Diphosphene Hot Paper

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A Boryl-Substituted Diphosphene: Synthesis, Structure, and Reaction with *n*-Butyllithium To Form a Stabilized Adduct by pπ-pπ Interaction

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Dedicated to Professor Takayuki Kawashima on the occasion of his 70th birthday

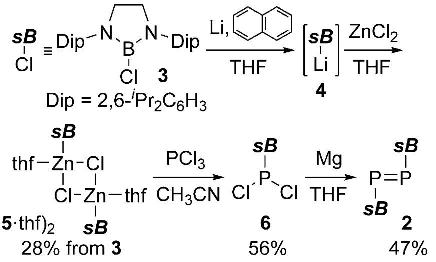
Abstract: *A boryl-substituted diphosphene was synthesized through the nucleophilic borylation of* PCl_3 *with a borylzinc reagent, followed by a reduction with Mg. A combined analysis of the resulting diboryldiphosphene by single-crystal X-ray diffraction, DFT calculations, and UV/Vis spectroscopy revealed a σ-electron-donating effect for the boryl substituent that was slightly weaker than that of the 2,4,6-tri-tert-butylphenyl (Mes*) ligand. The reaction of this diboryldiphosphene with* ^{n}*BuLi afforded a boryl-substituted phosphinophosphide that was, in comparison with the thermally unstable Mes*-substituted diaryldiphosphene, stabilized by a π-electron-accepting effect of the boryl substituent.*

Boryl substituents exhibit characteristic ambivalent substituent effects as σ-electron donors and π-electron acceptors. The synthesis and photophysical properties of boron-containing organic molecules have been thoroughly investigated, especially with respect to the substituent effects of the boryl group.[1] The π-acceptor properties of boryl substituents are due to a vacant p-orbital, which may accept electrons from adjacent atoms. The B−N bond length of aminoboranes, for example, is shorter than that of amine-boranes on account of pπ-pπ interactions.[2] But boryl substituents also exhibit strong σ-donor properties due to the relatively low electronegativity of the second-row element boron (2.04, Pauling), which is reflected in for example, the strong *trans* influence of boryl ligands in transition-metal-boryl complexes.[3]

In contrast to the well-understood substituent effect of the boryl group in organic and coordination chemistry, the effects in main group chemistry remain relatively unexplored, probably due to the limited availability of boryl-substituted main-group-element compounds. After we had reported the boryllithium compound as a boron nucleophile,[4] others and we used this compound to generate novel E−B bonds using the nucleophilic borylation of electrophilic main group reagents.[5] Some of the resulting compounds showed interesting redox chemistry at the main group element, for example, the direct reaction of a borylsilylene with dihydrogen,[5m] or the formation of divalent group 13 radical species.[5o] However, these studies on boryl anion-derived main-group-element compounds did not reveal any information regarding the substituent effect of boryl groups on the redox chemistry.

Since the isolation of Mes*P=PMes* (**1**, Mes* = 2,4,6-tri-*tert*-butylphenyl), diphosphenes, that is, compounds with a P=P double bond, have attracted much attention on account of their narrower HOMO–LUMO gap relative to that of diazo (N=N) species.[6] The photophysical properties of the P=P double bond is strongly influenced by the substituents on the phosphorus atoms. So far, aryl,[6a,b] alkyl,[7] silyl,[8] thio,[9] and amino-substituted[10] diphosphenes have been reported. Although two computational studies on boryl-substituted diphosphenes have been reported,[11] such species have not yet been investigated experimentally.[12] Herein, we report the synthesis, structure, properties, and reactivity of a diboryldiphosphene. A characterization of this diphosphene by UV/Vis spectroscopy, cyclic voltammetry, and DFT calculations revealed that the boryl substituents act as σ-donor substituents. Moreover, this diboryldiphosphene reacts with ^{n}BuLi to furnish an isolable phosphinophosphide, which is stabilized by pπ–pπ interactions between the boron and the phosphorus atoms. This behavior is thus markedly different to that of the Mes*-substituted diarylphosphene **1**.

