COMMUNICATION

Isolation and Characterization of Radical Anions Derived from a Boryl-Substituted Diphosphene

Shun-suke Asami,[a] Shintaro Ishida,[b] Takeaki Iwamoto,[b] Katsunori Suzuki,[a] and Makoto Yamashita*[c][d]

This paper is dedicated to Professor Takayuki Kawashima on the occasion of his 70th birthday.

Abstract: Radical anions of a diphosphene with two boryl substituents were isolated and characterized by single-crystal X-ray diffraction analysis, electron spin resonance (ESR) and UV-vis absorption spectroscopy, as well as DFT calculations. The structural analysis of the radical anions revealed an elongation of the P=P bond and a contraction of the B-P bonds relative to the neutral diphosphene. The UV-vis spectra of these radical anions showed a strong absorption in the visible region, which was assigned to SOMO-related transitions on the basis of DFT calculations. The ESR spectra revealed that the hyperfine coupling constant with the phosphorus nuclei is the smallest so far reported. The results of the DFT calculations furthermore suggest that this should be attributed to a soaking of spin density to vacant p-orbitals of the boryl substituents.

*T*he high reactivity of molecular phosphorus-centered radicals has attracted much attention in organic chemistry, biology, and functional materials.[1] In the gas phase, such radicals can be observed as monomeric species using electron-diffraction analysis, while they exist in solution as diphosphanes with P-P bonds.[2] In the presence of suitable N-based substituents, such diphosphanes can reversibly liberate monomeric radicals upon elevating the temperature.[3] The introduction of bulky substituents or the induction of a delocalization of the spin density over a π-conjugated system has enabled the isolation of phosphorus-centered radical species and their structural characterization in the solid state.[4] This strategy has also been successful for the isolation of multiphosphorus-centered radical species that involve two to four phosphorus atoms (Figure 1).[5] Among these, cationic radical species, obtained from the oxidation of carbene-coordinated diphosphorus compounds or Trip-substituted

diphosphanes, exhibit P-P multiple bond character as a result of the delocalization of spin density.[5c,5d]

Diphosphenes, i.e., species with P=P double bonds, should accept one electron to form radical anion species, because the π*-orbital of the diphosphenes is energetically lower than that of diazo (N=N) compounds, which is due to the smaller overlap of the 3 p orbitals on the P atoms compared to the 2 p orbitals on the N atoms.[6] Indeed, some diphosphenes can be reduced chemically or electrochemically to afford the corresponding anion radicals (Scheme 1).[7] Such radical anions can also be generated by one-electron oxidation of dianionic diphosphanes or by fragmentation of dianionic tetraphosphanes.[8] Although these diphosphene radical anions could be detected by ESR spectroscopy [hyperfine coupling constants: $a(^{31}P)$ = 41-55 G], examples of stable diphosphene radical anions that have been structurally characterized by X-ray diffraction analysis still remain elusive.
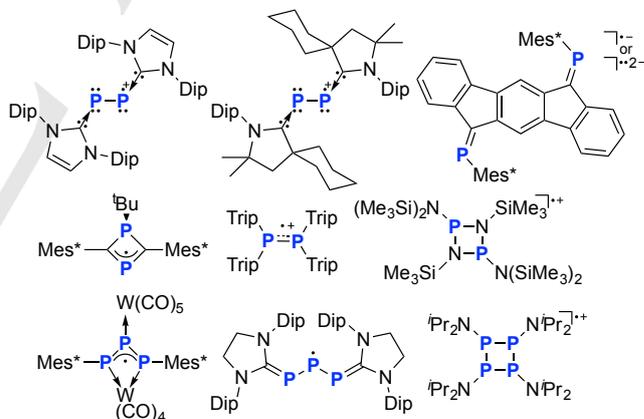
Figure 1. Structurally characterized multiphosphorus-centered radical species [Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$, Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$, Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$]

R = Mes*, (Me$_3$Si)$_3$C, 2,6-Mes$_2$C$_6$H$_3$, Tbt, Bbt, ^{t}Bu, Ph, Cy
Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$, Tbt = 2,4,6-[(Me$_3$Si)$_2$CH]$_3$C$_6$H$_2$
Bbt = 2,6-[(Me$_3$Si)$_2$CH]$_2$-4-[(Me$_3$Si)$_3$C]C$_6$H$_2$
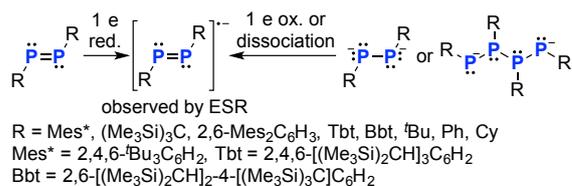
Scheme 1. Methods to generate persistent diphosphene radical anions.

