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Activation of N_2O and SO_2 by the P−B Bond System. Reversible Binding of SO_2 by the P−O−B Geminal Frustrated Lewis Pair

Natalia Szynkiewicz, Jarosław Chojnacki, and Rafał Grubba*

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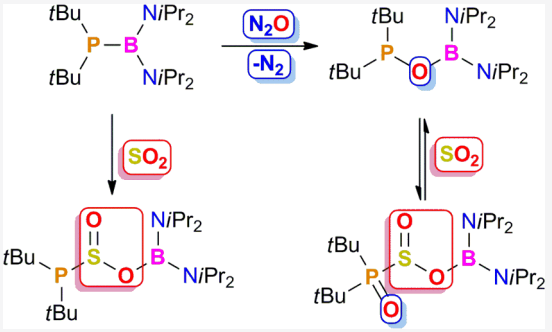
ABSTRACT: Herein, we present the first transformation of borylphosphine into borylphosphinite using nitrous oxide. Borylphosphine reacts with N_2O via insertion of a single oxygen atom into the P−B bond and formation of a P−O−B bond system. Borylphosphine and borylphosphinite capture SO_2 and activate it in an irreversible and reversible manner, respectively.



1. INTRODUCTION

Metal-free catalysis based on systems that mimic the reactivity of transition metal compounds toward hydrogen and greenhouse gases is currently one of the most widely studied fields of main-group element chemistry.[1,2] We are searching for compounds that not only capture small molecules but also enable their clean and efficient conversion into complex organic derivatives or their decomposition into more environmentally friendly species. The challenge is to develop agents capable of fixing highly reactive molecules such as SO_2 with the formation of selected products as well as activating species that kinetically or thermodynamically reluctant to decompose and be reduced, such as N_2O or CO_2, without employing harsh reaction conditions.

Despite its high oxidation potential, N_2O is kinetically inert, and only highly oxophilic compounds are known to react with N_2O under mild conditions.[3] Thus, these reactions are extremely selective and proceed via oxygen atom transfer and release of N_2. The covalent capture of N_2O may be achieved by frustrated Lewis pairs (FLPs)[4−6] or N-heterocyclic carbenes (NHCs),[7,8] leading to the formation of stable adducts involving an intact N_2O moiety: $R_3PNNOBR_3$ or NHC-NNO, respectively. Upon thermal or photochemical activation, these adducts decompose and liberate dinitrogen, giving $R_3P(O)BR_3$ or the corresponding urea. Although in NHC-(N_2O), the C−N bond is relatively strong, phosphorus is prone to oxidation, and zwitterionic $R_3P(N_2O)BR_3$ compounds are "kinetically trapped" due to the presence of the highly electrophilic borane. The product is stable only when the Lewis acid is sufficiently strong and coordination of borane to the oxygen atom is faster than phosphine oxidation.[4,5,9]

Unlike N_2O, SO_2 is a toxic and a more reactive Lewis acidic molecule that is considered a S-containing feedstock for chemicals. SO_2 reacts with a wide range of organic species, typically as an oxidizing agent, and forms stable adducts with amines, of which solid adducts are utilized as easily handled sulfur dioxide surrogates in organic syntheses.[10] While nitrogen base−SO_2 adducts are well characterized, reaction with phosphines results in the formation of phosphine oxides and phosphine sulfides in a 2:1 ratio.[11] Very recently, Dielmann et al. isolated the first phosphine−SO_2 adducts.[12] The slow decomposition of these compounds helped to elucidate the mechanism of their oxidation: nucleophilic attack by the phosphine at the sulfur atom of SO_2 followed by the formation of a P−O bond with elimination of SO.[12] Phosphine−SO_2 adducts may be stabilized in the presence of Lewis acids, for instance, by using FLPs. Inter- and intramolecular FLPs bind SO_2, yielding the corresponding $R_3P/N-S(O)-O-B/SiR_3$ as a linear or cyclic zwitterions upon formation of P−S (or N−S) and B−O (or Si−O and Al−O) bonds, respectively.[13−15] Unlike FLPs, stable boryl(phosphino)carbene was found not only to capture but also to activate the SO_2 molecule in an unprecedented manner, giving sulfine derivatives $R_2P(O)-C(SO)-BR_2$.[16]

Our group has a research interest in the synthesis and reactivity of low-valent P,B-based systems[17−20] with applica-