Diboryldiphosphene **2** was synthesized from chloroborane **3** in four steps (Scheme 1). The transmetallation of the boryllithium compound **4**, which was prepared from **3**, with 1.2 equivalents of $ZnCl_2$ afforded THF-coordinated dimeric borylzinc chloride $(\mathbf{5}\cdot thf)_2$ using a procedure similar to that of previously reported borylzinc species.[13] This direct substitution at the main group element with a nucleophilic borylzinc reagent stands in stark contrast to the reductive dehalogenation of aminodibromobithmuthane(III), which is converted into a diborylbismuthene through a Bi^I intermediate, reported by Jones et al.[5q] The reaction of isolated $(\mathbf{5}\cdot thf)_2$ with PCl_3 in



Scheme 1. Synthesis of diboryldiphosphene **2.**

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acetonitrile resulted in the formation of boryldichlorophosphine **6**. The observed B−P bond length of 1.952(2) Å in **6** is close to the sum of the covalent radii of the B and P atoms (1.98 Å),[14] which suggests the absence of any pπ–pπ interactions. A subsequent reduction of **6** with magnesium in THF furnished diboryldiphosphene **2** in moderate yield. In the ^{31}P NMR spectrum of **2** in C_6D_6, two magnetically equivalent phosphorus nuclei were observed at δ_P 605 ppm, which are comparable, albeit slightly low-field-shifted, to the resonances of carbon-substituted symmetrical *trans*-diphosphenes ($\delta_P \approx 477$–600 ppm).[6a,b,7,15] The electropositive boryl substituents may contribute to the low-field shift of these resonances, considering that the chemical shifts of symmetrical diphosphenes with electropositive silyl substituents (electronegativity of Si: 1.90, Pauling) are further downfield-shifted (δ_P 735, 818 ppm).[16] The ^{11}B NMR spectrum of **2** showed a broad signal at δ_B 30 ppm.

The centrosymmetric molecular structure of **2** was determined by single-crystal X-ray diffraction analysis (Figure 1). The observed P=P bond length of 2.0655(17) Å is slightly longer than those of previously reported carbon-substituted diphosphenes [1.985(3)[17]–2.051(2) Å[18]]. The two boron-containing planes are oriented almost perpendicular to the planar B-P=P-B moiety, exhibiting a dihedral N2-B1-P1-P1* angle of −83.2(2)°. This structure stands in stark contrast to the perpendicular and coplanar conformers that were observed for the recently reported diboryldibismuthene.[5q] The B1–P1 bond length of 1.936(3) Å in **2** is similar to the B−P bond length in **6** [1.952(2) Å], indicating a single-bond character for this bond, due to little overlap between the 2p and 3p orbitals of the boron and phosphorus atoms, respectively. The observed B1-P1-P1* angle of 95.83(9)° is relatively small, but still within the range of the corresponding C-P-P angles of symmetrical carbon-substituted diphosphenes [93.22(5)°[19]-114.9(1)°[18]]. DFT calculations at the B3LYP/6-31G(d) level of theory revealed the following features (for details, see the Supporting Information): a) the HOMO exhibits features of the nonbonding lone pair on the phosphorus atoms, b) the HOMO-7 and the LUMO correspond to the π and π* orbitals of the P=P double bond, and c) the HOMO-1 is predominantly characterized by contributions from the π-type orbital of the diazaborole moieties.

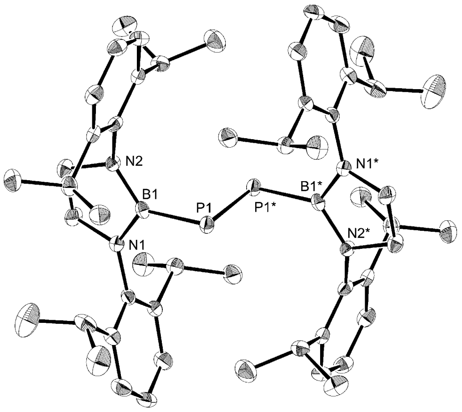
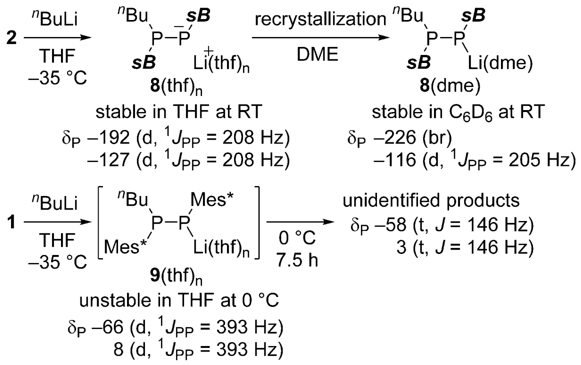


Figure 1. Molecular structure of **2** (thermal ellipsoids set at 50% probability, hydrogen atoms omitted for clarity; asterisks denote atoms generated by symmetry operation), Selected bond lengths [Å] and angles [°]: P1–B1 1.936(3), N1–B1 1.418(4), N2–B1 1.424(4), P1–P1* 2.0655(17); P1*-P1-B1 95.83(9), N1-B1-N2 108.3(2), P1-P1-B1-N1 95.8-(2).