Meanwhile, boryl substituents exhibit extraordinary π-acceptor properties due to the vacant p-orbital on B that is able to

[a]   Mr. S.-s. Asami, Dr. K. Suzuki
        Department of Applied Chemistry, Faculty of Science and
        Engineering, Chuo University
        1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan
[b]   Prof. Dr. S. Ishida, Prof. Dr. T. Iwamoto
        Department of Chemistry, Graduate School of Science, Tohoku
        University, 980-8578 Sendai (Japan)
        Homepage: http://www.ssoc.chem.tohoku.ac.jp/en_index.html
[c]   Prof. Dr. M. Yamashita
        Department of Applied Chemistry, Graduate School of Engineering,
        Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603,
        Japan
        E-mail: makoto@oec.apchem.nagoya-u.ac.jp
        Homepage: http://oec.apchem.nagoya-u.ac.jp/index-e.html
[d]   Prof. Dr. M. Yamashita
        Research Development Initiative, Chuo University
        1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

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        the document.((Please delete this text if not appropriate))

accept electrons of adjacent heteroatoms with a lone pair. In borylphosphanes, the bond length of the B-P bond is generally shorter than those of phosphine-boranes on account of pπ-pπ interactions.[9] In addition, stabilization of anionic species by delocalization of electron density to a vacant p orbital on B has also been reported. Using boryl anions for a nucleophilic borylation,[10] we recently reported the first example of a boryl-substituted diphosphene,[11] which revealed that the σ-donor and π-acceptor properties of the boryl group were able to stabilize an anionic ^{n}BuLi adduct of diphosphene. In this paper, we present the synthesis and isolation of radical anions derived from diboryldiphosphene, which were characterized experimentally by single-crystal X-ray diffraction analysis, ESR and UV-vis spectroscopy, as well as theoretically by DFT calculations. The latter showed in combination with the ESR results that spin density is delocalized over the B and P atoms on account of the π-accepting effect of the boryl groups.