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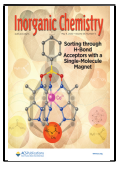

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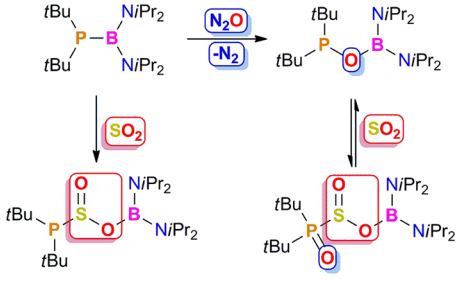
tions in the activation of small inorganic molecules. We pay special attention to amino-substituted phosphinoboranes[19] and diphosphinoboranes,[20] borylphosphine-like species containing a very long single P−B bond with a pyramidal P atom and a planar B atom.[21] As a continuation of our studies, we decided to explore the reactivity of these species toward inert N_2O and highly reactive SO_2. From a series of monomeric diaminophosphinoboranes recently synthesized by us, we tested the reactivity of tBu$_2$P−B(NiPr$_2$)$_2$ (**1**)[19] due to its high nucleophilicity and the presence of tBu and NiPr$_2$ substituents, which should promote the crystallization of activation products.

2. RESULTS AND DISCUSSION

The reaction of a toluene solution of **1** with N_2O (1 atm) at room temperature led to complete conversion of the parent P−B compound into borylphosphinite **2** after 24 h (Scheme 1). Furthermore, during the reaction, vigorous gas evolution was observed.

Scheme 1. Reaction of 1 with Nitrous Oxide and Reactions of 1 and 2 with Sulfur Dioxide



The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture displays a singlet at 144.7 ppm, which is strongly shifted downfield in comparison to the resonance of parent **1** (−8.0 ppm). Moreover, contrary to the spectrum of **1**, in which a broad signal was observed, the corresponding spectrum of **2** shows a sharp resonance, indicating the loss of direct phosphorus−boron coupling. Notably, the $^{31}P\{^1H\}$ chemical shift of **2** is in the typical region for phosphinites (e.g., for iPr$_2$POPh, 149 ppm). These spectral data indicated that newly formed **2** possesses a tBu$_2$PO phosphinite moiety. The ^{11}B NMR spectrum of **2** shows a singlet at 26.7 ppm, which is shifted upfield in comparison to the corresponding signal of **1** (39.5 ppm) and has a typical value for tricoordinated boron compounds with N-donor ligands.[19,20,22] Analytically pure **2** was quantitatively obtained by solvent evaporation as an air-stable, white crystalline solid (94% yield). Crystals of **2** suitable for X-ray analysis were formed from a concentrated petroleum ether solution at −80 °C. X-ray structure determination unambiguously confirmed the identity of **2** and showed that a single oxygen atom was inserted into the P−B bond (Figure 1).

The boron and both nitrogen atoms exhibit trigonal planar geometry, whereas the phosphorus atom is pyramidal. The N1−B1 [1.465(1) Å], N2−B1 [1.424(2) Å], and B1−O2 [1.413(1) Å] bond distances are significantly shorter than the corresponding single covalent bonds (sum of the single-covalent bond radii for B and N, 1.56 Å; that for B and O, 1.48 Å),[23] which suggests substantial π-donor interactions between N and O atoms with a boron center. The P1−O1 distance of

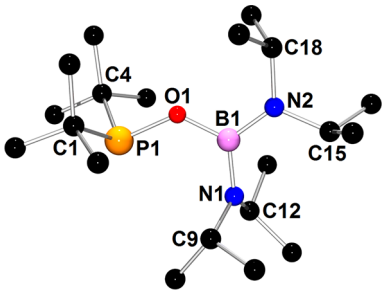


Figure 1. X-ray structure of **2** showing the atom numbering scheme. The H atoms have been omitted for the sake of clarity.

1.6582(9) Å is similar to those observed for compounds with phosphinite moieties attached to boryl groups.[22,24,25] The P−O−B angle is 126.51(7)°. Interestingly, P, O, B, and both N atoms lie in almost the same plane. This striking structural feature of **2** can be explained on the basis of NBO analysis. The O1 and B1 atoms display sp^2 hybridization; furthermore, the unhybridized p lone pair on the O1 atom interacts with the B1 atom, resulting in π-bonding. Additionally, significant donor−acceptor interactions were also observed between the nitrogen atoms and the B1 atom. Notably, there is no significant interaction between the P1 atom and the B1 center.