To better understand the electronic effects of the boryl substituents in **2**, the compound was subjected to UV/Vis spectroscopy, cyclic voltammetry, and further DFT calculations. The UV/Vis spectrum of **2** showed two absorption maxima at 310 nm ($\varepsilon = 5700$) and 400 nm ($\varepsilon = 680$; Figure S10), which are slightly blue-shifted relative to the absorptions of Mes*-substituted diarylphosphene **1** (325, 460–532 nm),[6] indicating a larger HOMO–LUMO gap of **1** relative to that of **2**. The cyclic voltammogram of **2** in THF (supporting electrolyte: 0.1 M [^{n}Bu$_4$N][BF$_4$]) showed a reversible reduction wave at −2.24 V (vs. Cp_2Fe/Cp_2Fe^+; Figures S16 and S17), which is lower than that of **1** (−2.36 V),[20] suggesting a lower LUMO level in **2** relative to that in **1**. A structural optimization of **1** and **2** at the B3LYP/6-31G(d) level of theory was able to reproduce the crystallographically obtained structures, albeit with slightly deviated dihedral angles. For comparison, diphenyldiphosphene PhP=PPh (**7**) was calculated as a model compound (for details, see the Supporting Information). These calculations revealed that the presence of the boryl substituents in **2** raise the energy levels of all P=P-related orbitals (n, π, π*) relative to those of **7**. Due to the introduction of three electron-donating *tert*-butyl groups on each phenyl substituent in **1** compared to **7**, the change in energy levels of the corresponding orbitals is consistent with the trends observed by UV/Vis spectroscopy and cyclic voltammetry.

Addition of ^{n}BuLi to diboryldiphosphene **2** at −35 °C in THF afforded the stable adduct **8**(thf)$_n$, which exhibited two doublets in the ^{31}P NMR spectrum at δ_P −192 (P-Li) and δ_P −127 ppm (P-^{n}Bu; Scheme 2). The relatively large coupling constant ($^1J_{PP} = 208$ Hz) is indicative of direct bonding between two inequivalent phosphorus nuclei. Considering that the ^{11}B and ^{7}Li NMR spectra of **8**(thf)$_n$ showed two distinct broad signals and one sharp singlet signal, respectively, the Li cation should be dissociated from the phosphide center to form a solvent-separated ion pair. In THF, this species was found to be stable at room temperature for 9.5 h. In contrast, treatment of **1** with ^{n}BuLi at −35 °C in THF led to



Scheme 2. Addition of ^{n}BuLi to diboryldiphosphene **1** and **2**.

the appearance of two doublet signals at δ_P −66 and δ_P 8 ppm, indicating the formation of ^{n}BuLi adduct **9**(thf)$_n$.[21] However, this species gradually decomposed at 0°C over the course of 7 h to generate unidentified species exhibiting two triplets in the ^{31}P NMR spectrum at δ_P −58 and δ_P 3 ppm. The extraordinary stability of **8**(thf)$_n$ relative to **9**(thf)$_n$ should most likely be attributed to the presence of pπ–pπ interactions between the boryl substituent and the phosphide unit in **8**(thf)$_n$. Although the isolation of **8**(thf)$_n$ was not successful, recrystallization of **8**(thf)$_n$ from hexane in the presence of 1 equiv of DME furnished **8**(dme) as a crystalline solid. The ^{31}P NMR spectrum of **8**(dme) in C_6D_6 exhibited one doublet signal at δ_P −116 ppm (P-^{n}Bu, $^1J_{PP} = 205$ Hz) and one broad multiplet signal at δ_P −226 ppm. For **8**(dme), only one very broad ^{11}B NMR signal was observed at δ_B 34 ppm, while the ^{7}Li NMR signal in C_6D_6 exhibited a doublet of doublet at δ_{Li} −4.43 ppm. The observed coupling constants of $^1J_{PLi} = 82$ Hz and $^2J_{PLi} = 3$ Hz should be attributed to interactions between lithium and the two inequivalent phosphorus atoms. In their entirety, the results of this multinuclear NMR analysis indicates that **8**(dme) exists in C_6D_6 as a contact ion pair with P–Li bond in C_6D_6 solution.

