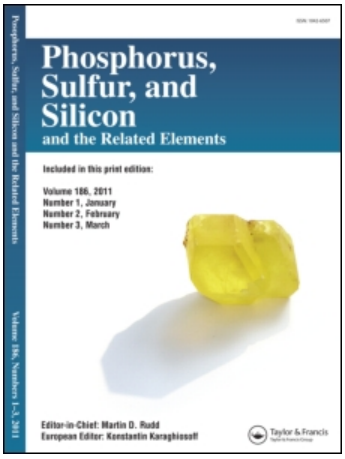

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Norihiro Tokitoh[a]; Akihiro Tsurusaki[a]; Takahiro Sasamori[a]
[a] Institute for Chemical Research, Kyoto University, Kyoto, Japan

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A Unique Thermal Reaction of 9-Anthryldiphosphene Leading to the Formation of a Triphosphirane Derivative

Norihiro Tokitoh, Akihiro Tsurusaki, and Takahiro Sasamori
Institute for Chemical Research, Kyoto University, Kyoto, Japan

Heating of a 9-anthryldiphosphene kinetically stabilized by 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl substituent (denoted as Bbt) group, BbtP = P(9-Anth) (9-Anth = 9-anthryl), with (n-Bu)$_3$P=Te afforded 1,2-bis(9-Anth)-3-Bbt-triphosphirane in moderate yield. The structural parameters and physical properties of the isolated triphosphirane were determined by spectroscopic and X-ray crystallographic analyses.

Keywords 9-Anthryldiphosphene; diphosphene; phosphine telluride; triphosphirane

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.[1] Up to now, several examples of stable diphosphenes and diarsenes (RAs=AsR) have been synthesized by taking advantage of steric protection with bulky substituents,[1,2] following the isolation of the first stable diphosphene, Mes*P=PMes* (Mes* = 2,4,6-tri-*t*-butylphenyl), reported by Yoshifuji et al.[3] We have also succeeded in the synthesis and characterization of the first stable distibenes (ArSb=SbAr) and dibismuthenes (ArBi=BiAr) by taking advantage of efficient steric protection

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Dedicated to Professor Marian Mikołajczyk from the CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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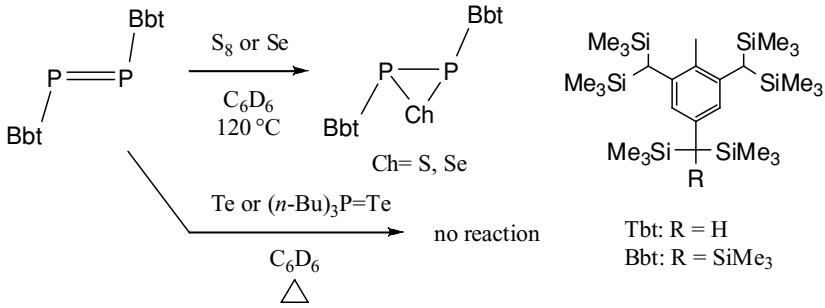
Address correspondence to Norihiro Tokitoh, Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp

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.[4] Evidence has shown that such stable doubly bonded systems between heavier group 15 elements should be good precursors for the corresponding heterocycles,[5] especially in the case of chalcogenation reactions.[6] For example, sulfurization and selenization reactions of kinetically stabilized diphosphenes such as Mes*P=PMes*[3] and BbtP=PBbt[7] using elemental sulfur and selenium were reported to give the corresponding thia- and selenadiphosphiranes as final stable products, respectively, (Scheme 1),[7,8] while sulfurization reactions of BbtSb=SbBbt and BbtBi=BiBbt using elemental sulfur afforded the corresponding four-, five-, and six-membered heterocycles containing sulfur and pnictogen (Sb or Bi) atoms.[6,9] We have reported that the thermal tellurization reactions of BbtP=PBbt with elemental tellurium and (n-Bu)$_3$P=Te were unsuccessful and resulted in the recovery of BbtP=PBbt, in contrast to the case of the tellurization reactions of the analogous distibene and dibismuthene, where the treatment of BbtE=EBbt (E = Sb, Bi) with (n-Bu)$_3$P=Te afforded the corresponding telluradipnictiranes.[10] The inertness of BbtP=PBbt toward the tellurization reagents mentioned above is likely due to the extreme steric hindrance around the P=P moiety.