According to calculations of nucleophilic (f_N) and electrophilic (f_E) Fukui functions, in **2**, both P and B atoms are neutral with values of f_N and f_E, respectively, close to zero. The nucleophilic properties of phosphorus decreased in comparison to those of parent **1** (f_N = 0.277), while the electrophilicity of the boron atom remained unchanged.

We did not observe the formation of adduct **1** with N_2O containing a PNNOB structural motif similar to those obtained in reactions involving P- and B-based FLPs and N_2O.[4,5] Considering that the Lewis acidic properties of the B center in **1** are quenched due to strong π-donation from N atoms,[19] we assume that coordination of the terminal O atom of the N_2O molecule to B is very weak and that oxidation of the tBu$_2$P phosphanyl group is favored. Consequently, oxidation of **1** by N_2O leads to the formation of **2** bearing a P−O−B skeleton with simultaneous liberation of N_2. Insertion of a single oxygen atom into a single covalent bond is very rare[22,26,27] except in biological systems utilizing monooxygenases.[28] The insertion of an oxygen atom into a P−B bond was observed for the first time by Nöth and Schrägle in the reaction of Et$_2$P−B(NMe$_2$)$_2$ with O_2, which gave Et$_2$P(=O)−O−B(NMe$_2$)$_2$.[29] An alternative method was proposed by Pringle and co-workers. Therein, Me$_3$NO was used as an oxidizing agent that enables the insertion of the single O atom to form P−O−B species.[22] The presented reaction of **1** with N_2O constitutes a simple and effective method of synthesizing borylphosphinites, an emerging class of compounds with applications in the activation of small molecules[24,25] and the synthesis of transition metal catalysts.[22]

Next, we tested the reactivity of **1** toward the electrophilic SO_2 molecule [$f_E(SO_2)$ = 0.525]. The reaction of **1** with gaseous SO_2 (1 atm) in toluene was performed at room temperature for 5 min. After evaporation of the solvent-pure product, **3** was isolated quantitatively as a yellowish solid (98% yield) (Scheme 1). X-ray-quality crystals of **3** were obtained from a saturated petroleum ether solution at −20 °C. $^{31}P\{^1H\}$ NMR spectroscopy reveals that the reaction of **1** with SO_2 is very clean, with **3** as the only main product. The $^{31}P\{^1H\}$

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spectrum of **3** shows a downfield-shifted sharp singlet at 111.4 ppm. The ^{11}B spectrum of **3** displays a resonance at 26.4 ppm with almost the same value of the chemical shift as observed for **2**, indicating the same coordination environment of the B atom in both **2** and **3**. X-ray structural analysis of **3** confirms that the aforementioned reaction proceeds via insertion of the SO_2 molecule into a single P−B bond (Figure 2).

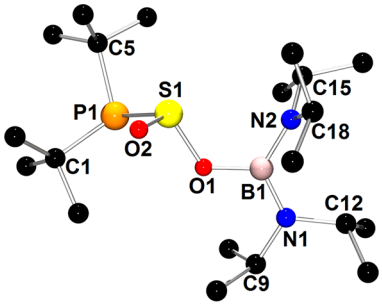

Figure 2. X-ray structure of **3** showing the atom numbering scheme. The H atoms have been omitted for the sake of clarity. One molecule of the two present in the asymmetric unit was selected.

The pyramidal geometry around the P1 atom and planar geometries around B1 at the N1 and N2 atoms are clearly visible. The geometry at S1 is pyramidal due to the presence of a lone pair of electrons. Similar to those in **2**, in **3**, the O1−B1 [1.426(2) Å], N1−B1 [1.402(2) Å], and N2−B1 [1.453(2) Å] distances are significantly shorter than typical single covalent bonds, indicating π-interactions with the boron center. The P1−S1 [2.2176(7) Å] and S1−O1 [1.634(1) Å] bond lengths are very close to the expected distances for the corresponding single covalent bonds (sum of the single covalent bond radii for P and S, 2.14 Å; that for S and O, 1.66 Å),[23] whereas the S1−O2 [1.476(1) Å] distance is typical for a S=O bond (sum of the double covalent bond radii for S and O, 1.51 Å).[30] Due to sp^2 hybridization of the O1 and B1 atoms, S1, O1, B1, and N1 are almost coplanar. Moreover, the value of the B1−O1−S1 angle [118.74(8)°] indicates sp^2 hybridization of the O1 atom.

