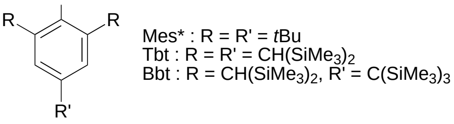
Synthesis and Structure of the First Stable Phosphabismuthene**

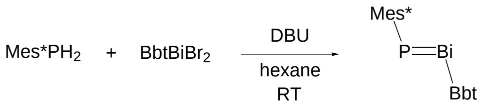
Takahiro Sasamori, Nobuhiro Takeda, Mizue Fujio, Masahiro Kimura, Shigeru Nagase, and Norihiro Tokitoh*

There has been much interest in doubly bonded compounds between Group 15 elements, that is, heavier congeners of azo compounds, since the first isolation of a stable diphosphene, Mes*P=PMes* (Mes* = 2,4,6-tri-*tert*-butylphenyl), by Yoshifuji et al. in 1981.[1] In 1980s, several examples of kinetically stabilized diphosphenes (RP=PR)[2] and diarsenes (RAs=AsR)[3] have been synthesized and fully characterized. In contrast, much heavier analogues, that is, distibene (RSb=SbR)[4] and dibismuthene (RBi=BiR),[5] have only been reported very recently by us, where the first isolation of stable distibene and dibismuthene was achieved by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) (Scheme 1).[6] Later on, Power and co-workers also described the syntheses of another series of distibenes and dibismuthene containing bulky 2,6-$Ar_2C_6H_3$ groups (Ar = mesityl or 2,4,6-triisopropylphenyl).[7] Thus, homonuclear doubly bonded systems between heavier Group 15 elements are no longer imaginary species even in the case of bismuth, and the next target molecules are heteronuclear doubly bonded systems, which may be key compounds of great importance in the systematic elucidation of the intrinsic nature of low-coordinate compounds of heavier main group elements. While some examples of phosphaarsenes and phosphastibenes are reported,[8, 9] no heteronuclear double bonds between bismuth and the other Group 15 elements have been described probably because of the weakness of π bond between Bi and another atom due to the difference of the size of the p orbitals. Very recently, however, we succeeded in the synthesis of the first stable stibabismuthene (BbtSb=BiBbt),[10] which is the first example of a heteronuclear doubly bonded system containing a bismuth atom, by taking advantage of a new type of steric protection group, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt).[11] Herein, we report the first synthesis of a stable phosphabismuthene, that is, a novel doubly bonded system between phosphorus and bismuth atoms, in which the exceedingly different size of p orbitals is overcome.



Scheme 1. Some steric protection groups.

The condensation reaction of $BbtBiBr_2$ with Mes^*PH_2 in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in hexane at room temperature afforded a deep orange powder (Scheme 2), the ^{31}P NMR spectrum of which showed a broad singlet at $\delta = 612$ along with a small peak for Mes^*PH_2 ($\delta = -130$). Since the low-field chemical shift of $\delta = 612$ is characteristic of a low-coordinate phosphorus atom, this result strongly suggests the formation of phosphabismuthene **1** in this reaction. In addition, the broadening of the signal, which is considered to be due to the 9/2 nuclear spin of the adjacent Bi atom, is also regarded as an evidence for the P=Bi double bond of **1**. The yield of **1** was estimated to be 91 % on the basis of a comparison of the integrals of the ^1H NMR signals compared with those of TbtH added as an internal standard. Although phosphabismuthene **1** was very difficult to purify by chromatographic separation owing to its extreme high reactivity toward moisture and air, recrystallization of the orange powder from hexane at −40 °C afforded **1** · 0.5 hexane as green single crystals. It is noteworthy that compound **1** is not only a new member of a novel class of heteronuclear doubly bonded systems between heavier Group 15 elements but also the first example of a stable species with a double bond between the third and sixth row main group elements.



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Scheme 2. Synthesis of phosphabismuthene **1**.