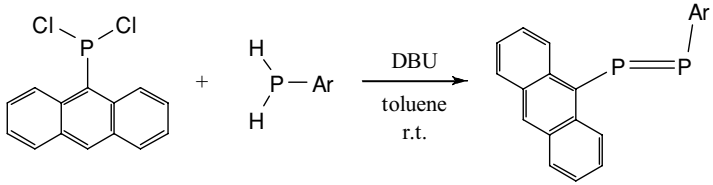
SCHEME 1

However, we have recently reported the synthesis of the first stable 9-anthryldiphosphene **1a**, TbtP=P(9-Anth), bearing a less hindered combination of steric protection groups—Tbt and 9-anthryl—at the P=P unit.[11] Since **1a** is expected to have enough space for reaction with tellurization reagents, we have examined the reaction of **1a** with (n-Bu)$_3$P=Te with the expectation of obtaining the corresponding telluradiphosphirane, which should be an interesting and important species from the viewpoint of heteroatom chemistry.[12] With a view to making closer comparison of the reactivity toward tellurization reaction

between BbtP=PBbt (**2**) and the 9-anthryldiphosphene, we have attempted the tellurization reaction of BbtP=P(9-Anth) (**1b**), which has a Bbt group at the phosphorus atom instead of the Tbt group of **1a**.

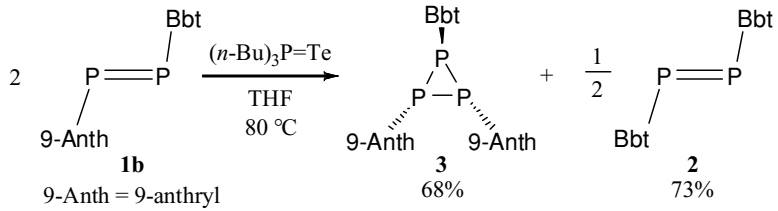
RESULTS AND DISCUSSION

9-Anthryldiphosphene **1b** was synthesized according to the reported procedure as shown in Scheme 2.[11,13] When a bright-red solution of **1b** in THF was treated with an excess (10 equiv.) of (n-Bu)$_3$P=Te at 80°C (sealed tube) for 98 h, the solution turned deep red and a yellow solid precipitated. The ^{31}P NMR spectrum of the crude mixture showed the formation of BbtP=PBbt (**2**) and an unexpected product, the triphosphirane **3**, along with the recovery of (n-Bu)$_3$P=Te as the expense of the starting material (Scheme 3). Filtration of the reaction mixture afforded yellow precipitates, which were found to be triphosphirane **3**, in 68% yield. Alternatively, GPLC purification of the concentrated filtrate afforded diphosphene **2** in 73% yield. The ^{31}P NMR spectrum of the crude mixture indicated almost quantitative recovery of (n-Bu)$_3$P=Te, since no signal for other tributylphosphine derivatives such as (n-Bu)$_3$P or (n-Bu)$_3$P=O was observed. Surprisingly, heating of 9-anthryldiphosphene **1b** in the absence of (n-Bu)$_3$P=Te under the same conditions (in THF at 80°C for 98 h) resulted in the almost quantitative recovery of **1b**, but the formation



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

SCHEME 2



9-Anth = 9-anthryl

SCHEME 3

of only a trace amount of triphosphirane **3**. This fact suggests that (*n*-Bu)$_3$P=Te would work as a kind of catalyst in the thermal reaction of **1b** leading to the formation of **2** and **3** under these conditions. Although the reaction mechanism for the formation of **3** is unclear at present, the corresponding telluradiphosphirane derivative, which would be highly reactive, may be a key intermediate.