Notably, the insertion of SO_2 into the P−B bond is irreversible. Solid **3** is stable under vacuum and does not regenerate parent **1**. In contrast to **2**, compound **3** is prone to hydrolysis and must be handled under an inert atmosphere.

According to the Gibbs free energy profile, insertion of the SO_2 molecule into the P−B bond proceeds via a two-step mechanism analogous to the one we have recently elucidated for the reaction of **1** with CO_2[19] (see the Supporting Information for details). In the first step, the phosphorus atom binds with the sulfur atom, resulting in intermediate **1**-SO_2 adduct **I** (Figure S23). The second, rate-determining step proceeds via a transition state with a four-membered PSOB ring. The simultaneous formation of B−O and cleavage of the P−B bond give final product **3**. The formation of **3** is thermodynamically favored, with a free energy value (ΔG°_{298}) of −33.7 kcal/mol, and more energetically favored than the corresponding insertion of a CO_2 molecule (−20.1 kcal/mol).[19] Moreover, as the linear CO_2 molecule has to bend during fixation and is less electrophilic than SO_2, the energy barrier $\Delta G^\ddagger$ of 14.4 kcal/mol for the formation of **3** is significantly lower than $\Delta G^\ddagger$ for the reaction of **1** with CO_2 (27.3 kcal/mol).[19]

Compound **2** can be considered as geminal phosphinoborane in which the phosphanyl and boryl groups are separated by a single oxygen atom. Geminal methylene- or oxygen-bridged phosphinoboranes are preorganized FLPs with intramolecular donor and acceptor sites oriented in the same direction for optimal interaction with the substrate.[24,25,31,32] Intramolecular self-quenching of Lewis acid and base centers is not observed, as the formation of strained three-membered PCB or POB rings is not thermodynamically favored.[24,31] Despite the mild Lewis acidity of the boron center, methylene-bridged geminal FLPs bind and/or activate, e.g., H_2, CO_2, or SO_2,[31,32] while oxygen-bridged ones bind and/or activate, e.g., CO_2 or CS_2.[24,25] The interesting structural features of **2** and recent advances in the chemistry of geminal FLPs encourage us to study the reactivity of **2** toward small inorganic molecules. We performed reactions of **2** with a series of inorganic gases: H_2, CO_2, and SO_2. All of these reactions were carried out under the same mild conditions: toluene as the solvent, room temperature, and 1 atm pressure of the gaseous reagent. We did not detect the formation of any products in the case of reactions involving H_2 and CO_2. In contrast, borylphosphinite **2** reacted rapidly with SO_2 (Scheme 1). $^{31}P\{^1H\}$ NMR spectroscopic analysis of the reaction mixture showed the appearance of a new sharp singlet at 81.0 ppm, which is significantly shifted to a lower frequency compared to that of borylphosphinite **2** (144.7 ppm). Otherwise, the ^{11}B NMR spectra of the reaction solution consist of only one signal at 27.0 ppm with a chemical shift very similar to those observed for **2** (26.7 ppm). Complete conversion of **2** to new product **4** is observed after a few minutes, and no other products are present in the reaction mixture. Cooling the reaction mixture to −80 °C yielded yellow crystals, which were characterized as tBu$_2$P(=O)−S(=O)−O−B(NiPr$_2$)$_2$ (**4**) on the basis of NMR spectroscopy and X-ray structural analyses. The molecular structure of **4** is presented in Figure 3.

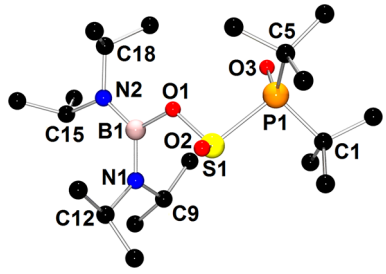

Figure 3. X-ray structure of **4** showing the atom numbering scheme. The H atoms have been omitted for the sake of clarity.

The phosphinyl tBu$_2$P(=O) group is linked to the (iPr$_2$N)B boryl group via the SO_2 moiety. In comparison to **2**, **4** retains planar geometries around the B1, N1, and N2 atoms. The geometry and metric parameters of the P1−S1(O2)−O1−B1 skeleton in **4** resemble those observed for the analogous structural motif in compound **3**. The S1=O2 and P1=O3 bonds are *anti*-oriented to each other, and the O2−S1−P1−O3 torsion angle is −142.01(8)°.