As described in our previous report, the cyclic voltammogram of boryl-substituted diphosphene **1** exhibited a reversible reduction wave at $E_{1/2}$ = −2.24 eV.[11] The chemical one-electron reduction of **1** with KC$_8$ in the presence/absence of [2.2.2]-cryptand in THF at −35 °C generated purple crystalline solids of radical anions [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ and [**1**$^{\cdot}$]$^-$[K(cryptand)]$^+$ in 60% and 69% yield, respectively (Scheme 2), and these products were structurally characterized by single-crystal X-ray diffraction analysis (Figure 2). In the crystal, one of the two P atoms in [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ is coordinated to a potassium cation to form a contact ion pair with η^3- and η^6-interaction from the two Dip rings. In contrast, [**1**$^{\cdot}$]$^-$[K(cryptand)]$^+$ exists as a separated ion pair. The P-P bond lengths in [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ [2.1112(9) Å] and [**1**$^{\cdot}$]$^-$[K(cryptand)]$^+$ [2.1453(19) Å] are longer than that in neutral diphosphene **1** [2.0655(17) Å][11] and those in the previously reported carbon-substituted diphosphenes [1.985(3)[12] – 2.051(2)[13] Å], but still shorter than conventional P-P single bonds (~ 2.2 Å).[14] In addition, the B-P bond distances in [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ (av. 1.904 Å) and [**1**$^{\cdot}$]$^-$[K(cryptand)]$^+$ (av. 1.922 Å) contract upon the one-electron reduction of **1** [B-P: 1.936(3) Å]. The two B-containing planes in [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ adopt an almost coplanar orientation with respect to the planar [B-P=P-B] moiety, while one of the two B-containing planes is twisted relative to the P=P double bond. The structural features of these radical anions stand thus in stark contrast to the structure of **1**, in which both the two boron-containing planes adopt a perpendicular orientation relative to the central P=P double bond. The thus obtained structural data indicate that these radical anions exhibit a multiple-bond character for the P-P and P-B bonds, probably due to a delocalization of unpaired electrons and anionic charges over the [B-P-P-B] moiety.
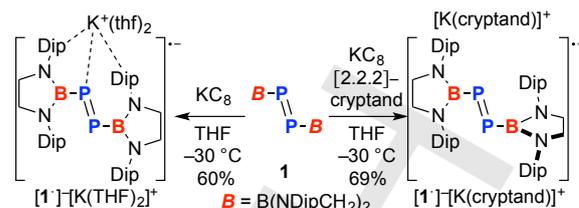
Scheme 2. Synthesis of the radical anions [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ and [**1**$^{\cdot}$]$^-$[K(cryptand)]$^+$.
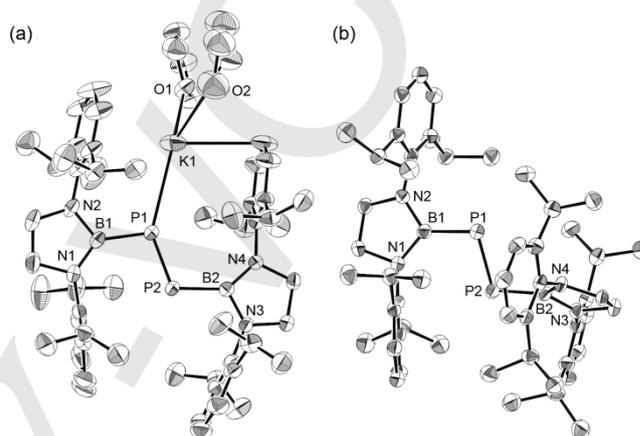
Figure 2. Crystal structures of [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ and [**1**$^{\cdot}$]$^-$[K(cryptand)]$^+$ (thermal ellipsoids set at 50 % probability; hydrogen atoms, minor parts of disordered THF molecules, and [K(cryptand)]$^+$ cation omitted for clarity, for details, see Supporting Information).

The ESR and UV-vis absorption spectra clearly confirmed the presence of unpaired electrons in [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ and [**1**$^{\cdot}$]$^-$[K(cryptand)]$^+$. Both compounds exhibited identical ESR spectra at room temperature, which show that [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ exists mainly as a separated ion pair in THF (for details, see Supporting Information). Leaving the solutions of two compounds for hours did not alter the spectra, indicating both species are stable at room temperature. In the ESR spectrum of [**1**$^{\cdot}$]$^-$[K(cryptand)]$^+$ (Figure 3), a triplet signal was observed at g = 2.013, which arises from the two magnetically equivalent P nuclei. This result is comparable to those of previously reported diphosphene-derived radical anions (g = 2.007 – 2.018).[7] The magnitude of hyperfine coupling with the two phosphorus nuclei [$a(^{31}P)$ = 37.3 G] is significantly smaller in [**1**$^{\cdot}$]$^-$[K(cryptand)]$^+$ than in all other previously reported persistent diphosphene radical anions (41-55 G).[7] Including the contribution of the B nuclei [$a(^{10}B)$ = 0.7 G; $a(^{11}B)$ = 2.0 G] into a simulation allowed a close reproduction of the observed spectrum. These results indicate that, in contrast to the case of carbon-substituted diphosphenes, the spin density on the P atoms soaks into the vacant p-orbitals of the B atoms. The UV-vis absorption spectra of these radical anions in THF showed characteristic absorption maxima at 513 nm (Figure 4), which are slightly blue-shifted compared to those of previously reported diphosphene radical anions.[7f,7g] The identical absorption maxima and ESR spectra of these two species supported the notion that [**1**$^{\cdot}$]$^-$[K(THF)$_2$]$^+$ exists as a separated ion pair in THF. In the longer wavelength region, shoulders of relatively low intensity were