The molecular structure of **1** was determined by X-ray crystallographic analysis (Figure 1).[12] This molecule has a *trans* configuration with a C-Bi-P-C torsion angle of 179.79(9)°. The length of the P−Bi bond of **1** is 2.4541(6) Å, which is the midpoint between the E−E bond lengths of the corresponding diphosphene (Mes*P=PMes* (**2**), 2.034(2) Å)[1] and dibismuthenes (TbtBi=BiTbt (**3**), 2.8206(8) Å[5] and BbtBi=BiBbt (**4**), 2.8699(6) Å[13]). This P−Bi bond length is about 8 % shorter than the sum of the covalent radii of the phosphorus and bismuth atoms (2.66 Å)

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[*] Prof. N. Tokitoh, Dr. N. Takeda
Institute for Chemical Research, Kyoto University
Gokasho, Uji, Kyoto 611-0011 (Japan)
Fax: (+81)774-38-3209
E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp
T. Sasamori
Graduate School of Science, Kyushu University
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581 (Japan)
Dr. M. Fujio
Institute for Fundamental Research of Organic Chemistry,
Kyushu University
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581 (Japan)
M. Kimura
Graduate School of Science, Tokyo Metropolitan University
Hachioji, Tokyo 192-0397 (Japan)
Prof. S. Nagase
Institute for Molecular Science
Myodaiji, Okazaki 444-8585 (Japan)

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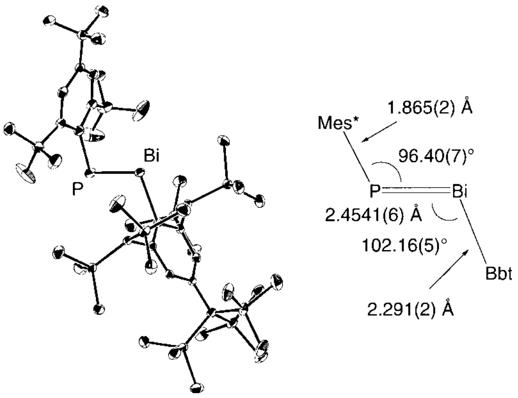

Figure 1. Left: Molecular structure of **1** (ORTEP drawing; thermal ellipsoid plot (50% probability)). The fragment of solvated hexane was omitted for clarity. Right: Schematic drawing of **1** with some selected bond lengths and angles.

as well as the E=E bond lengths of the doubly bonded system between heavier Group 15 elements, which are known to be about 8% shorter than the corresponding E–E single bonds.[14] On the other hand, the Bi-P-C and P-Bi-C angles of **1** were found to be 96.40(7)° and 102.16(5)° respectively. The considerably wider angle at the Bi atom than that at the P atom may be surprising, because the angles at pnictogens generally become smaller with increasing atomic number (from N to Bi). It is well known that the heavier pnictogens have a stronger tendency to maintain the $(ns)^2(np)^3$ valence electron configuration because of the larger size difference and energy gap between the valence s and p orbitals.[15] The results of theoretical calculations for RP=BiR′ systems,[16] which are summarized in Table 1, lead us to a reasonable understanding. All the optimized structures for RP=BiR′ systems show very similar bond lengths for their P–Bi bond (ca. 2.43 Å), which are almost consistent with the experimentally obtained P–Bi bond lengths of **1**. By contrast, the bond angles at the phosphorus and bismuth atoms vary in these systems. The optimized geometry of PhP=BiPh (**5**) showed no distinct difference between angles at the phosphorus atom (97.0°) and the bismuth atom (96.6°) in contrast to the experimentally obtained values of **1**. On the other hand, a theoretically optimized structure of the more sterically congested system, Mes*P=BiBbt (**1**), was found to have structural parameters (95.3° for P and 104.4° for Bi) almost the same as the experimentally obtained values. The optimized structural parameters for the reversibly substituted model system BbtP=BiMes* (**6**) showed a widened angle at the P atom (104.8°) and almost the same angle at the Bi atom (94.1°) as that of PhP=BiPh (**5**). In addition, the P-Bi-C angle of HP=BiBbt (**7**) system was also found to be widened to 103.1°, which is almost the same value as that of **1**. These results indicate that the wider angle at the Bi atom determined from the X-ray crystallographic analysis of **1** is probably due to the steric repulsion not between the substituents (Mes* and Bbt group) but between the bulky Bbt group and the central P=Bi moiety.

