ^{31}P NMR signals for the two phosphorus atoms and the ^1H NMR signals for the two Tbt and Bbt groups are observed equivalently in both **1a** and **1b**. These NMR spectroscopic features of **1a** and **1b** suggest that there is no restricted rotation of the substituents in solution. Accordingly, in solution the severe steric repulsion of Tbt or Bbt groups in **1a** and **1b** might slightly elongate the P=P double bonds compared with those of diphosphenes **5** and **6**, and the overlapping of π-orbitals of the phosphorus atoms might be decreased. Therefore, their absorption maxima for the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions were observed in the longer wavelength region in solution, probably owing to the more weakened π bonds between phosphorus atoms than those of **5** and **6**. In addition, the absorption maximum for the $\pi \rightarrow \pi^*$ transition of Bbt-substituted diphosphene **1b** was slightly red shifted compared with the Tbt-substituted compound (**1a**). The bathochromic effect here observed might

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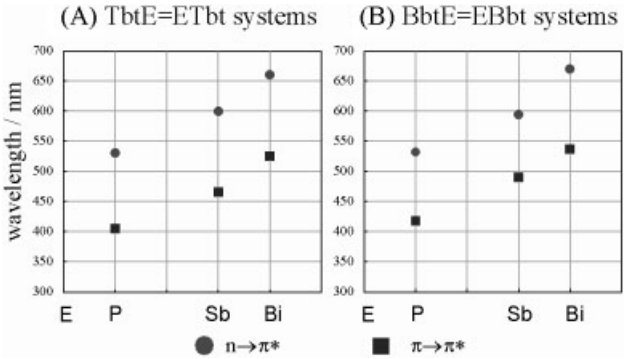


Figure 4. Absorption maxima for (A) TbtE=ETbt and (B) BbtE=EBbt

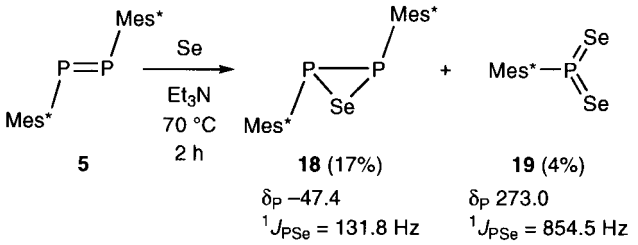
indicate a slightly longer P=P double bond of **1b** than that of **1a** in solution.

Since the UV/visible spectra of these double-bond systems are sensitive to the substituents on the central atoms, it is interesting to compare the absorption maxima for the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions among a series of the RE=ER (E = P, Sb, Bi) systems having the same substituents. In Fig. 4 are shown the $\pi \rightarrow \pi^*$ (squares) and $n \rightarrow \pi^*$ (circles) transitions for the series of Tbt- and Bbt-substituted RE=ER systems (R = Tbt and Bbt, E = P, Sb, and Bi), although the corresponding diarsenes, TbtAs=AsTbt and BbtAs=AsBbt, are missing. In both series of Tbt and Bbt derivatives, it can be seen that their $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions shift to the longer wavelength region as the element row is descended. These trends for the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions indicate the weakening of the π bond as the principal quantum number is increased, and it is consistent with the results of calculations [HF/DZ(d,p)] on the frontier orbital energy gaps of HE=EH (E = P, As, Sb, and Bi).[16] In addition, similar trends are also observed for the absorption maxima of 2,6-Mes_2-C_6H_3 and 2,6-Tip_2-C_6H_3 derivatives.[7c]

Reactions of Tbt- and Bbt-substituted diphosphenes

Kinetic stabilization (in other words, steric protection by bulky substituents) has some problems caused by the congestion of the substituents, e.g. difficulty in the preparation of precursors of the desired substances and/or low intermolecular reactivity of the stabilized compound. In order to elucidate the reactivities of the diphosphene **1a** and **1b** having extremely bulky Tbt and Bbt groups, their reactions with elemental sulfur and selenium were examined. We examined the reaction of **1b** with elemental selenium first because ^{77}Se NMR spectroscopic data would be helpful in analyses of the reaction products.

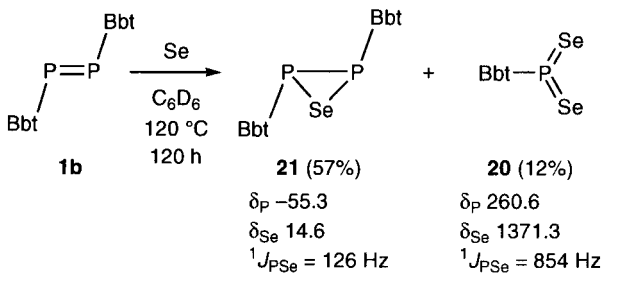
Yoshifuji *et al.* have reported the reaction of



Scheme 2

Mes*P=PMes* (**5**) with elemental selenium activated by triethylamine leading to the formation of the corresponding selenadiphosphirane derivative **18** and diselenoxophosphorane derivative **19** (Scheme 2).[17] When diphosphene **1b** was treated with gray selenium in benzene-d_6 at 120 °C for 120 h in a sealed tube, a green crude solution was obtained, indicating the formation of the corresponding diselenoxophosphorane **20** (Scheme 3). The ^{31}P and ^{77}Se NMR spectra of the crude mixture indicate the formation of the selenadiphosphirane derivative **21** ($\delta_p = -55.3$, $\delta_{Se} = 14.6$, $^1J_{SeP} = 126$ Hz) and diselenoxophosphorane **20** ($\delta_p = 260.6$, $\delta_{Se} = 1371.3$, $^1J_{SeP} = 854$ Hz), judging from their characteristic chemical shifts, coupling patterns and coupling constants, which were similar to those of **18** and **19**. Diselenoxophosphorane **20** could not be isolated owing to its extremely high sensitivity to light as well as **19**. On the other hand, the selenadiphosphirane **21** is stable under ambient conditions, and **21** was easily isolated and purified as orange crystals in 57% yield by HPLC separation. Counting backwards from the isolated yield of **21** (57%), the yield of **20** could be estimated to be 12% on the basis of a comparison of the integrals of the ^{1}H NMR signals with those of **21** in the crude mixture. Hence it was found that the diselenoxophosphorane **20** and selenadiphosphirane **21** were formed by the reaction of the diphosphene **1b** with elemental selenium as in the case of **5**. However, it was not necessary to use triethylamine for the activation of gray selenium in this case.