A single-crystal X-ray diffraction analysis on **8**(dme) suggested stabilizing pπ-pπ interactions between the anionic phosphorus atom and the adjacent boron atom (Figure 2). Single crystals of **8**(dme) contained two independent molecules of **8**(dme) and one molecule of hexane per unit cell. The two independent molecules differ with respect to each other with regard to the orientation of the diazaborole ring connected to the P2 atom. In **8**(dme), the P–B bond lengths within the phosphide moiety [1.896(3)/1.898(3) Å] were slightly shorter than those in the ^{n}Bu-substituted phosphinyl moiety in **8**(dme) [1.933(3)/1.954(3) Å]. The angle sum around the phosphorus atoms (P1: 341.3/335.5°, P2: 322.1/312.7°) demonstrate that the pyramidalization of P1 was less pronounced than that of P2. These structural features indicate the existence of pπ-pπ interactions between P1 and the boron atom, probably due to the existence of two lone pairs on P1, and reveal that **8**(dme) exists as contact ion pair in the crystalline state.

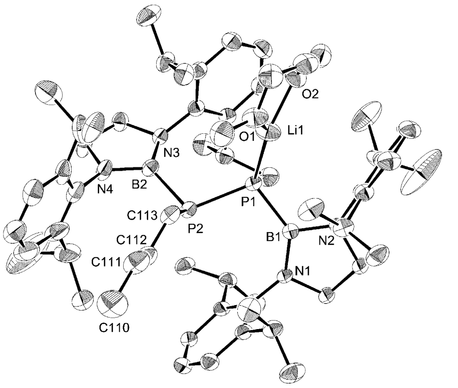


Figure 2. Molecular structure of **8**(dme) (thermal ellipsoids set at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: N1–B1 1.448 (4), N2–B1 1.457 (4), P1–B1 1.896 (3); N1-B1-N2 105.2(17) N3-B2 1.445 (4), N4-B2 1.434 (4), P2-B2 1.933 (3), P1-P2 2.1775 (11).

The presence of stabilizing pπ–pπ interactions between the anionic phosphorus atom and the adjacent boron atom in **8**(dme) was also corroborated by DFT calculations. The structural optimization of the two independent structures encountered in the unit cells afforded two energetically similar structures, and an imaginary frequency was not found. The HOMO and the HOMO-1 of **8**(dme) correspond to the P=B π-bond and a lone pair on the phosphorus atom, respectively (Figure 3). An NBO analysis of the resulting two structures provided estimated second-order perturbation energies of 46.78 and 54.67 kcal mol^{-1}, which suggest the existence of donor–acceptor interactions between the phosphorus and boron atoms. These interactions may very likely be the key factor for the stabilization of boryl-substituted phosphinophosphide **8**(dme).

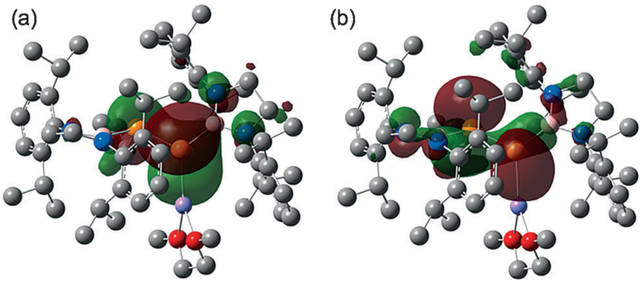


Figure 3. a) HOMO and b) HOMO-1 of **8**(dme) (only one of the two energetically similar structures is shown; hydrogen atoms omitted for clarity; color code: gray = carbon, blue = nitrogen, orange = phosphorus, pale pink = boron, purple = lithium, red = oxygen).

In summary, boryl-substituted diphosphene **2** was synthesized by a nucleophilic borylation of PCl_3 using a borylzinc reangent. A single-crystal X-ray diffraction analysis in combination with DFT calculations and an analysis of UV/Vis spectroscopic results revealed a σ-donating effect of the boryl substituents in **2** that is slightly weaker than that of the Mes* substituent. The reaction of **2** with ^{n}BuLi resulted in the formation of a phosphinophosphide that was stabilized by a π-accepting effect of boryl substituent, which was confirmed by single-crystal X-ray diffraction analysis and DFT calculations.

