Singlet Dioxygen Fixation

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Reaction of Singlet Dioxygen with Phosphine–Borane Derivatives: From Transient Phosphine Peroxides to Crystalline Peroxoboronates**

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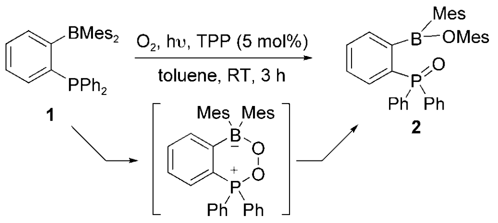
Dedicated to Dr. Bernard Meunier

The last two decades has witnessed a spectacular renaissance in main group chemistry.[1] Of particular interest are ambiphilic compounds that result from the combination of donor and acceptor moieties, typically involving Group 13 and 15 elements.[2] Most strikingly, the groups of D. W. Stephan and G. Erker have shown that phosphine–boranes R_2P-spacer-$B(C_6F_5)_2$ (R = *t*Bu or Mes (2,4,6-$Me_3C_6H_2$); spacer = *p*-C_6H_4 or CH_2CH_2) reversibly activate dihydrogen under mild conditions, opening new avenues in metal-free catalytic hydrogenation.[3] Recently, reversible binding of carbon dioxide has also been reported.[4] Moreover, our group has evidenced versatile coordination properties for mono- and polyphosphine–boranes featuring *o*-C_6H_4 linkers, which provide a better understanding of unusual interactions between transition metals and Lewis acids.[5] The borane moiety *ortho* to phosphorus was also exploited to stabilize highly reactive adducts of phosphines. Accordingly, the reaction of R_2P-(*o*-C_6H_4)$BMes_2$ with phenyl azide was shown to give a phosphazide that is dramatically stabilized by intramolecular a N→B interaction that undergoes an unusual photoisomerization process.[6] Furthermore, treatment of the *o*-phenylene phosphine–borane system with diethyl azodicarboxylate and phenyl isocyanate afforded stable versions of the zwitterionic intermediates involved in the Mitsunobu reaction and cyclooligomerization of isocyanates, respectively.[7]

Our continued interest in phosphine–borane compounds prompted us to investigate their behavior toward singlet dioxygen.[8,9] Very little is known about peroxidic adducts between phosphines and $^1O_2$. Indeed, the phosphadioxirane deriving from the tris(*o*-methoxyphenyl)phosphine is the only such adduct that has been characterized to date, thanks to low-temperature NMR techniques.[10] Herein we report that the presence of a Lewis acid in close proximity to the phosphorus center dramatically influences the fate of the reaction.[11] In particular, phosphine–boronates are shown to readily split $^1O_2$. The initially formed phosphine peroxides are stabilized by intramolecular O→B interactions, but spontaneously rearrange by B→O migration to give stable peroxoboronates.

We began to investigate the behavior of phosphine–borane compounds towards dioxygen with the previously described phosphine–borane **1**.[12] No sign of oxidation was observed after several hours when a toluene solution of **1** was subjected to air bubbling at room temperature.[13] In marked contrast, compound **1** rapidly reacted with $^1O_2$ (generated by irradiation of $^3O_2$ in the presence of tetraphenylporphyrin as photosensitizer) to afford a new compound **2** (Scheme 1). The mass spectrum (the ion $(M+Na)^+$ was found at *m*/*z* 565) indicated the incorporation of two oxygen atoms, and ^1H NMR spectroscopy revealed the desymmetrization of the two mesityl substituents at boron. Single crystals were obtained in Et_2O at −20 °C, and the molecular structure of **2** was unambiguously established by an X-ray diffraction study (Figure 1, left). Accordingly, the phosphine–borane compound **1** has split the $^1O_2$ molecule. One oxygen atom sits at phosphorus (leading to a phosphine oxide moiety), and the other has been inserted into one of the B–Mes bonds. The boron atom is in a trigonal planar environment, which



Scheme 1. Fixation of $^1O_2$ by the phosphine–borane **1**. TPP = tetraphenylporphyrin.