Next, we examined the reaction of **1b** with elemental sulfur. Yoshifuji and co-workers have already reported the reactions of Mes*P=PMes* (**5**) with elemental sulfur activated by triethylamine leading to the formation of a



Scheme 3

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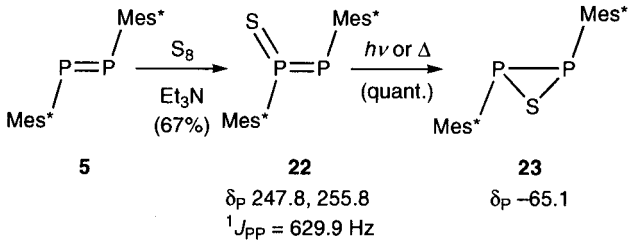
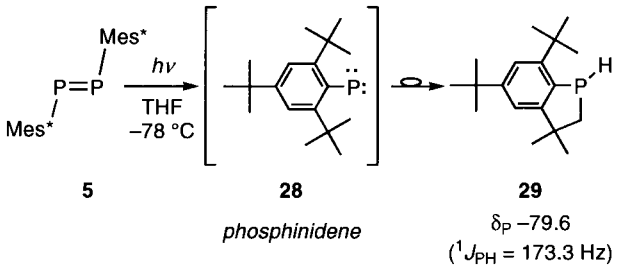


Scheme 4



Scheme 6

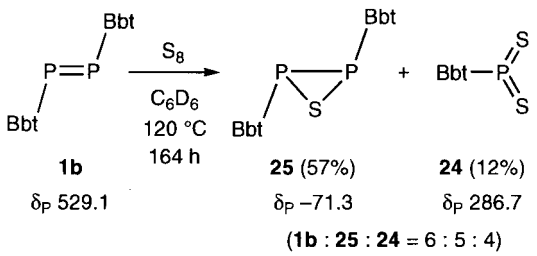
yellow intermediate **22**, which underwent ready thermal or photochemical isomerization to give thiadiphosphirane **23** (Scheme 4).[18] When a benzene-d_6 solution of **1b** and elemental sulfur (S_8, 5 equiv. as S) was heated at 120 °C in a sealed tube for 120 h, the resulting red solution showed characteristic signals at 529.1, 286.7 and −71.3 ppm by ^{31}P NMR spectroscopy. The observation of these three signals indicates the presence of remaining diphosphene **1b** (529.1 ppm) and the formation of dithioxophosphorane **24** (286.7 ppm) and thiadiphosphirane **25** (−71.3 ppm), as inferred from analogy with the reaction of **1b** with elemental selenium (Scheme 5). Furthermore, when the solution was heated at 120 °C for 42 h, the ^{1}H NMR spectrum showed the peaks for **1b, 24**, and **25** with the ratio of 6:4:5 and the reaction did not go to completion. Thus, the sulfurization reaction of diphosphene **1b** proceeded more slowly than the selenization reaction of **1b**. In contrast to the sulfurization reaction of Mes*P=PMes* (**5**), diphosphene-1-sulfide derivative **26** [BbtP(S)=PBbt] was not observed in this reaction. On the other hand, the reaction of **1b** with an excess amount of elemental sulfur (S_8, 10 equiv. as S) in the presence of triethylamine (10 equiv.) at 120 °C in benzene-d_6 for 40 h resulted in the formation of thiadiphosphirane **25** as a main product. Since **1b** completely disappeared under the reaction conditions, **25** could be isolated by HPLC purification as air- and moisture-stable orange crystals in 88% yield. Here, it was found that triethylamine would promote the sulfurization reaction of diphosphene **1b**.

Taking into account of these results, it can be concluded that diphosphene **1b** has enough reaction space around the central P=P bond, although the Bbt groups are extremely bulky and very effective steric protecting groups to avoid the oligomerization of the reactive P=P bonds.

The synthesis and isolation of Bbt-substituted thia- and selenadiphosphirane derivatives by the reactions of **1b** with elemental sulfur and selenium naturally prompted us to examine the reaction of **1b** with elemental tellurium to synthesize the heavier analogue, i.e. telluradiphosphirane derivative **27**, since there is only one example of telluradiphosphirane derivatives[19] and no example of a telluradiphosphirane derivative has been structurally characterized. However, no change was observed by ^{31}P and ^{1}H NMR spectroscopy when a C_6D_6 suspension of **1b** and elemental tellurium (5 equiv.) was heated even at 150 °C for 1 week in a sealed tube. The use of Bu_3P=Te (2 equiv.) instead of elemental tellurium at 120 °C for 1 week also resulted in the quantitative recovery of **1b**.

Yoshifuji *et al.* reported that the phosphinidene **28** was generated as an intermediate in the photolysis (100 W, −78 °C, THF) of **5**, where **28** underwent immediate intramolecular cyclization to give the corresponding phosophaindane derivative **29** (Scheme 6).[20] The intermediate **28** could not be trapped intermolecularly by MeOH, probably owing to the very fast intramolecular cyclization of **28** and the extreme congestion around the central phosphorus atom surrounded by the *test*-butyl groups at *ortho*-positions. On the other hand, a Tbt or Bbt group has enough space around the 1-position to avoid intramolecular cyclization, in contrast to the Mes* group. Indeed, the Tbt-substituted stibinidene (**30**; Tbt–Sb:), which is a heavier congener of phosphinidene **31**, was successfully trapped by 2,3-dimethyl-1,3-butadiene via [1 + 4] cycloaddition without any intramolecular cyclization.[21] Taking into consideration of the features of **1a** and **1b** in solution, we examined the dissociation reaction of the diphosphene **1a** having Tbt groups leading to the formation of the corresponding phosphinidene derivative **31**.