observed at ~670 nm (δ 80-140), which are red-shifted in comparison to that of a Tbt-substituted diphosphene radical anion.[7g] This shift should be attributed to the energetic lowering of the SOMO on account of the π-accepting substituent effect of the boryl groups. As a result, the absorption edge extends up to 750 nm. Based on time-dependent DFT (TD-DFT) calculations on [**1**·]$^-$, these absorptions were assigned to SOMO-related transitions, including a symmetry forbidden *n*-SOMO transition with a small oscillator strength (*f* = 0.0001) at 726 nm (for details of the DFT calculations, *vide infra*).
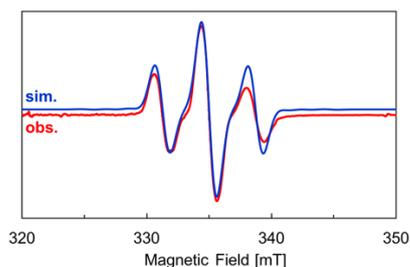
Figure 3. ESR spectrum of [**1**·]$^-$[K(cryptand)]$^+$ in THF at 298 K (red) and simulated ESR spectrum (blue) using the following parameters: *g* = 2.0125, $a(^{31}P)$ = 37.3 G, $a(^{10}B)$ = 0.7 G, and $a(^{11}B)$ = 2.0 G. The simulation was performed on four isotopomers (^{11}B-^{11}B):(^{11}B-^{10}B):(^{10}B-^{11}B):(^{10}B-^{10}B) in a 64:16:16:4 ratio (calculated from the natural abundance of boron nuclei; ^{11}B/^{10}B=80:20). The difference between observed and simulated spectra at ~337 mT is due to a slow tumbling motion on the ESR timescale.
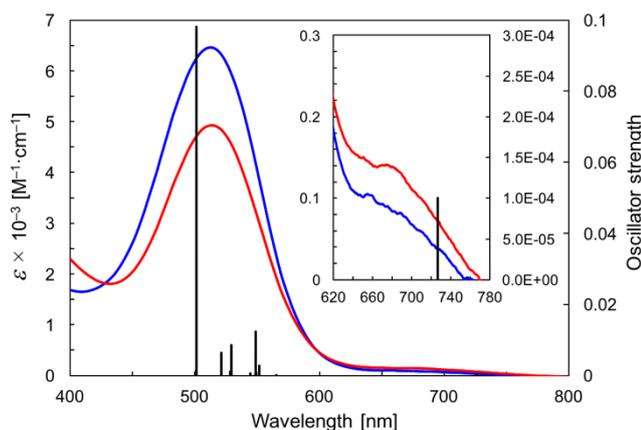
Figure 4. UV-vis spectra of [**1**·]$^-$[K(THF)$_2$]$^+$ (red) and [**1**·]$^-$[K(cryptand)]$^+$ (blue) in THF (125 μM) at room temperature, together with transitions of [**1**·]$^-$ (black) calculated at the UB3LYP/6-31G(d) level of theory; inset: expanded spectra and oscillator strength for the 620-780 nm region.

DFT calculations on the free radical anion [**1**·]$^-$ revealed characteristic molecular orbitals that describe pπ-pπ interactions between the B and P atoms (Figure 5). Using the anionic part of [**1**·]$^-$[K(THF)$_2$]$^+$ in the crystal structure as an initial geometry, the optimized structure of [**1**·]$^-$ revealed two B-containing planes that adopted an almost coplanar orientation relative to the [B-P=P-B] moiety, which stands in contrast to the experimentally obtained structure of [**1**·]$^-$[K(THF)$_2$]$^+$.[15] The SOMO of [**1**·]$^-$ consists of a π^*-