Table 1. Calculated structures of phosphabismuthenes.[16]

RP=BiR′		Angle [°]		Length [Å]
		R–P–Bi	P–Bi–R′	
Ph–P=Bi–Ph[a]	**5**	97.0	96.6	2.427
Mes*–P=Bi–Bbt	**1**	95.3	104.4	2.440
Bbt–P=Bi–Mes*	**6**	104.8	94.1	2.442
H–P=Bi–Bbt	**7**	90.0	103.0	2.428

[a] The phenyl groups are fixed perpendicularly to the C-P-Bi plane.

The UV/Vis spectrum of **1** in hexane shows characteristically red-shifted absorption maxima at 455 (ε 10000), 540 (sh, 1000), and 670 (300) nm, while the previously known heavier congeners of azo compounds show only two absorption maxima corresponding to the symmetry-allowed $\pi \rightarrow \pi^*$ and symmetry-forbidden $n \rightarrow \pi^*$ electron transitions at wavelengths longer than 300 nm in all cases. The λ_{max} value of 455 nm, which is attributable to the $\pi \rightarrow \pi^*$ transition of the P=Bi chromophore, lies in the middle between the $\pi \rightarrow \pi^*$ transition of Mes*P=PMes* (**2**: λ_{max} 340 nm (ε 7690))[1] and that of BbtBi=BiBbt (**4**: λ_{max} 537 nm (ε 6000)).[13] Although the latter two λ_{max} values observed for **1** (540 and 670 nm) are most likely due to the $n \rightarrow \pi^*$ transitions and one of them at 540 nm is reasonably found in the middle between the λ_{max} value of **2** (460 nm (ε 1360)) and that of **4** (670 nm (sh, ε 20)), another one at 670 nm lies at a strangely longer wavelength. Although we have no clear explanation for the additional $n \rightarrow \pi^*$ transition observed in longer wavelength region for **1**, it could be consistent with the assumption that heteronuclear doubly bonded systems between heavier Group 15 elements should have two weak $n \rightarrow \pi^*$ transitions due to two chemically distinct lone pairs on the phosphorus and the bismuth atoms in addition to one strong $\pi \rightarrow \pi^*$ transition. These outcomes for phosphabismuthene **1** discussed above are also of great importance for understanding the spectroscopic properties of BbtSb=BiBbt, which we reported previously.[10]

Thus, **1** features a double bond between the phosphorus and the bismuth atom in the solid state and even in solution, as suggested by the NMR and UV/Vis spectra and X-ray crystallographic analysis. Further investigation of the physical and chemical properties of **1** is currently in progress. Now, as for heavier Group 15 elements, not only the homonuclear doubly bonded compounds but also the heteronuclear systems have been obtained as stable compounds, even in the case of elements from rows that differ by more than one (i.e. P and Bi), when they are kinetically well stabilized. The concept of kinetic stabilization should be very helpful for the synthesis of unprecedented doubly bonded systems such as As=Sb, As=Bi, Sb=Si, and Bi=Si.

Experimental Section

1: DBU (15.0 µL, 0.10 mmol) was added dropwise by means of a syringe to a solution of Mes*PH$_2$ (14.7 mg, 0.053 mmol) and BbtBiBr$_2$ (51.0 mg, 0.051 mmol) in hexane (10 mL) at room temperature (ca. 25 °C). The resulting orange solution was stirred at the same temperature for 14 h. After filtration through Celite, the filtrate was evaporated. The residue (orange powder, 57.0 mg) contained **1** as a main product (0.046 mmol, 91%, estimated by ^{1}H NMR spectroscopy by using TbtH as an internal standard), along with a small amount of Mes*PH$_2$ and DBU. **1**: m.p. 120.0–121.2 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.25$ (s, 36H), 0.40 (s, 27H), 1.41 (s, 9H), 1.68 (s, 2H), 1.70 (s, 18H), 7.58 (s, 2H), 7.84 (s, 2H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 2.29$ (q), 6.11 (q), 22.80 (s), 32.96 (q), 33.98 (s), 37.02

(q), 38.46 (s), 40.61 (d), 119.79(d), 128.52 (s), 131.05 (d), 144.59 (s), 150.66 (s), 152.30 (s), 159.59 (s), a signal assignable to *ipso*-^{13}C of Bbt group was not observed.; ^{31}P NMR (121 MHz, C_6D_6): $\delta = 612.0$; UV/vis (*n*-hexane): λ_{max} (ε) = 455 (10000), 540 (sh, 1000), and 670 nm (300); high-resolution MS (FAB): m/z: 1109.5511($[M+H]^+$), calcd for $C_{48}H_{97}Si_7PBi$ 1109.5516. Slow evaporation of a hexane solution of the residue in a refrigerator at $-40\,^\circ$C fixed in a glovebox filled with argon gave green crystals of $\mathbf{1}\cdot$0.5 hexane.