Although the thermolysis (85 °C, 30 h) and photolysis (100 W, 3 h) of a C_6D_6 solution of **1a** in the presence of 2,3-dimethyl-1,3-butadiene (10 equiv.) was examined in expectation of trapping the intermediary phosphinidene **31**, no phospholene derivative **32**, i.e. the expected [1 + 4] cycloadduct of **31** with 2,3-dimethyl-1,3-butadiene, was observed and diphosphene **1a** was completely



Scheme 5

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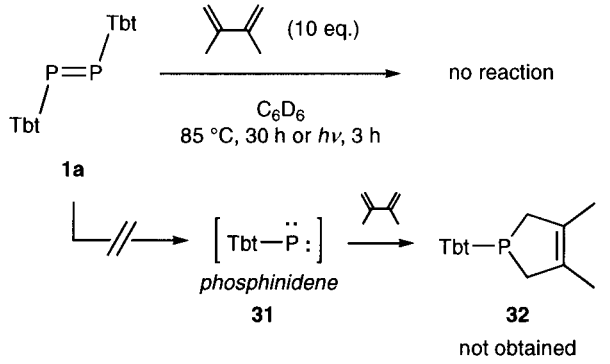

Scheme 7

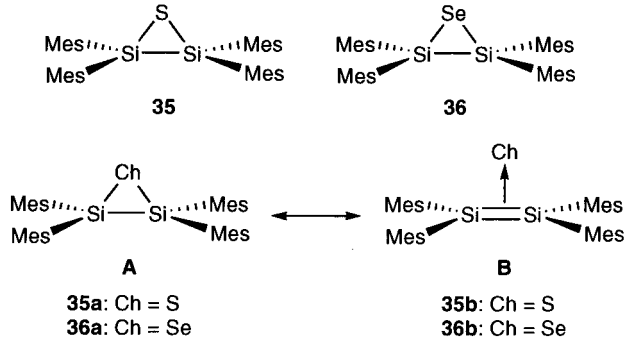

Chart 3

recovered (Scheme 7). However, the generation of phosphinidene **31** in these thermolysis and photolysis reactions is not completely unlikely because the retro [1 + 4] reaction of **32** might occur under these conditions or the trapping reaction of **31** with 2,3-dimethyl-1,3-butadiene might be much slower than the dimerization reaction of **31** giving the starting material **1a**. Therefore, no conclusive result on the generation of the phosphinidene was obtained in these thermolysis and photolysis reactions. Since it was conceivable that **29** was produced not via phosphinidene **28** but via some other radical intermediates and there has been no report on the intermolecular trapping reaction of a phosphinidene generated from a diphosphene so far, it is not clear whether a phosphinidene is generated by the thermal or photochemical cleavage of the P=P double bond of a diphosphene.

Structures of Bbt-substituted thia- and selenadiphosphiranes

Although the syntheses of several types of thiadiphosphiranes have been reported,[22] there is only one example of structural characterization.[22a] Therefore, the x-ray crystallographic analysis of the newly obtained thiadiphosphirane **25** is interesting in view of the structural analysis of thiadiphosphirane derivatives. On the other hand, there have been two structurally characterized selenadiphosphirane derivatives, **33**[23a] and **34**.[23b] However, their three-membered ring skeletons are considerably affected by the electronic perturbation due to their peculiar substituents such as Cp* and R_f (Chart 2). From this point of view, the structure of **21** is interesting

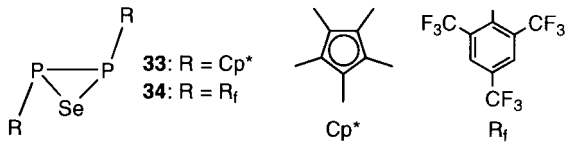

Chart 2

because the Bbt group has very little thermodynamic influence on the central skeleton. Fortunately, single crystals of [**25**·0.5hexane] and [**21**·0.5hexane] were obtained by recrystallization from hexane at 0 °C, and their structures were determined by x-ray crystallographic analysis. In Figures 5–8 are shown the ORTEP drawings and selected bond lengths and angles of the thiadiphosphirane **25** and the selenadiphosphirane **21**. In both cases the two Bbt groups are oriented in a *trans* configuration with respect to the central chalcogenadiphosphirane skeleton.

Concerning the thia- and selenadisiliranes **35**[24] and **36**,[25] having a three-membered ring with two silicon and one chalcogen (sulfur or selenium) atoms, a resonance structure model (**A** and **B**) between a three-membered ring (**35a** and **36a**) and a π complex (**35b** and **36b**) has been proposed to account for their crystal structures (see Chart 3).[26]

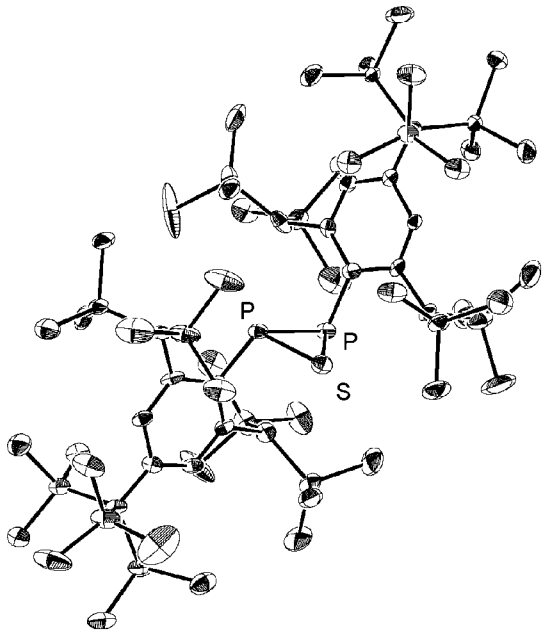

Figure 5. ORTEP drawing of the major part of thiadiphoaphirane **25** with thermal ellipsoid plot (50% probability). The fragment of solvated hexane was omitted for clarity