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Keywords: boron · boryllithium · diphosphenes · main group chemistry · substituent effects

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[1] a) "Boron-Containing Polymers": A. Doshi, F. Jäkle in *Comprehensive Inorganic Chemistry II*, 2nd ed. (Ed.: J. R. Poeppelmeier), Elsevier, Amsterdam, **2013**, pp. 861–891; b) Y.-L. Rao, H. Amarne, S. Wang, *Coord. Chem. Rev.* **2012**, *256*, 759–770; c) F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985–4022; d) C. A. Swamy, R. N. Priyanka, P. Thilagar, *Dalton Trans.* **2014**, *43*, 4067–4075; e) X. Yin, J. Chen, R. A. Lalancette, T. B. Marder, F. Jäkle, *Angew. Chem. Int. Ed.* **2014**, *53*, 9761–9765; *Angew. Chem.* **2014**, *126*, 9919–9923; f) L. Ji, R. M. Edkins, L. J. Sewell, A. Beeby, A. S. Batsanov, K. Fucke, M. Drafz, J. A. K. Howard, O. Moutounet, F. Ibersiene, A. Boucekkine, E. Furet, Z. Liu, J.-F. Halet, C. Katan, T. B. Marder, *Chem. Eur. J.* **2014**, *20*, 13618–13635; g) H. Braunschweig, V. Dyakonov, B. Engels, Z. Falk, C. Hörl, J. H. Klein, T. Kramer, H. Kraus, I. Krummenacher, C. Lambert, C. Walter, *Angew. Chem. Int. Ed.* **2013**, *52*, 12852–12855; *Angew. Chem.* **2013**, *125*, 13088–13092; h) L. Weber, D. Eickhoff, T. B. Marder, M. A. Fox, P. J. Low, A. D. Dwyer, D. J. Tozer, S. Schwedler, A. Brockhinke, H.-G. Stammler, B. Neumann, *Chem. Eur. J.* **2012**, *18*, 1369–1382; i) L. Weber, J. Halama, L. Böhling, A. Chrostowska, A. Dargelos, H.-G. Stammler, B. Neumann, *Eur. J. Inorg. Chem.* **2011**, 3091–3101; j) P. Chen, R. A. Lalancette, F. Jäkle, *J. Am. Chem. Soc.* **2011**, *133*, 8802–8805; k) L. Weber, V. Werner, M. A. Fox, T. B. Marder, S. Schwedler, A. Brockhinke, H.-G. Stammler, B. Neumann, *Dalton Trans.* **2009**, 1339–1351; l) C. D. Entwistle, J. C. Collings, A. Steffen, L.-O. Palsson, A. Beeby, D. Albesa-Jove, J. M. Burke, A. S. Batsanov, J. A. K. Howard, J. A. Mosely, S.-Y. Poon, W.-Y. Wong, F. Ibersiene, S. Fathallah, A. Boucekkine, J.-F. Halet, T. B. Marder, *J. Mater. Chem.* **2009**, *19*, 7532–7544.

[2] P. Brint, B. Sangchakr, P. W. Fowler, *J. Chem. Soc. Faraday Trans. 2* **1989**, *85*, 29–37.

[3] J. Zhu, Z. Y. Lin, T. B. Marder, *Inorg. Chem.* **2005**, *44*, 9384–9390.

[4] a) Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113–115; b) Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069–16079; c) M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *Chem. Lett.* **2008**, *37*, 802–803.