Additionally, we investigated whether compound **4** could transform into a hypothetical tautomer with the formula tBu$_2$P−O−S(=O)−O−B(iPr$_2$N)$_2$ (**4′**). To this end, we modeled and optimized the structure of tautomer **4′** using DFT methods (see Figure S38). By calculating the free energy value, we found that transformation of **4** into **4′** is not

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thermodynamically favored with a ΔG°_{298} of 4.3 kcal/mol (Figure S25), which indicates that tautomer **4** is preferred both in the solid state and in solution.

Interestingly, **2** reacts with SO_2 during the formation of **4** in a reversible manner. Without an SO_2 atmosphere, compound **4** slowly decomposed at room temperature both in the solid state and in solution into starting borylphosphinite **2**. The gentle heating of solid **4** under vacuum up to 35 °C for 2 h leads to complete regeneration of **2** (Figure S19).

To the best of our knowledge, the reaction of **2** with SO_2 is the first example of a reversible activation of the SO_2 molecule by a P-based system. The combinations of strong Lewis basic phosphines with strong Lewis acidic boranes form irreversibly stable zwitterionic adducts with SO_2 due to strong P−S and B−O interactions.[13,15] Recently, the first stable adducts of highly nucleophilic phosphines and SO_2 were isolated, but they decompose at room or elevated temperatures to $R_3P{=}O$, $R_3P{=}S$, and SO.[12] The product of activation of SO_2 by boryl(phosphino)carbene decomposes above −25 °C to uncharacterized compounds.[16] The reaction of **2** with SO_2 can be formally seen as the insertion of SO_2 into the P−B bond of the hypothetical tautomer of $t\mathrm{Bu_2P{-}O{-}B(NiPr_2)_2}$ (**2**) with the formula $t\mathrm{Bu_2P(=O){-}B(NiPr_2)_2}$. If we replace the boryl group with H, it resembles a well-known tautomerism of phosphinous acid [$R_2P{-}O{-}H$ vs $R_2P(=O){-}H$].[33,34] In this context, the reaction of **2** cannot be treated as analogous to the oxidation of phosphine by SO_2.

On the grounds of DFT calculations, we proposed a reaction mechanism that supports this statement (Figure 4). Despite

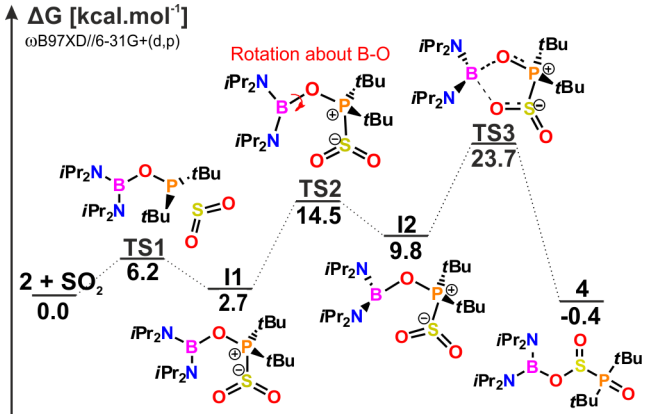

Figure 4. Gibbs free energy profile of the reaction of **2** with SO_2.

the neutral character of phosphorus (f_N = 0.008 for **2** in comparison to a value of 0.277 for **1**), the reaction starts with an electrophilic attack by the SO_2 molecule on the P lone pair, giving intermediate **I1**. Via rotation about the B−O bond, the **2**-SO_2 adduct adopts a conformation that enables the interaction of boron and the **O**SO oxygen atom (**I2**). It leads to simultaneous formation of **B**−**O**SO and cleavage of the **B**−**O**P bond with migration of the linking B−**O**−P oxygen atom to phosphorus via five-membered OBOPS transition state **TS3**. The resulting product **4** is formed reversibly, and in the absence of an SO_2 atmosphere, an equilibrium is established between parent **2** and **4**, which is justified by the calculated value of free energy ΔG°_{298} of −0.4 kcal/mol.