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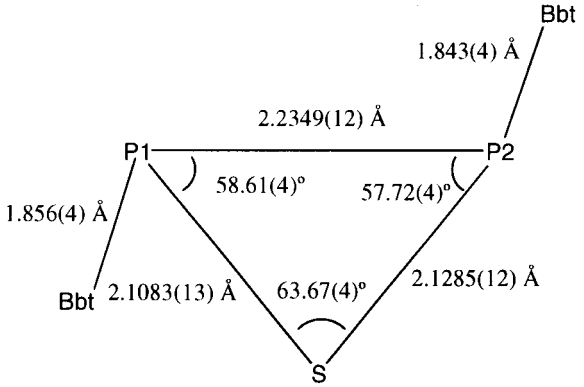
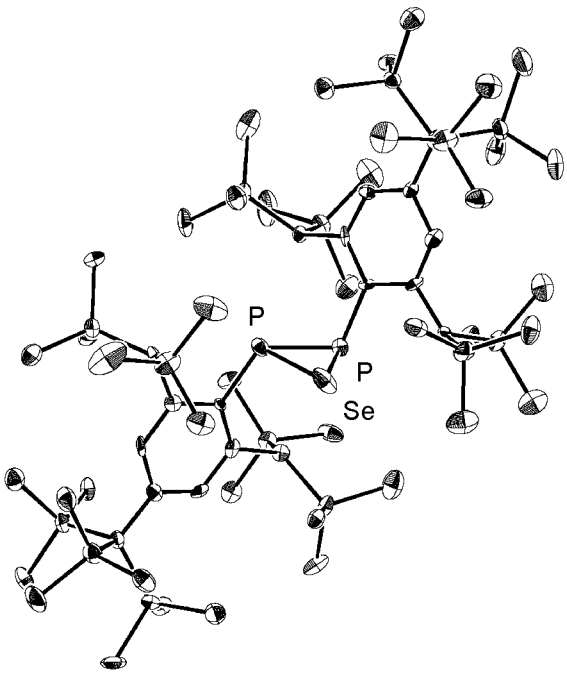


Figure 6. Selected bond lengths and bond angles of **25** (major part)

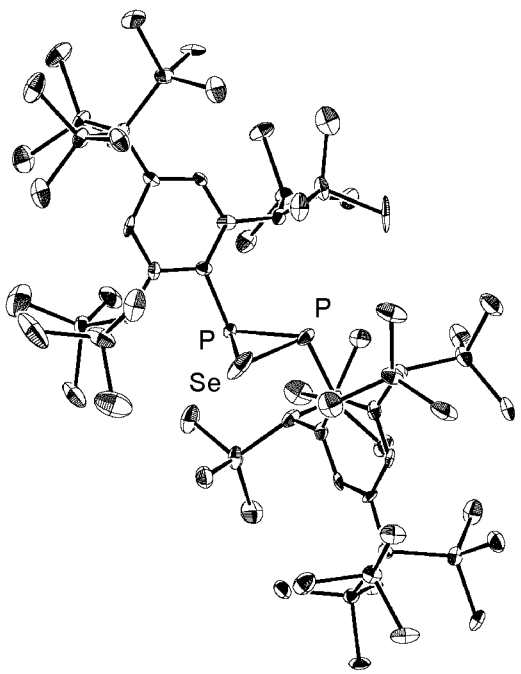
On the other hand, the bond lengths of the P—P bond [2.2349(12) Å] and the P—S bond [2.1083(13) Å and 2.1285(12) Å] in the thiadiphosphirane **25** are almost comparable to the corresponding typical single-bond lengths [P—P single bond, ca 2.2–2.3 Å;[8,9] P—S single bond, 2.14 Å (sum of covalent radii)[26]]. In the case of selenadiphosphirane **21**, the lengths of the P—P bond [fragment A, 2.250(3); fragment B, 2.239(4) Å] and the P—Se bond [fragment A, 2.250(3) and 2.270(3) Å; fragment B, 2.257(4) and 2.259 (4) Å] are within the range of the typical P—P single bond lengths (ca 2.2–2.3 Å) and the sum of single-bond covalent radii for phosphorus and selenium (P—Se single bond, 2.27 Å[26]), respectively. Thus, it was found that thia- and selenadiphosphiranes **25** and **21** have a three-membered ring which consists of reasonable single bonds and almost no character of a π complex, in contrast to the case of chalcogenadisiliranes **35** and **36**. Since the previously reported chalcogenadiphosphiranes **23, 33** and **34** have similar features to those of Bbt-substituted compounds in the geometries of their three-membered rings, these central three-membered ring skeletons may be little affected by substituents. In addition, the structural optimization at the B3LYP/6–311G(2d,p) level of 2,3-dimethyl- and 2,3-diphenylchalcogenadiphosphirane models **37**–**40** revealed that the structural parameters for their thia- and selenadiphosphirane skeletons are very similar to those obtained experimentally for **25** and **21**, respectively (Table 3), suggesting the reliable single bond character of the chalcogenadiphosphiranes.

Summary

New stable diphosphenes having Tbt and Bbt groups, **1a** and **1b**, were synthesized and their structures were definitively determined by x-ray crystallographic analysis. It was found that the extremely overcrowded diphosphenes **1a** and **1b** have interesting structures with intertwined substituents to preserve the central P═P double bond lengths in the solid state. In solution,



Fragment A



Fragment B
(major part)

Figure 7. ORTEP drawing of selenadiphoaphirane **21** with thermal ellipsoid plot (50% probability). The fragment of solvated hexane was omitted for clarity

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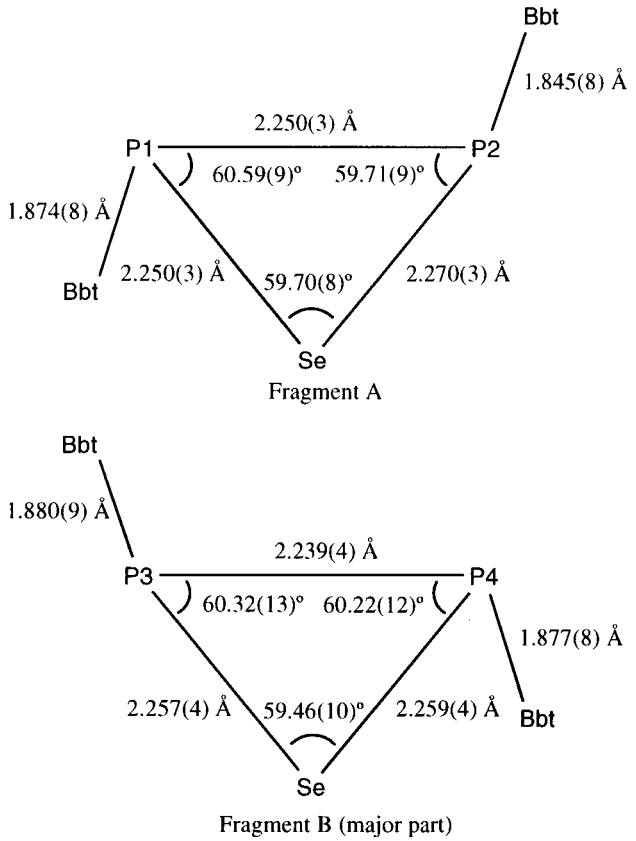