[5] a) Y. Segawa, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.* **2007**, *46*, 6710–6713; *Angew. Chem.* **2007**, *119*, 6830–6833; b) M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *J. Am. Chem. Soc.* **2007**, *129*, 9570–9571; c) T. Terabayashi, T. Kajiwara, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14162–14163; d) K. Nozaki, Y. Aramaki, M. Yamashita, S.-H. Ueng, M. Malacria, E. Lacôte, D. P. Curran, *J. Am. Chem. Soc.* **2010**, *132*, 11449–11451; e) Y. Hayashi, Y. Segawa, M. Yamashita, K. Nozaki, *Chem. Commun.* **2011**, *47*, 5888–5890; f) Y. Okuno, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.* **2011**, *50*, 920–923; *Angew. Chem.* **2011**, *123*, 950–953; g) Y. Okuno, M. Yamashita, K. Nozaki, *Eur. J. Org. Chem.* **2011**, 3951–3958; h) N. Dettenrieder, Y. Aramaki, B. M. Wolf, C. Maichle-Mössmer, X. Zhao, M. Yamashita, K. Nozaki, R. Anwander, *Angew. Chem. Int. Ed.* **2014**, *53*, 6259–6262; *Angew. Chem.* **2014**, *126*, 6373–6377; i) S. Li, J. Cheng, Y. Chen, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2011**, *50*, 6360–6363; *Angew. Chem.* **2011**, *123*, 6484–6487; j) B. Wang, M. Nishiura, J. Cheng, Z. Hou, *Dalton Trans.* **2014**, *43*, 14215–14218; k) A. V. Protchenko, L. M. A. Saleh, D. Vidovic, D. Dange, C. Jones, P. Mountford, S. Aldridge, *Chem. Commun.* **2010**, *46*, 8546–8548; l) L. M. A. Saleh, K. H. Birjkumar, A. V. Protchenko, A. D. Schwarz, S. Aldridge, C. Jones, N. Kaltsoyannis, P. Mountford, *J. Am. Chem. Soc.* **2011**, *133*, 3836–3839; m) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500–6503; n) A. V. Protchenko, D. Dange, M. P. Blake, A. D. Schwarz, C. Jones, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2014**, *136*, 10902–10905; o) A. V. Protchenko, D. Dange, J. R. Harmer, C. Y. Tang, A. D. Schwarz, M. J. Kelly, N. Phillips, R. Tirfoin, K. H. Birjkumar, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *Nat. Chem.* **2014**, *6*, 315–319; p) A. V. Protchenko, D. Dange, A. D. Schwarz, C. Y. Tang, N. Phillips, P. Mountford, C. Jones, S. Aldridge, *Chem. Commun.* **2014**, *50*, 3841–3844; q) D. Dange, A. Davey, J. A. B. Abdalla, S. Aldridge, C. Jones, *Chem. Commun.* **2015**, *51*, 7128–7131; r) N. Dettenrieder, H. M. Dietrich, C. Schädle, C. Maichle-Mössmer, K. W. Törnroos, R. Anwander, *Angew. Chem. Int. Ed.* **2012**, *51*, 4461–4465; *Angew. Chem.* **2012**, *124*, 4537–4541; s) N. Dettenrieder, C. O. Hollfelder, L. N. Jende, C. Maichle-Mössmer, R. Anwander, *Organometallics* **2014**, *33*, 1528–1531; t) N. Dettenrieder, C. Schädle, C. Maichle-Mössmer, P. Sirsch, R. Anwander, *J. Am. Chem. Soc.* **2014**, *136*, 886–889; u) M. Kaaz, J. Bender, D. Forster, W. Frey, M. Nieger, D. Gudat, *Dalton Trans.* **2014**, *43*, 680–689; v) H. Kisu, H. Sakaino, F. Ito, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2016**, *138*, 3548–3552; w) W. Lu, H. Hu, Y. Li, R. Ganguly, R. Kinjo, *J. Am. Chem. Soc.* **2016**, *138*, 6650–6661; x) A. Rit, J. Campos, H. Niu, S. Aldridge, *Nat. Chem.* DOI 10.1038/nchem.2597.

[6] a) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589; b) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1982**, *104*, 6167–6167; c) L. Weber, *Chem. Rev.* **1992**, *92*, 1839–1906; d) T. Baumgartner, R. Réau, *Chem. Rev.* **2006**, *106*, 4681–4727.

[7] A. H. Cowley, J. E. Kilduff, T. H. Newman, M. Pakulski, *J. Am. Chem. Soc.* **1982**, *104*, 5820–5821.

[8] a) A. H. Cowley, P. C. Knueppel, C. M. Nunn, *Organometallics* **1989**, *8*, 2490–2492; b) L. Weber, G. Meine, R. Boese, N. Augart, *Organometallics* **1987**, *6*, 2484–2488.

[9] L. N. Markovskii, V. D. Romanenko, M. I. Povolotskii, A. V. Ruban, E. O. Klebanskii, *Zh. Obshch. Khim.* **1986**, *56*, 2157–2158.

[10] a) E. Niecke, R. Rüger, M. Lysek, S. Pohl, W. Schoeller, *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 486–487; *Angew. Chem.* **1983**, *95*, 495–496; b) E. Niecke, R. Rüger, *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 155–156; *Angew. Chem.* **1983**, *95*, 154–155.