In the ^{31}P NMR spectrum, triphosphirane **3** showed the signals of a characteristic A_2B-pattern in the high-field region at –93.1 ppm (doublet) and –127.6 ppm (triplet) with the coupling constant of $^1J_{PP} = 188$ Hz. Since the observed NMR spectral data (δ_P and $^1J_{PP}$ value) of **3** are similar to those of previously reported triphosphiranes,[14] the bulky combination of Bbt and 9-anthryl groups, should not electronically affect the central triphosphirane skeleton.

In addition, the X-ray crystallographic analysis revealed the structural parameters of **3** as shown in Figure 1. The P–P bond lengths of **3** are 2.2144(14), 2.2136(13), and 2.2408(14) Å; these values are within the range of typical P–P single bond lengths (ca. 2.2 Å)[15] but are slightly shorter than those of six-membered ring oligophosphanes [e.g., $(PhP)_6$; 2.237(5) Å][16] probably due to the "banana-bonds" in three-membered ring systems.[17] The bulky Bbt group is oriented toward the opposite side of the two 9-anthryl groups, which face each other with a distance of ca. 3.2–4.3 Å.[18] The bond length between the phosphorus atoms P(2) and P(3), both of which are bonded to a 9-anthryl group, is longer than those of P(1)–P(2) and P(1)–P(3), probably due to the steric repulsion between the facing two 9-anthryl groups.

Theoretical calculations[19] revealed that the structural parameters for the parent triphosphirane **4** with the same configuration as that of **3** are almost similar to those experimentally observed for **3**. Furthermore, in the theoretically optimized structure of 1,2-bis(9-anthryl)-3-(2,6-dimethylphenyl)triphosphirane **5**, which is a model compound of **3** having a 2,6-dimethylphenyl group instead of a Bbt group, the two 9-anthryl groups were found to step aside from each other and twist around to avoid the steric repulsion as shown in Figure 2. Therefore, the unique geometry of **3**, where the two 9-anthryl groups are facing parallel to each other, is most likely due to the packing force in the crystalline state.

In summary, it was found that the thermal reaction of anthryldiphosphene **1b** in the presence of (*n*-Bu)$_3$P=Te afforded the triphosphirane **3** and the diphosphene **2**. Furthermore, (*n*-Bu)$_3$P=Te is necessary for the effective transformation of **1b**, giving **2** and **3**. Further investigations on the properties of triphosphirane **3** are currently in progress.

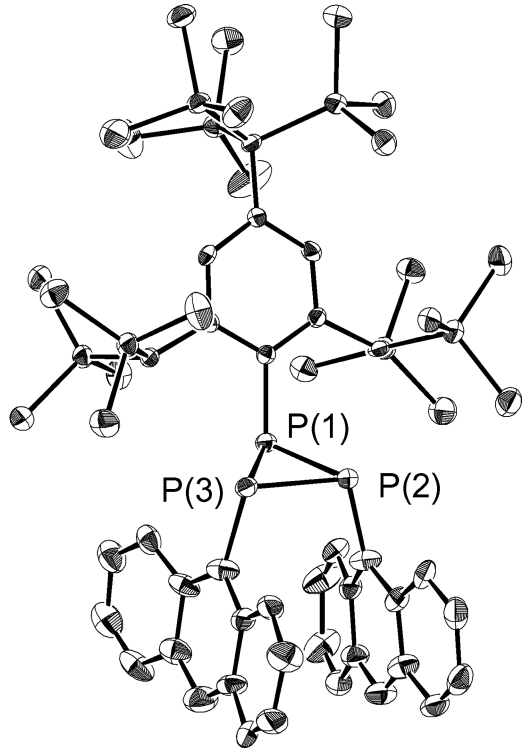


FIGURE 1 Molecular structure of triphosphirane **3** in the crystal (displacement ellipsoids are drawn at the 50% probability level). The hydrogen atoms are omitted for clarity. Selected structural parameters: P(1)–P(2): 2.2144(14) Å, P(1)–P(3): 2.2136(13) Å, P(2)–P(3): 2.2408(14) Å, P(2)–P(1)–P(3): 60.80(4)°, P(1)–P(2)–P(3): 59.58(4)°, P(1)–P(3)–P(2): 59.62(4)°.