Figure 8. Selected bond lengths and bond angles of **21**

however, the NMR and UV/visible spectral data implied that the entanglements between the substituents were solved and the severe steric repulsion of Tbt or Bbt groups of **1a** or **1b** might slightly elongate and weaken the P═P double bond.

On the other hand, it was found that **1a** and **1b** can react with elemental sulfur and selenium to give thia- and selenadiphosphiranes, respectively, in spite of the extreme bulkiness of Tbt and Bbt groups. While Tbt and Bbt groups are very effective steric protecting groups to prevent the oligomerization of reactive chemical bonds, they still have sufficient reaction space around the 1-position for reactions with some small molecules. The concept of kinetic stabilization with Tbt and Bbt groups should certainly be of great use for the construction and elucidation of the physical and chemical properties of unprecedented, reactive chemical bonds.[27] Furthermore, cooperative theoretical verification of the experimental outcome will become very important for elucidating the intrinsic nature of new chemical bondings between heavier main group elements.

EXPERIMENTAL

General procedure. All experiments were performed under an argon atmosphere unless stated otherwise. All solvents were dried by standard methods and freshly distilled prior to use. ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM AL-400 or JEOL JNM AL-300 spectrometer. Signals due to $CHCl_3$ (7.25 ppm) and C_6D_5H (7.15 ppm) were used as references in ^{1}H NMR, and those due to $CDCl_3$ (77 ppm) and C_6D_6 (128 ppm) were used in ^{13}C NMR. Multiplicity of signals in ^{13}C NMR spectra was determined by the DEPT technique. ^{31}P NMR (121 MHz) and ^{77}Se NMR (57 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL AL-300 spectrometer using 85% H_3PO_4 in water (0 ppm) and diphenyl diselenide (460 ppm) as an external standard, respectively. High- and low-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. HPLC (high-performance liquid chromatography) was performed on an LC-908 or LC-918 instrument (Japan Analytical Industry) equipped with JAIGEL 1H and 2H columns (eluent: chloroform or toluene). Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. Electronic spectra were recorded on a JASCO V530 UV/visible or JASCO Ubest-50 UV/visible 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 or 1064 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 Institute for Chemical Research, Kyoto University. TbtBr[28] and BbtBr[29] were prepared according to the reported procedures.

*Preparation of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}dichlorophosphine (**4a**).* To a solution of TbtBr (3.16 g, 5.00 mmol) in THF (45 ml) was added *tert*-butyllithium (2.24 M pentane solution, 4.9 ml, 11.0 mmol) at − 78 °C. After 30 min, PCl_3 (0.70 ml, 8.0 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 17 h. The solvents

Table 3. Theoretically optimized structural parameters for thia- and selenadiphosphiranes [B3LYP/6–311G(2d,p)][a]

Ch / RP—PR		Bond lengths (Å)		Bond angles (°)	
		P—P	P—Ch	P—Ch—P	Ch—P—P
Ch = S					
R = Me	**37**	2.221	2.162	61.8	59.1
R = Ph	**38**	2.244	2.155	62.8	58.6
Ch = Se					
R = Me	**39**	2.222	2.311	57.5	61.3
R = Ph	**40**	2.245	2.306	58.3	60.9

[a] These models have a *C*2 rotational axis passing through the chalcogen atom and the midpoint of the P—P bond.

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were evaporated under reduced pressure and 100 ml of hexane were 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–ethanol to afford $TbtPCl_2$ (**4a**, 2.65 g, 81%). **4a**: colorless powder, m.p. 172.7–174.9 °C (decomp.). Found: C, 49.64; H, 9.11%. Calcd for $C_{27}H_{59}Si_6PCl_2$: C, 49.57; H, 9.09%. ^{1}H NMR (400 MHz, $CDCl_3$), $\delta = 0.07$ (s, 36H), 0.09 (s, 18H), 1.40 (s, 1H), 2.98 (d, $^4J_{PH} = 10.7$ Hz, 1H), 3.07 (d, $^4J_{PH} = 8.7$ Hz, 1H), 6.33 (d, $^4J_{PH} = 4.6$ Hz, 1H), 6.47 (brs, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$), $\delta = 0.77$ ($CH_3 \times 2$), 1.18 (CH_3), 26.81 (d, $^3J_{PC} = 18.1$ Hz, *C*H), 27.04 (d, $^3J_{PC} = 26.4$ Hz, *C*H), 31.64 (*C*H), 123.20 (*C*H), 127.43 (d, $^1J_{PC} = 67.6$ Hz), 127.81 (*C*H), 149.57, 151.72 (d, $^2J_{PC} = 33.8$ Hz), 152.35 (d, $^2J_{PC} = 23.9$ Hz). ^{31}P NMR (121 MHz, C_6D_6), $\delta = 164.2$. HRMS (FAB), found: *m/z* 654.2324 ($[M]^+$). Calcd for $C_{27}H_{59}{}^{35}Cl^{37}ClSi_6P$ ($[M]^+$): 654.2318.