[11] a) D. Usharani, A. Poduska, J. F. Nixon, E. D. Jemmis, *Chem. Eur. J.* **2009**, *15*, 8429–8442; b) S. Vogt-Geisse, H. F. Schaefer, *J. Chem. Theory Comput.* **2012**, *8*, 1663–1670.

[12] For related boryl-substituted disilenes, see: a) K. Takeuchi, M. Ikoshi, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2010**, *132*, 930–931; b) K. Takeuchi, M. Ichinohe, A. Sekiguchi, *Organometallics* **2011**, *30*, 2044–2050. For a boryl-substituted dibismuthene, see: ref. [5q].

[13] a) T. Kajiwara, T. Terabayashi, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.* **2008**, *47*, 6606–6610; *Angew. Chem.* **2008**, *120*, 6708–6712; b) J. Campos, S. Aldridge, *Angew. Chem. Int. Ed.* **2015**, *54*, 14159–14163; *Angew. Chem.* **2015**, *127*, 14365–14369.

[14] J. Emsley, *The Elements*, 3rd ed., Oxford University Press, New York, **1998**.

[15] a) M. Yoshifuji, S. Sasaki, D. Shiomi, T. Niitsu, N. Inamoto, *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *49–50*, 325–328; b) M. Yoshifuji, S. Sasaki, N. Inamoto, *J. Chem. Soc. Chem. Commun.* **1989**, 1732–1733; c) P. Jutzi, U. Meyer, B. Krebs, M. Dartmann, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 919–921; *Angew. Chem.* **1986**, *98*, 894–895; d) M. Scholz, H. W. Roesky, D. Stalke, K. Keller, F. T. Edelmann, *J. Organomet. Chem.* **1989**, *366*, 73–85; e) H. Ranaivonjatovo, J. Escudié, C. Couret, J. Satgé, *Phosphorus Sulfur Silicon Relat. Elem.* **1987**, *31*, 81–87.

[16] a) N. Wiberg, A. Wörner, H.-W. Lerner, K. Karaghiosoff, *Z. Naturforsch. B* **2002**, *57*, 1027 – 1035; b) V. Cappello, J. Baumgartner, A. Dransfeld, M. Flock, K. Hassler, *Eur. J. Inorg. Chem.* **2006**, 2393 – 2405.

[17] E. Urnėžius, J. D. Protasiewicz, *Main Group Chem.* **1996**, *1*, 369 – 372.

[18] T. Sasamori, N. Takeda, N. Tokitoh, *J. Phys. Org. Chem.* **2003**, *16*, 450 – 462.

[19] M. Sakagami, T. Sasamori, H. Sakai, Y. Furukawa, N. Tokitoh, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 1132 – 1143.

[20] A. J. Bard, A. H. Cowley, J. E. Kilduff, J. K. Leland, N. C. Norman, M. Pakulski, G. A. Heath, *J. Chem. Soc. Dalton Trans.* **1987**, 249 – 251.

[21] Treatment of **1** with ^{n}BuLi in THF at room temperature affords adduct **9**, which exhibits two doublets at δ_P −9 and δ_P 81 ppm ($^{1}J_{PP}$ = 344 Hz) in its ^{31}P NMR spectrum. The discrepancy of the ^{31}P NMR chemical shifts may be attributed to the measurement of **9** at lower temperature (0 °C). For details, see: M. Yoshifuji, K. Shibayama, N. Inamoto, *Chem. Lett.* **1984**, *13*, 115 – 118.

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Communications

Diphosphene

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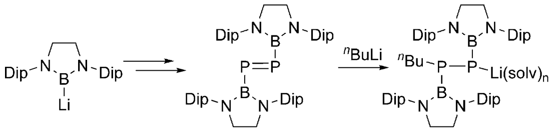
A Boryl-Substituted Diphosphene: Synthesis, Structure, and Reaction with *n*-Butyllithium To Form a Stabilized Adduct by pπ-pπ Interaction



stabilized by pπ-pπ interaction

A boryl-substituted diphosphene was synthesized using a borylzinc reagent (see picture). An analysis of the species revealed an σ-electron-donating effect of the boryl substituents. The reaction of the diboryldiphosphene with *n*-butyllithium afforded a boryl-substituted phosphinophosphide that was stabilized by a π-electron-accepting effect of the boryl substituents.