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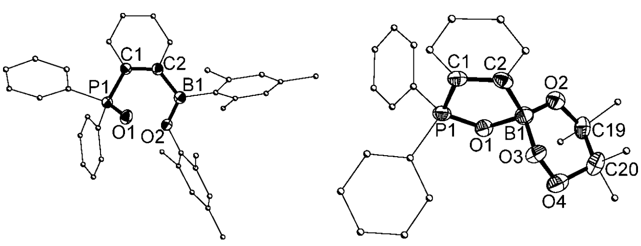
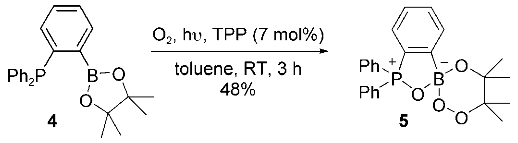


Figure 1. Molecular views of **2** (left) and **5** (right) in the solid state (ellipsoids set at 50% probability). Phenyl, mesityl, and methyl groups are simplified and the hydrogen atoms are omitted for clarity. For **5**, only one of the two independent molecules present in the asymmetric unit is shown. Selected bond lengths [Å] and angles [°]: **2**: P1–O1 1.484(1), B1–O2 1.359(2). **5**: P1–O1 1.534(3), B1–O1 1.647(6), B1–O2 1.408(6), B1–O3 1.454(6), O3–O4 1.473(4); P1-O1-B1 112.4(3), O2-B1-O3 115.1(4).

corresponds with the ^{11}B NMR signal observed at $\delta =$ 34.7 ppm.

From a mechanistic viewpoint, it is most likely that $^1O_2$ is first trapped by the ambiphilic phosphine–borane **1**, and the ensuing phosphine peroxide **3** then rearranges by migration of a mesityl group from boron to oxygen.[14] No intermediate could be detected by ^{31}P NMR monitoring at −80 °C, suggesting that the rearrangement **3**→**2** proceeds spontaneously. Furthermore, the reaction is totally regioselective, with the oxygen atom being inserted into one of the B−Mes bond but not into the $B-C_6H_4PPh_2$ bond.

To study the influence of the substituents at boron, the two mesityl groups were replaced by a pinacol unit. The phosphine–boronate **4**[15] was also found to react spontaneously with $^1O_2$ (but not with $^3O_2$), leading to a single compound **5** (Scheme 2). The mass spectrum indicated the incorporation of two oxygen atoms and the low field shift of the ^{31}P NMR signal (from $\delta = -4.1$ ppm for **4** to $\delta = +46.0$ ppm for **5**) substantiated the oxidation of the phosphorus atom. Furthermore, the presence of two sets of ^{1}H and ^{13}C NMR signals for the CMe_2 groups revealed the desymmetrization of the pinacol moiety, and the ^{11}B NMR resonance signal observed at $\delta = +15.9$ ppm (compared to +31.1 ppm for **4**) suggested a tetracoordinate environment around boron. Compound **5** was isolated as a white moisture-sensitive solid by recrystallisation from diethyl ether at −20 °C, and its molecular structure was definitely confirmed by X-ray crystallography (Figure 1, right). The phosphine–boronate **4** has thus split the dioxygen molecule in a similar fashion to that observed with **1**. In this case, one oxygen atom bridges the phosphorus and boron atoms, whilst the other oxygen atom has been inserted into the B(pin) ring, leading to a B-O-O skeleton. When the reaction of **4** with $^1O_2$ was performed with a circa 1:1 mixture of $(^{16}O)_2$ and $(^{18}O)_2$, the three isotopomers $(^{16}O)_2$, $(^{16}O^{18}O)$, and $(^{18}O)_2$ of **5** were observed by mass spectrometry.[15] The scrambling of the labeled oxygen atoms suggests a bimolecular process for the rearrangement of the initially formed **4**:$^1O_2$ adduct into **5**.



Scheme 2. Fixation of $^1O_2$ by the phosphine–boronate **4**.

Organylperoxides of Group 13 elements (>E-O-O-R, with E = B, Al, Ga, or In) have attracted a surge of interest in the last two decades as key intermediates in autoxidation processes and as potential oxygen transfer reagents. However, these compounds are usually extremely reactive and rather unstable,[16] which often prevents their isolation and complete characterization. The first alkylperoxides of a Group 13 element to be structurally authenticated were the dimeric $[\{(tBu)_2E(\mu\text{-}OOtBu)\}_2]$ (E = Ga, In)[17] and dinuclear $[(tBuOO)(tBuO)Al(\mu\text{-}OtBu)_2Al(mesal)_2]$ (mesal = methyl salicylate) derivatives.[18] Recently, Uhl et al. took advantage of the peculiar electronic properties of the $CH(SiMe_3)_2$ group to prepare and crystallographically characterize a monomeric aluminum peroxide and several original di- and trinuclear gallium peroxides,[19] all featuring oxidizing peroxo moieties (E-O-O) and also reducing E−C bonds. Not much is known either about the related organylperoxides of boron. To date, only one such compound has been characterized by X-ray diffraction: in 2009, Piers et al. described an endoperoxide adduct of a NHC-stabilized 9-boraanthracene.[20]