*Synthesis of bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}diphosphene (**1a**).* To a THF solution (3 ml) of $TbtPCl_2$ (**4a**) (124.3 mg, 0.19 mmol) was added Mg metal (54.6 mg, 2.24 mmol) at room temperature. After the reaction mixture had been stirred for 30 min, the color of the solution changed to deep red and then deep violet. The solvent was evaporated under reduced pressure and 30 ml of hexane were added to the residue. Insoluble inorganic salts were removed by filtration through Celite to give a red solution. Removal of the solvent from the filtrate followed by separation with GPLC (toluene) afforded diphosphene **1a** (106.7 mg, 96%). **1a**: red solid, m.p. 202.7–204.5 °C (decomp.). Found: C, 56.94; H, 10.06%. Calcd for $C_{54}H_{118}Si_{12}P_2 \cdot 0.5C_6H_{14}$: C, 56.74; H, 10.19%. ^{1}H NMR (300 MHz, C_6D_6), $\delta = 0.21$ (s, 36H), 0.27 (s, 72H), 1.55 (s, 2H), 3.22 (brs, 2H), 3.28 (brs, 2H), 6.74 (brs, 2H), 6.82 (brs, 2H). ^{31}P NMR (121 MHz, C_6D_6), $\delta = 531.8$. FT-Raman (Nd:YAG laser, 1064 nm), 609 cm^{-1} ($\nu_{P=P}$). UV/vis (hexane), λ_{max} 530 nm (ε 2000), 405 nm (13 000). LRMS (FAB), found: *m/z* 1166 ($[M + H]^+$). Calcd for $C_{54}H_{119}Si_{12}P_2$ ($[M + H]^+$): 1166.

*Preparation of {2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}dichlorophosphine (**4b**).* To a solution of BbtBr (5.63 g, 8.00 mmol) in THF (80 ml) was added *tert*-butyllithium (2.3 M pentane solution, 7.8 ml, 17.6 mmol) at − 78 °C. After 30 min, PCl_3 (1.1 ml, 12.0 mmol) was added. After the reaction mixture had been stirred at − 78 °C for 3 h, LiCl (3.42 g, 80.7 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 13 h. The solvents were evaporated under reduced pressure and 100 ml of hexane were 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–ethanol to afford $BbtPCl_2$ (**4b**, 4.02 g, 69%). **4b**: colorless powder, m.p. 174.8–176.2 °C (decomp.). Found: C, 49.50; H, 9.42%. Calcd for $C_{30}H_{67}Si_7PCl_2$: C, 49.61; H, 9.30%. ^{1}H NMR (400 MHz, $CDCl_3$), $\delta = 0.09$ (s, 36H), 0.27 (s, 27H), 3.17 (d, $^4J_{PH} = 11.6$ Hz, 2H), 6.78 (d, $^4J_{PH} = 4.6$ Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$), $\delta = 1.70$ (CH_3), 5.60 (CH_3), 23.68, 27.73 (d, $^3J_{PC} = 25.5$ Hz, *C*H), 127.83 (*C*H), 129.22 (d, $^1J_{PC} = 67.5$ Hz), 151.16, 151.30 (d, $^2J_{PC} = 26.3$ Hz). ^{31}P NMR (121 MHz, $CDCl_3$), $\delta = 162.6$. HRMS (FAB), found: *m/z* 725.2814 ($[M + H]^+$). Calcd for $C_{30}H_{68}{}^{35}Cl_2Si_7P$ ($[M + H]^+$): 725.2821.

*Synthesis of bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}diphosphene (**1b**).* To a THF solution (3 ml) of $BbtPCl_2$ (**4b**) (726.3 mg, 1.00 mmol) was added Mg metal (243.1 mg, 10.0 mmol) at room temperature. After the reaction mixture had been stirred for 10 min, the solution turned deep red and then deep violet. The solvent was evaporated under reduced pressure and 100 ml of hexane were added to the residue. Insoluble inorganic salts were removed by filtration through Celite. The removal of the solvent from the filtrate gave red crystals of diphosphene **1b** (700.6 mg, quant.). **1b**: red crystals, m.p. >350 °C. Found: C, 54.37; H, 10.48%. Calcd for $C_{60}H_{134}Si_{14}P_2$: C, 54.98; H, 10.30%. ^{1}H NMR (300 MHz, C_6D_6), $\delta = 0.31$ (s, 72H), 0.40 (s, 54H), 3.49 (brs, 4H), 7.11 (s, 4H). ^{13}C NMR (75 MHz, C_6D_6), $\delta = 2.12$ (q), 5.70 (q), 22.81 (s), 32.08 (d), 127.61 (d), 139.57 (s), 147.70 (s), 148.53 (s). ^{31}P NMR (121 MHz, C_6D_6), $\delta = 529.0$. FT-Raman (Nd:YAG laser, 1064 nm), 603 cm^{-1} ($\nu_{P=P}$). UV/visible (hexane), λ_{max} 532 nm (ε 1000), 418 nm (12 000). HRMS (FAB), found: *m/z* 1308.6736 ($[M]^+$). Calcd for $C_{60}H_{134}Si_{14}P_2$ ($[M]^+$): 1308.6731.

*Reaction of diphosphene **1b** with elemental selenium.* A benzene-d_6 suspension (0.7 ml) of BbtP=PBbt (**1b**) (130.8 mg, 0.10 mmol) and elemental selenium (10.8 mg, 0.13 mmol) was degassed and sealed in an NMR tube. When the suspension had been heated at 120 °C for 120 h, the signals of **1b** disappeared and the signals which correspond to diselenoxophosphorane **20** and selenadiphosphirane **21** were observed with a ratio of 2:9 in the ^{1}H NMR spectrum. The reaction mixture was separated by HPLC (toluene) to give 77.4 mg of 2,3-bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)-methyl]phenyl}selenadiphosphirane (**21**, 57%) and 18.5 mg of BbtH (30%). Pure orange crystals of [**21**·0.5hexane] were obtained by slow recrystallization from hexane in a refrigerator at 0 °C. **21**: orange crystals, m.p. 244.6–245.8 °C (decomp.). Found: C, 52.84; H, 9.65%. Calcd for $C_{60}H_{134}Si_{14}P_2Se \cdot 0.5C_6H_{14}$: C, 52.81; H, 9.92%. ^{1}H NMR (400 MHz, C_6D_6), $\delta = 0.33$ (s, 54H), 0.36 (s, 36H), 0.41 (s, 36H), 3.29–3.32 (m, 4H), 6.85 (s, 4H). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 50 °C), $\delta = 2.82$ (CH_3), 2.85 (CH_3), 6.07 (CH_3), 22.81, 31.0–31.2 (m, *C*H), 128.24 (*C*H), 133.3–134.3 (m), 146.29, 149.4–149.6 (m). ^{31}P NMR (121 MHz, C_6D_6), $\delta = -55.3$. ^{77}Se