EXPERIMENTAL

All experiments were performed under an argon atmosphere unless otherwise noted. Solvents used for the reactions were purified by The Ultimate Solvent System (Glass Contour Company).[20] BbtP=P(9-Anth) was prepared according to the procedures similar to those for TbtP=P(9-Anth).[11] ^{1}H NMR (300 MHz) spectra were measured in C_6D_6 with a JEOL JNM AL-300 spectrometer using a signal due to C_6D_5H (7.15 ppm) as a reference. ^{31}P NMR (121 MHz) spectra were measured in C_6D_6 with a JEOL AL-300 spectrometer using a signal for 85% H_3PO_4 in water (0 ppm) as an external standard. High-resolution mass spectral data were obtained with a JEOL JMS-700 spectrometer. Gel permeation liquid chromatography (GPLC) was performed with an LC-918

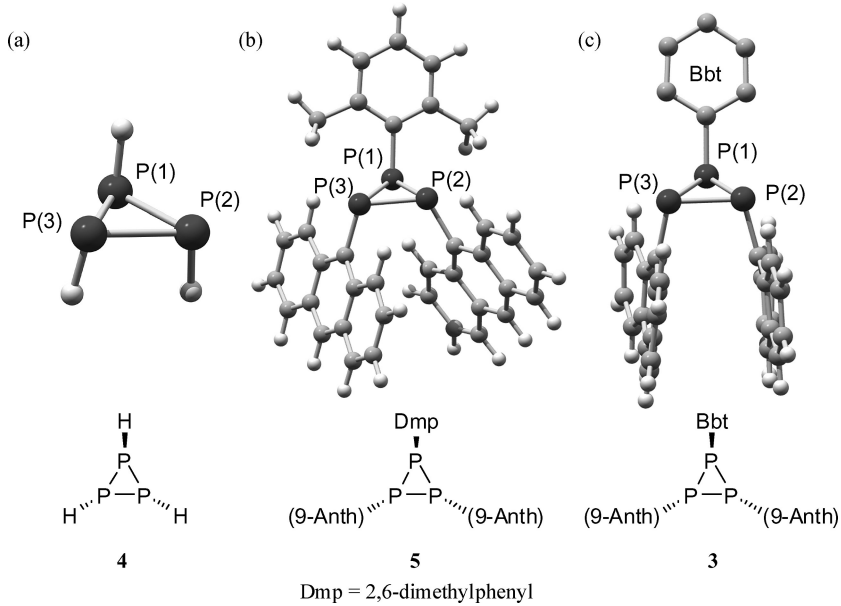


FIGURE 2 (a) Optimized structure of the parent triphosphirane **4**; selected structural parameters: P(1)–P(2): 2.242 Å, P(1)–P(3): 2.242 Å, P(2)–P(3): 2.259 Å, P(2)–P(1)–P(3): 60.5°, P(1)–P(2)–P(3): 59.7°, P(1)–P(3)–P(2): 59.7°. (b) Optimized structure of triphosphirane **5**; selected structural parameters: P(1)–P(2): 2.237 Å, P(1)–P(3): 2.277 Å, P(2)–P(3): 2.259 Å, P(2)–P(1)–P(3): 60.0°, P(1)–P(2)–P(3): 60.8°, P(1)–P(3)–P(2): 59.1°. (c) Experimentally observed structure of **3**. The substituents of the Bbt group are omitted for clarity.

(Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: toluene). The melting point was determined with a Yanaco micro melting point apparatus and is uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

Triphosphirane (3)

A THF suspension (0.6 mL) of BbtP=P(9-Anth) (**1b**, 60.4 mg, 0.070 mmol) and (n-Bu)$_3$P=Te[21] (231 mg, 0.70 mmol) was degassed and sealed in an NMR tube. After heating of the mixture at 80°C for 98 h, the bright red color of the reaction mixture changed to deep red, and a yellow powder precipitated. After the signals for **1b** almost disappeared, the yellow suspension was separated by filtration, and the yellow insoluble materials were washed with hexane. The solvent of the mother liquid

was removed under reduced pressure, and the residue was separated by GPLC to afford BbtP=PBbt (**2**, 16.7 mg, 0.013 mmol, 73%) as red crystals. The yellow solid thus obtained was dissolved in toluene and filtered through a glass filter to remove the inorganic salt. The filtrate was evaporated under reduced pressure to afford triphosphirane **3** (25.7 mg, 0.024 mmol, 68 %) as yellow crystals. **3**: mp 263°C (decomp.). ^{1}H NMR (300 MHz, C_6D_6, 40°C) $\delta = 0.39$ (s, 36H), 0.43 (s, 27H), 4.07 (s, 2H), 6.82 (br s, 4H), 6.89 (pseudotriplet, $^3J_{HH} = 6.8$ Hz, 4H), 7.07 (d, $^4J_{PH} = 2.5$ Hz, 2H), 7.26 (d, $^3J_{HH} = 8.9$ Hz, 4H), 7.46 (s, 2H), 9.11 (d, $^3J_{HH} = 8.5$ Hz, 4H). ^{31}P NMR (121 MHz, C_6D_6, r.t.) $\delta = -92.9$, -127.4 (A_2B spin pattern, $^1J_{PP} = 188$ Hz). The signals observed in the ^{13}C NMR spectrum could not be assigned. Anal. Found: C, 64.15; H 8.00%. Calcd for $C_{58}H_{85}P_3Si_7 \cdot H_2O$: C, 63.92; H, 8.05%. HRMS (FAB) m/z, found: 1071.4335 ($[M+H]^+$), calcd for $C_{58}H_{86}P_3Si_7$ ($[M+H]^+$): 1071.4327.

Single crystals of **3** suitable for X-ray diffraction were obtained by slow recrystallization from THF/toluene at –40°C. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71069$ Å) at –170°C to $2\theta_{max} = 51°$. The structure was solved by direct methods (SHELXS-97[22]) and refined by full-matrix least-squares procedures on F2 for all reflections (SHELXL-97[22]). All hydrogen atoms were placed using AFIX instructions. Crystal data for **3** ($C_{58}H_{85}P_3Si_7$): M = 1071.80, T = 103(2) K, monoclinic, $P2_1/n$ (no.14), $a = 9.5518(3)$ Å, $b = 27.2459(8)$ Å, $c = 22.9089(8)$ Å, $\beta = 94.2967(11)°$, V = 5945.2(3) Å^3, Z = 4, $D_{calc} = 1.197$ g cm^{-3}, $\mu = 0.277$ mm^{-1}, $2\theta_{max} = 51.0$, 52034 measured reflections, 11040 independent reflections [$R_{int} = 0.1143$], 634 refined parameters, GOF = 1.036, $R_1 = 0.0558$ and w$R_2 = 0.1019$ [$I > 2\sigma(I)$], $R_1 = 0.1195$ and w$R_2 = 0.1158$ [for all data], largest diff. peak and hole 0.710 and –0.410 e.Å^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 670466 for **3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.).

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[19] The calculations were performed using Gaussian 03W package at B3LYP/6-31G(d) level. It was confirmed that the optimized structures have minimum energies using frequency calculations.

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