Compound **5** thus provides a rare example of a structurally authenticated B-O-O skeleton, and the first included in a peroxoboronate moiety.[21–24] The O1−P1 bond distance of **5** (1.534(3) Å) is significantly longer than that of **2** (1.484(1) Å), in agreement with the additional interaction of O1 toward B (O1−B1: 1.647(6) Å). The ensuing five-membered ring is almost planar, and the six-membered ring linked in a spiro fashion at boron adopts a chair conformation. The B−O bond is slightly shorter for the boron–alkoxide than for the boron–peroxide linkage (B1−O2: 1.408(6) Å versus B1−O3: 1.454(6) Å). The O3−O4 distance (1.473(4) Å) falls in the typical range for alkylperoxides of Group 13 elements,[17–19] and the torsion angle across the O3−O4 bond (60.8°) is similar to those observed by Uhl et al. in gallium endoperoxides[19b–d] (values of more than 90° are encountered in acyclic peroxides).

At this stage, it should be noted that the peroxo skeleton of >E-O-O-R compounds usually comes from a dioxygen molecule (insertion into E−C bonds) or a hydroperoxide (condensation reaction), whereas for **5**, the B-O-O fragment is obtained by insertion of one oxygen atom into a B−O bond.

To gain more insight into the structure and relative stability of the various phosphine–borane: $^1O_2$ adducts, DFT calculations were performed at the B3PW91/SDD(P,B),6-31G**(other atoms) level of theory on the model compound **I** featuring an ethylene glycol unit at boron.[15] The optimized structures of the dioxygen adducts **II**–**IV** are shown in Figure 2. In the cyclic adduct **II**, the O1−O2 distance is 1.54 Å and the boron atom does not interact with the phosphadioxirane moiety (the BO1 and BO2 distances exceed 2.7 Å). The formation of **II** from **I** + $^1O_2$ is strongly favored thermodynamically ($\Delta G_{\mathbf{I}\rightarrow\mathbf{II}} = -32.8$ kcal mol^{-1}). In marked contrast with that predicted computationally for simple phosphines,[25] the corresponding phosphine peroxide

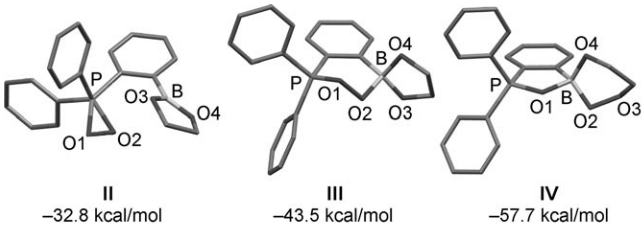
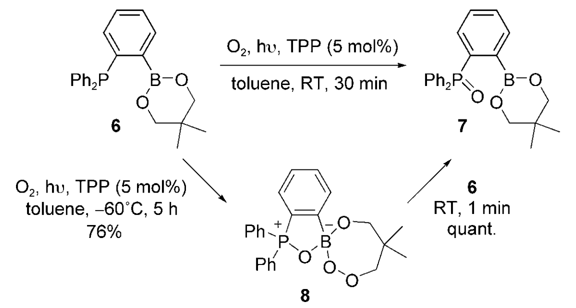


Figure 2. Optimized geometries and relative energies of the $^1O_2$ adducts deriving from the model phosphine–boronate **I** (free energies G at 25 °C relative to $\mathbf{I}+{}^1O_2$).

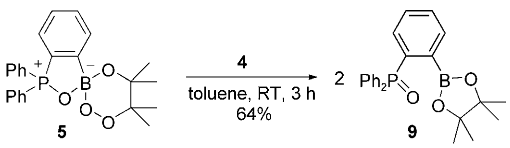
derivative **III** was also found to be a minimum on the potential energy surface, located 10.7 kcal mol^{-1} lower in energy.[26] Compound **III** is stabilized by a strong intramolecular O→B interaction (B–O2 distance: 1.554 Å). Overall, the phosphine–borane skeleton bridges the two oxygen atoms (O1–O2 1.50 Å), leading to a puckered six-membered ring. Finally, the peroxoboronate form **IV** (related to **5**) is a further 14.2 kcal mol^{-1} lower in energy compared to **III**, and its optimized geometry reproduced well the structure determined crystallographically (O2–O3 1.46 Å).