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NMR (57 MHz, C_6D_6), $\delta = 14.6$ (t, $^1J_{SeP} = 126$ Hz). LRMS (FAB), found: *m/z* 1389 ($[M]^+$). Calcd for $C_{60}H_{134}Si_{14}P_2Se$ ($[M]^+$): 1389. **20**: ^{1}H NMR (300 MHz, C_6D_6), $\delta = 0.25$ (s, 18H), 0.30 (s, 18H), 0.32 (s, 27H), 3.02 (d, $^4J_{HP} = 4$ Hz, 2H), 6.91 (d, $^4J_{HP} = 6$ Hz, 2H). ^{31}P NMR (121 MHz, C_6D_6), $\delta = 260.6$. ^{77}Se NMR (57 MHz, C_6D_6), $\delta = 1371.3$ (d, $^1J_{SeP} = 854$ Hz).

*Reaction of diphosphene **1b** with elemental sulfur.* A benzene-d_6 suspension (0.7 ml) of BbtP═PBbt (**1b**) (68.2 mg, 0.05 mmol) and elemental sulfur (S_8, 7.5 mg, 0.23 mmol as S) was degassed and sealed in an NMR tube. When the suspension had been heated at 120 °C for 120 h, the signals which correspond to diphosphene **1b**, dithioxophosphorane **24** and thiadiphosphirane **25** were observed with a ratio of 6:4:5 in the ^{1}H NMR spectrum. The reaction mixture was separated by PTLC (hexane) to give 54.6 mg of a 6:5 mixture of diphosphene **1b** (43%) and 2,3-bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}thiadiphosphirane (**25**, 36%) and 29.4 mg of BbtH. **25**: orange crystals, m.p. 258.2–262.5 °C (decomp.). Found: C, 53.58; H, 10.18%. Calcd for $C_{60}H_{134}Si_{14}P_2S$: C, 53.66; H, 10.66%. ^{1}H NMR (300 MHz, C_6D_6), $\delta = 0.32$ (s, 54H), 0.33 (s, 36H), 0.37 (s, 36H), 3.15–3.18 (m, 4H), 6.83 (s, 4H). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6, 50 °C), $\delta = 2.20$ (CH_3), 2.44 (CH_3), 5.74 (CH_3), 22.60, 30.2–30.4 (m, CH), 128.16 (CH), 133.2–134.3 (m), 146.50, 149.5–149.7 (m). ^{31}P NMR (121 MHz, C_6D_6), $\delta = -71.3$. HRMS (FAB), found: *m/z* 1341.6525 ($[M + H]^+$). Calcd for $C_{60}H_{135}Si_{14}P_2S$ ($[M + H]^+$): 1341.6530. **24**: ^{1}H NMR (300 MHz, C_6D_6), $\delta = 0.24$ (s, 18H), 0.29 (s, 18H), 0.30 (s, 27H), 2.61 (d, $^4J_{HP} = 4$ Hz, 2H), 6.94 (d, $^4J_{HP} = 6$ Hz, 2H). ^{31}P NMR (121 MHz, C_6D_6), $\delta = 286.7$.

*Reaction of diphosphene **1b** with elemental sulfur in the presence of triethylamine.* A benzene-d_6 suspension (0.7 ml) of BbtP═PBbt (**1b**) (130.8 mg, 0.10 mmol), elemental sulfur (S_8, 32.1 mg, 1.00 mmol as S), and triethylamine (0.15 ml, 1.0 mmol) was degassed and sealed in an NMR tube. When the suspension had been heated at 120 °C for 40 h, the signals of **1b** disappeared and the signals corresponding to thiadiphosphirane **25** were observed in the ^{1}H NMR spectrum as a main product. The reaction mixture was separated by HPLC (toluene) to give 118.5 mg of thiadiphosphirane **25** (88%).

*Reaction of diphosphene **1b** with elemental tellurium.* A benzene-d_6 suspension (0.7 ml) of BbtP═PBbt (**1b**) (85.4 mg, 0.06 mmol) and elemental tellurium (41.6 mg, 0.32 mmol) was degassed and sealed in an NMR tube. When the suspension had been heated at 120 °C for 40 h and monitored by ^{1}H NMR spectroscopy, no change was observed in the ^{1}H NMR spectrum. Even after additional heating at 150 °C for 1 week, the ^{1}H NMR spectrum of the suspension showed no change.

*Reaction of diphosphene **1b** with Bu_3P═Te.* A benzene-d_6 suspension (0.7 ml) of BbtP═PBbt (**1b**) (134.2 mg, 0.10 mmol) and Bu_3P═Te (67.5 mg, 0.20 mmol) was degassed and sealed in an NMR tube. When the suspension had been heated at 80 °C for 140 h, monitoring by ^{1}H NMR spectroscopy showed no change. After the additional heating at 120 °C for 1 week, no change was observed in the ^{1}H NMR spectrum of the suspension.

*Thermolysis and photolysis of diphosphene **1a** in the presence of 2,3-dimethyl-1,3-butadiene.* A benzene-d_6 solution (0.7 ml) of TbtP═PTbt (**1a**) (61.2 mg, 0.05 mmol) and 2,3-dimethyl-1,3-butadiene (0.06 ml, 0.53 mmol) was degassed and sealed in an NMR tube. When the solution had been heated at 85 °C for 30 h, no change was observed in the ^{1}H NMR spectrum. The sealed tube was further irradiated with a medium-pressure mercury lamp (100 W) at room temperature for 3 h, but no exchange was observed.