type orbital of the P=P moiety in **1** and two vacant p-orbitals on the B atoms, indicating a delocalization of spin density over the [B-P=P-B] moiety. The HOMO and HOMO-1 correspond to lone pairs on the P atoms and a bonding π-orbital, respectively. These results are consistent with an elongation of the P-P bond and a contraction of the B-P bonds in [**1**·]$^-$[K(THF)$_2$]$^+$ and [**1**·]$^-$ [K(cryptand)]$^+$. The Wiberg bond indexes of [**1**·]$^-$ (P-B: 1.21, 1.21; P-P: 1.26) also support a multiple-bond character, which is consistent with the delocalization of the unpaired electron density over the [B-P=P-B] moiety. The calculated Mulliken spin density distribution (P: 0.415, 0.407; B 0.042, 0.043) agreed well with the hyperfine coupling constants observed in the ESR spectrum. The results of an NBO analysis on [**1**·]$^-$ suggest that donor-acceptor interactions exist between P and B (second-order perturbation energies: 29.63 and 29.58 kcal/mol), and that they are comparable to those between N and B (~26 kcal/mol). Considering these results in their entity, the radical anion [**1**·]$^-$ is characterized by a π-accepting effect of the boryl substituents and should be described ideally by resonance structures **A**-**D** (Scheme 3), which are consistent with an elongated P-P bond, contracted B-P bonds, and a distribution of the unpaired electron that is predominantly centered on the P atoms, but contains also small yet significant contributions from B atoms.
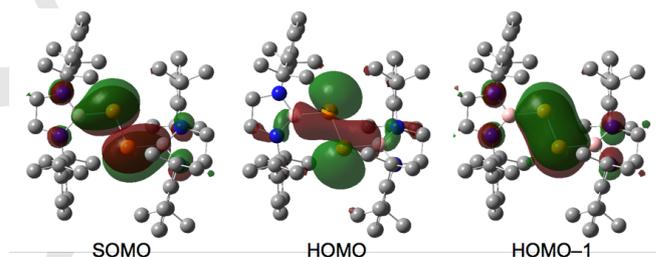
Figure 5. Selected molecular orbitals of free radical anion [**1**·]$^-$ calculated at the UB3LYP/6-31G(d) level of theory (hydrogen atoms omitted for clarity, gray: carbon, blue: nitrogen, orange: phosphorus, pale peach: boron).
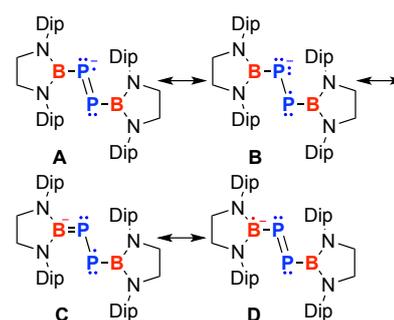
Scheme 3. Resonance structures **A**-**D** for radical anion [**1**·]$^-$ (for each structure an isomer exists that is obtained from a 180° rotation around the C_2 axis bisecting the P-P bond).

In summary, the diphosphene radical anions [**1**·]$^-$[K(THF)$_2$]$^+$ and [**1**·]$^-$[K(cryptand)]$^+$ were isolated and characterized by single-crystal X-ray diffraction analysis, UV-vis and ESR spectroscopy, as well as DFT calculations. The results revealed that the radical

anions are characterized by the π-accepting properties of the boryl substituents, and that the spin density is delocalized over the B-P=P-B moiety.

Acknowledgements

Keywords: boron • substituent effect • radical anion • diphosphene

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[15]   The optimized structure of the contact ion pair [**1**]⁻[K(THF)₂]⁺ is similar to the free anion [**1**]⁻ derived from [**1**]⁻[K(THF)₂]⁺. The optimization of the anionic part of [**1**]⁻[K(cryptand)]⁺ also generated the free anion with a similar structure and a slightly higher energy (0.23 kcal/mol). The discussion herein is therefore based on the free anion that was obtained from the optimization of [**1**]⁻[K(THF)₂]⁺.

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COMMUNICATION

Isolation of diphosphene radical anions stabilized by π-accepting boryl substituents
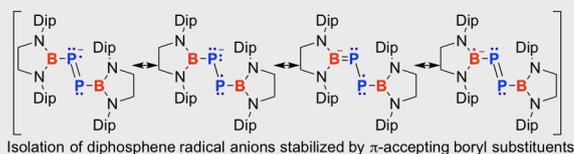
Shun-suke Asami, Shintaro Ishida,
Takeaki Iwamoto, Katsunori Suzuki,
Makoto Yamashita*

Isolation and Characterization of Radical Anions Derived from a Boryl-Substituted Diphosphene

Radical anions of a diphosphene with two boryl substituents were isolated and characterized by X-ray analysis, ESR and UV-vis spectroscopy, as well as DFT calculations. All the structural analysis of the radical anions suggested a soaking of spin density to vacant p-orbitals of the boryl substituents.