To substantiate the generality of the reaction observed between **4** and $^1O_2$, we then investigated the behavior of the related phosphine–borane compound **6**[15] featuring a six-membered-ring boronate. In this case, reaction of **6** with $^1O_2$ under the same conditions afforded the phosphine oxide–boronate **7** (Scheme 3), as deduced from mass spectrometry (incorporation of a single oxygen atom) and NMR spectroscopy (δ ^{31}P = +32.2 ppm and δ ^{11}B = +27.4 ppm). Taking into account the fact that **6** is reluctant toward oxidization by $^3O_2$, we speculated that the phosphine oxide **7** was formed by a side reaction between unreacted **6** and a $^1O_2$ adduct thereof. To prevent this comproportionation process, the reaction between **6** and $^1O_2$ was carried out at −60 °C. Gratifyingly, ^{31}P NMR spectroscopy revealed the exclusive formation of a new product **8** (δ = +52.9 ppm) that was isolated in 76% yield by precipitation from a dichloromethane/pentane mixture at −20 °C. All the spectroscopic data for **8** support a peroxoboronate structure analogous to **5**, which was unambiguously confirmed by crystallography.[15] The O–O distance of **8** (1.433(3) Å) is slightly shorter than that of **5**, whilst the torsion angle around the O–O bond widens to 98.7° as the result of the inclusion of the B-O-O-C skeleton in a seven-membered ring. Oxygen transfer between the peroxoboronate **8** and the starting material **6** readily occurs at room temperature, as substantiated by the instantaneous and quantitative formation of the phosphine oxide **7** upon mixing both reagents in a 1:1 ratio. This result confirms that **7** is formed from **6** and $^1O_2$ at room temperature.



Scheme 3. Fixation of $^1O_2$ by the phosphine–boronate **6**.

A similar oxygen transfer was also observed between the phosphine–boronate **4** and the ensuing peroxoboronate **5** (Scheme 4). This comproportionation reaction required 3 h at room temperature, and cleanly afforded the phosphine oxide **9**. Compound **9** was isolated in 64% yield after recrystallization in Et_2O/pentane and fully characterized by NMR and X-ray diffraction.[15] Finally, the ability of the peroxoboronates **5** and **8** to oxidize simple phosphines was examined using PPh_3 as a model substrate. According to ^{31}P NMR, the reaction proceeds cleanly in both cases, leading to Ph_3PO (δ = +25.0 ppm) together with the phosphine oxide **9** or **7**. In line with observations for the comproportionation reactions, the reaction proceeds faster with **8** than with **5**, complete conversion being achieved within 2 h at room temperature with **8** but requiring heating overnight at 100 °C with **5**.



Scheme 4. Oxygen transfer reaction from **5** to **4**.

In summary, *ortho*-phenylene phosphine–borane systems have been shown to readily react with singlet dioxygen. Starting from phosphine–boronates **4** and **6**, two stable peroxoboronates **5** and **8** have been isolated and fully characterized. The ability of these compounds to undergo oxygen transfer reactions has been substantiated. The potential application of such peroxoboronates as oxidizing agents and the extension of the present work to other phosphine–borane systems is currently under study in our group.

Experimental Section

All reactions and manipulations were carried out using standard Schlenk techniques. The NMR spectra were recorded at 25 °C.

General procedure for the reactions of the phosphine–borane compounds with $^1O_2$: A toluene solution of the phosphine–borane compound (concentrations ranging from 0.02 M to 0.09 M) containing 5–7 mol% of tetraphenylporphyrin was irradiated with a halogen lamp under a dried atmosphere of dioxygen until ^{31}P NMR spectroscopy indicated complete conversion. Toluene was removed under vacuum, and the residue was purified by crystallization in diethyl ether (for **2** and **5**) or precipitation in dichloromethane/pentane (for **8**).

2: ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6): δ = 37.8 ppm; ^{11}B NMR (160.5 MHz, $CDCl_3$): δ = 34.7. HRMS (ESI$^+$) calcd for $[M{+}Na]^+$ ($C_{36}H_{37}BO_2P^+$): 565.2444, found: 565.2443. **5**: ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 46.0 ppm; ^{11}B NMR (160.5 MHz, $CDCl_3$): δ = 15.9 ppm. HRMS (ESI$^+$) calcd for $[M{+}H]^+$ ($C_{24}H_{27}BO_4P^+$): 421.1740, found: 421.1757. **8:** ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6): δ = 52.9 ppm; ^{11}B NMR (160.5 MHz, C_6D_6): δ = 12.9 ppm. HRMS (CI$^+$) calcd for $[M{+}H]^+$ ($C_{23}H_{25}BO_4P^+$): 407.1584, found: 407.1578.

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[25] a) K. Nahm, Y. Li, J. D. Evanseck, K. N. Houk, C. S. Foote, *J. Am. Chem. Soc.* **1993**, *115*, 4879 – 4884; b) S. Tsuji, M. Kondo, K. Ishiguro, Y. Sawaki, *J. Org. Chem.* **1993**, *58*, 5055 – 5059.

[26] The phosphadioxirane **II** was predicted to rearrange into the phosphine peroxide **III** with a barrier height of only 5.1 kcal mol^{-1}.

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