3. CONCLUSIONS

Despite the low Lewis acidity of the boron center in the diaminophosphinoboranes, these compounds were successfully applied in the activation of small inorganic molecules. The phosphinoborane **1** containing direct P−B bond reacts with N_2O, leading to insertion of an oxygen atom into the P−B bond and formation of geminal P−O−B phosphinoborane **2**. Moreover, we compared the reactivity of phosphinoboranes (P−B) and geminal phosphinoboranes (P−O−B) toward SO_2. Our studies revealed that both systems capture and activate the SO_2 molecule in irreversible and reversible manners, respectively. The presented reactions constitute new synthetic methods for insertion of a single oxygen atom into the P−B bond and an unprecedented example of reversible activation of SO_2 by a P-based compound. As a continuation of this work, we are currently studying reactions of diphosphinoboranes possessing two P−B bonds with small molecules and these results will be published in due course.

4. EXPERIMENTAL SECTION

General Information. All manipulations were carried out under a dry argon atmosphere by using flame-dried Schlenk-type glassware on a vacuum line or in a glovebox. Solvents were dried by standard procedures over Na(K)/K/Na/benzophenone and distilled under argon. One-dimensional (^{31}P, ^{13}C, ^{11}B, and ^{1}H) and two-dimensional NMR spectra in a C_6D_6 or toluene-d_8 solution were recorded on a Bruker AV400 MHz spectrometer (external standard TMS for ^{1}H and ^{13}C; 85% H_3PO_4 for ^{31}P) at ambient temperature. Reaction progress was monitored by $^{31}P\{^{1}H\}$ and ^{11}B NMR spectra of reaction mixtures. The FTIR spectra of crystalline products were recorded using a Nicolet iS50 FT-IR spectrometer equipped with the Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory, and spectral analysis was carried out by using the OMNIC software package. Elemental analyses were performed at the University of Gdańsk using a Vario El Cube CHNS apparatus. Crystallographic analyses were performed on a STOE IPDS II diffractometer using Mo Kα radiation (λ = 0.71073 Å). Phosphinoborane **1** was synthesized via the procedure described in ref 19.

Preparation of 2. A solution of **1** (178 mg, 0.5 mmol) in toluene (3 mL) was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr, and backfilled with N_2O (1 atm). The solution was allowed to warm to room temperature and stirred for 24 h. $^{31}P\{^{1}H\}$ NMR of the colorless reaction mixture revealed a complete conversion of **1** into **2**. The solvent was evaporated, and the residue was dried under vacuum (0.01 Torr) giving **2** as a white, crystalline solid: yield 94% (175 mg, 0.470 mmol). The solid was dissolved in 1 cm^3 of petroleum ether and left at −80 °C to afford colorless, X-ray-quality crystals of **2** that were dried in vacuum: yield 65% (120 mg, 0.322 mmol); $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ 144.7 (s); ^{11}B NMR (C_6D_6) δ 26.7 (s); ^{1}H NMR (C_6D_6) δ 3.68 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2H, C*H*), 3.68 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2H, C*H*), 1.27 (d, $^{3}J_{HH}$ = 6.8 Hz, 24H, CHCH_3), 1.23 (d, $^{3}J_{PH}$ = 10.8 Hz, 18H, CCH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6) δ 46.5 (s, *C*HCH$_3$), 46.5 (s, *C*HCH$_3$), 35.0 [d, $^{1}J_{PC}$ = 31.8 Hz, *C*(CH$_3$)$_3$], 28.3 [d, $^{2}J_{PC}$ = 16.3 Hz, C(*C*H$_3$)$_3$], 24.3 (s, CHCH_3); IR (solid) ν 2960, 2863, 1469, 1431, 1363, 1295, 1238, 1189, 1151, 1115, 1020, 1007, 996, 876, 805, 787, 751 cm^{-1}. Elemental analysis. Calcd for $C_{20}H_{46}BN_2OP$: C, 64.51; H, 12.45; N, 7.52. Found: C, 64.24; H, 12.32; N, 7.42

Preparation of 3. A solution of **1** (178 mg, 0.5 mmol) in toluene (3 mL) was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr, and backfilled with SO_2 (1 atm). The solution was allowed to warm to room temperature and stirred for 5 min. $^{31}P\{^{1}H\}$ NMR of the yellow reaction mixture revealed a complete conversion of **1** to **3**. The solvent was evaporated, and the residue was dried under vacuum (0.01 Torr), giving **3** as a yellowish solid: yield 98% (205 mg, 0.488 mmol). The solid was dissolved in 1 cm^3 of petroleum ether and left at −20 °C to afford colorless, and X-ray-quality crystals of **3** were