*X-ray crystallographic analyses of [**1a**·benzene-d_6], [**1b**·hexane], [**21**·0.5hexane] and [**25**·0.5hexane].* Crystal data for [**1a**·benzene-d_6], [**1b**·hexane], [**21**·0.5hexane], [**25**·0.5hexane] are summarized in Table 4 and have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 194236-194239. The intensity data were collected on a Rigaku R-AXIS RAPID imaging plate detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at − 180 °C to $2\theta_{max} = 50°$ (55° for [**25**·0.5hexane]). The structure was solved by a direct method (SIR-97)[30] or (SHELXS-97)[31] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[31]

Single crystals of [**1a**·benzene-d_6] suitable for x-ray analysis were obtained by slow recrystallization from C_6D_6 in a sealed tube at room temperature. A deep-red, prismatic crystal was mounted on a glass fiber. The hexagonal skeleton of the solvated benzene was restrained using AFIX instructions. Two trimethylsilyl groups of the $CH(SiMe_3)_2$ group at the *para* position to one of the Tbt groups were disordered. The occupancies of methyl groups were refined (0.70:0.30 and 0.62:0.38). All hydrogen atoms were placed using AFIX instructions, and all the other atoms were refined anisotropically.

Single crystals of [**1b**·hexane] suitable for x-ray analysis were obtained by slow recrystallization from hexane in a refrigerator at −40 °C fixed in a glove-box filled with argon. A deep-red, prismatic crystal was mounted on a glass fiber. All trimethylsilyl groups of the $C(SiMe_3)_3$ groups at the *para* position to the two Bbt groups were disordered. The occupancies of trimethylsilyl groups were refined (0.67:0.33 and 0.84:0.16). The two Si—C bonds of the disordered trimethylsilyl groups of the minor parts were restrained to have the same Si—C distance using SADI instructions. The anisotropic

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Table 4. Crystal data for [**1a**·benzene-d_6], [**1b**·hexane], [**21**·0.5hexane] and [**25**·0.5hexane]

Parameter	[**1a**·benzene-d_6]	[**1b**·hexane]	[**21**·0.5hexane]	[**25**·0.5hexane]
Formula	$C_{60}H_{124}P_2Si_{12}$	$C_{66}H_{148}P_2Si_{14}$	$C_{63}H_{141}P_2SeSi_{14}$	$C_{63}H_{141}SP_2Si_{14}$
Formula weight	1244.61	1397.04	1432.92	1386.02
Crystal color, habit	Deep red, prismatic	Deep red, prismatic	Orange, prismatic	Orange, prismatic
Crystal dimensions (mm)	$0.60 \times 0.30 \times 0.20$	$0.60 \times 0.50 \times 0.40$	$0.30 \times 0.20 \times 0.10$	$0.50 \times 0.30 \times 0.20$
Temperature (°C)	−180	−180	−180	−180
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1$ (#4)	P-1 (#2)
Lattice parameters:				
a (Å)	11.9185(4)	13.4555(8)	18.2260(15)	12.9737(8)
b (Å)	25.5835(9)	21.8734(11)	12.779(9)	17.7976(15)
c (Å)	27.0386(8)	30.4453(17)	36.468(3)	19.0763(11)
α (°)	90	90	90	86.809(10)
β (°)	100.3242(9)	96.400(3)	91.363(4)	79.789(8)
γ (°)	90	90	90	87.278(10)
V (Å^3)	8111.0(5)	8904.7(9)	8491.4(11)	4325.1(5)
Z	4	4	4	2
D_{calc} (g cm^{-3})	1.019	1.042	1.121	1.064
Independent reflections	13985	15514	27777	18867
No. of parameters	693	853	1426	1299
R_1 [$I > \sigma(I)$]	0.087	0.096	0.094	0.068
wR_2 (all data)	0.246	0.231	0.196	0.179
GOF	0.929	1.103	1.08	1.089

temperature factors of four carbon atoms (in the minority of disordered trimethylsilyl groups) were restrained not to be non-positive values using ISOR instructions. All hydrogen atoms were placed using AFIX instructions, and all the other atoms were refined anisotropically except for one Si atom, which was in the minor part of the disordered trimethyl silyl groups and refined isotropically.

Single crystals of [**21**·0.5hexane] suitable for x-ray analysis were obtained by slow recrystallization from hexane in a refrigerator at 0 °C. An orange, prismatic crystal of [**21**·0.5hexane] was mounted on a glass fiber. The selenadiphosphirane ring of the fragment B was disordered. The occupancies of the disordered phosphorus and selenium atoms were refined (0.86:0.14). The minor part of the disordered selenadiphosphirane ring was restrained to have the same structure as the major part of the selenadiphosphirane ring using SAME instructions. All hydrogen atoms were placed using AFIX instructions. The disordered phosphorus and selenium atoms of the minor part were refined isotropically, and all the other non-hydrogen atoms were refined anisotropically.

Single crystals of [**25**·0.5hexane] suitable for x-ray analysis were obtained by slow recrystallization from hexane in a refrigerator at 0 °C. An orange, prismatic crystal of [**25**·0.5hexane] was mounted on a glass fiber. The molecule of thiadiphosphirane **25** was disordered. The occupancies of the disordered molecules were refined (0.74:0.26). The solvated hexane was disordered and their occupancies were refined (0.82:0.18). The benzene rings of the Bbt groups of the minor part were constrained to have right hexagonal structure using AFIX instructions. All hydrogen atoms were placed using AFIX instructions. Some carbon atoms and a silicon atom of the disordered Bbt groups of the minor part were refined isotropically, and all the other non-hydrogen atoms were refined anisotropically.

Theoretical calculations. All theoretical calculations were carried out using the Gaussian 98 program[32] with density functional theory at the B3LYP level.[33] In calculations for diphosphenes **1a, 1b**, **1a′** and **1b′**, the triple zeta basis set ([3s3p])[34] augmented by two sets of d polarization functions for P (d exponents 0.537 and 0.153) was used with an effective core potential, and the 6–31G(d) (for Si) and the 3–21G (for C and H) basis sets were used. The structural optimization of **1a, 1b**, **1a′** and **1b′** were done by OPT keywords without force-constant calculations. In calculations for chalcogenadiphosphiranes **37, 38, 39** and **40**, the 6–311G(2d, p) basis set was used for all atoms. Computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

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