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[12] Crystal data for $\mathbf{1}\cdot$0.5 hexane ($C_{51}H_{103}BiPSi_7$): $M_r = 1152.91$, $T = 93(2)$ K, triclinic, $P\bar{1}$ (no. 2), $a = 12.7372(2)$, $b = 14.6943(5)$, $c = 18.5933(5)$ Å, $\alpha = 107.5367(14)$, $\beta = 95.2385(15)$, $\gamma = 107.9837(5)^\circ$, $V = 3090.27(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.239\ \mathrm{g\,cm^{-3}}$, $\mu = 3.044\ \mathrm{mm^{-1}}$, $\lambda = 0.71070$ Å, $2\theta_{max} = 50.0$, 35164 measured reflections, 10813 independent reflections, 572 refined parameters, GOF = 1.034, $R_1 = 0.0201$ and $wR_2 = 0.0483$ ($I > 2\sigma(I)$), $R_1 = 0.0225$ and $wR_2 = 0.0489$ (for all data), largest difference peak and hole 1.106 and -0.476 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168594. 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). The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97). All hydrogens were placed using AFIX instructions.

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[16] Geometry optimization was carried out using the Gaussian 98 program with density functional theory at the B3LYP level. The triple zeta basis set ([3s3p]) augmented by two sets of d polarization functions for Bi (d exponents 0.229 and 0.069) and P (d exponents 0.537 and 0.153) and double zeta basis ([2s2p])set for Si were used with effective core potential; the 3-21G basis set was used for C and H.

Erodible Conducting Polymers for Potential Biomedical Applications[**]

Alexander N. Zelikin, David M. Lynn, Jian Farhadi, Ivan Martin, Venkatram Shastri,* and Robert Langer*

Electrically conducting polymers have been investigated for numerous applications, including organic substitutes for metals in electronic circuits,[1] coatings for electromagnetic shielding,[2] analytical and biological sensing devices,[3–5] and as substrates for the manipulation of mammalian cell growth and function.[6] From a separate standpoint, the development and application of biodegradable polymers has had a profound impact in numerous medical and surgical applications.[7] It occurred to us that the creation of biocompatible, degradable conducting polymers could open the door to a number of new biomedical applications.[8] Several groups have reported the synthesis and characterization of conducting poly(thiophene) derivatives containing hydrolyzable ester groups in the polymer backbone.[9] However, to our knowledge, the degradability and biocompatibility of these polymers has not been established, and the reduced environmental stability of oxidized polythiophenes could limit their application under physiological conditions.

Of the various electrically conducting polymers, polypyrrole (Ppy) has been the most widely studied material for potential biomedical applications because it is relatively stable to air and water and can be readily synthesized through chemical and electrochemical routes.[10] Additionally, Ppy is a suitable substrate for cell attachment and proliferation[6] and possesses excellent biocompatibility in vivo.[8, 11] Our attempts to synthesize biodegradable Ppy derivatives through the incorporation of backbone ester moieties (in analogy to the polythiophenes discussed above) have thus far been unsuccessful because of extensive side reactions accompanying pyrrole coupling chemistry and the generally poor oxidative stability of the requisite oligopyrrole intermediates. Herein, we report an alternative strategy for the design of *erodible* Ppy materials based on the chemical and electrochemical polymerization of β-substituted pyrrole monomers containing ionizable and/or hydrolyzable side groups [Eq. 1]. These polymers can be fabricated into conductive materials that erode slowly under physiological conditions and support the growth, proliferation, and differentiation of primary human cells in in vitro cell culture assays.

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[*] V. Shastri, R. Langer, A. N. Zelikin, D. M. Lynn
Department of Chemical Engineering, Room E25-342
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 (USA)
Fax: (+1) 617-258-8827
E-mail: shastriv@seas.upenn.edu, rlanger@mit.edu

J. Farhadi, I. Martin
Department of Surgery, Research Division
Kantonsspital Basel, Basel, (Switzerland)

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