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dried in vacuum. Yield of 75% (157 mg, 0.373 mmol). The compound **3** is thermally stable both in the toluene solution and in the solid state; it does not decompose upon being heating to 90 °C: $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ 111.4 (s); ^{11}B NMR (C_6D_6) δ 26.4 (s); ^{1}H NMR (C_6D_6) δ 3.42 (sept, $^{3}J_{HH}$ = 6.6 Hz, 4H, C*H*), 1.54 (d, $^{3}J_{PH}$ = 11.6 Hz, 9H, CCH_3), 1.32 (d, $^{3}J_{PH}$ = 10.8 Hz, 9H, CCH_3), 1.22 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CHCH_3), 1.21 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CHCH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6) δ 45.7 (s, *C*HCH$_3$), 37.7 [d, $^{1}J_{PC}$ = 40.9 Hz, *C*(CH$_3$)$_3$], 33.5 [d, $^{1}J_{PC}$ = 30.0 Hz, *C*(CH$_3$)$_3$], 30.3 [d, $^{2}J_{PC}$ = 12.7 Hz, C(*CH*$_3$)$_3$], 29.8 [d, $^{2}J_{PC}$ = 12.7 Hz, C(*CH*$_3$)$_3$], 22.6 (s, CH*CH*$_3$), 22.2 (s, CH*CH*$_3$); IR (solid) ν 2957, 2866, 1471, 1382, 1362, 1309, 1250, 1180, 1152, 1076, 1009, 979, 868, 802, 735 cm^{-1}. Elemental analysis. Calcd for $C_{20}H_{46}BN_2O_2PS$: C, 57.13; H, 11.03; N, 6.66; S, 7.63. Found: C, 56.92; H, 10.90; N, 6.62; S, 7.49.

Preparation of 4. A solution of **2** (198 mg, 0.5 mmol) in toluene (2 mL) was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr, and backfilled with SO_2 (1 atm). The solution was allowed to warm to room temperature and stirred for 5 min. $^{31}P\{^{1}H\}$ NMR of the yellow reaction mixture revealed a complete conversion of **2** to **4**. The X-ray-quality crystals were obtained from the SO_2-saturated toluene solution at −80 °C. Compound **4** is stable only in the presence of SO_2. Removing of the solvent over the yellow crystals as well as the evaporation of the solvent after reaction results in slow decomposition into substrate **2**. Drying of **4** under vacuum in the oil batch at 35 °C for 2 h leads to complete regeneration of the substrate. The formation of **4** is reversible, and in the presence of SO_2, the product is yielded again: $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ 81.0 (s); ^{11}B NMR (C_6D_6) δ 27.0 (s); ^{1}H NMR (C_6D_6) δ 3.39 (sept, $^{3}J_{HH}$ = 6.7 Hz, 4H, C*H*), 1.49 (d, $^{3}J_{PH}$ = 14.8 Hz, 9H, CCH_3), 1.29 (d, $^{3}J_{PH}$ = 13.8 Hz, 9H, CCH_3), 1.23 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CHCH_3), 1.19 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CHCH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6) δ 45.7 (s, *C*HCH$_3$), 41.3 [d, $^{1}J_{PC}$ = 31.8 Hz, *C*(CH$_3$)$_3$], 37.8 [d, $^{1}J_{PC}$ = 37.2 Hz, *C*(CH$_3$)$_3$], 27.4 [s, C(*CH*$_3$)$_3$], 26.4 [s, C(*CH*$_3$)$_3$], 22.2 (s, CH*CH*$_3$), 21.8 (s, CH*CH*$_3$); IR (solid) ν 2967, 2930, 2872, 1468, 1398, 1382, 1362, 1311, 1249, 1169, 1096, 1073, 1011, 974, 867, 804, 752 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00435.

Crystallographic details, spectroscopic details, and computational details (PDF)

Accession Codes

CCDC 1959420−1959422 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Rafał Grubba − *Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland;* orcid.org/0000-0001-6965-2304; Email: rafal.grubba@pg.edu.pl

Authors

Natalia Szynkiewicz − *Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland*

Jarosław Chojnacki − *Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c00435

Notes

The authors declare no competing financial interest.

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