

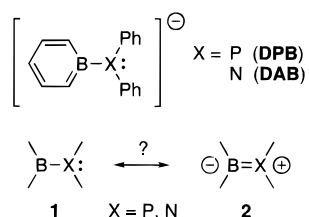
Direct Crystallographic Comparison of P–B and N–B π -Bonding: Structural Studies of Diphenylphosphido- and Diphenylamidoboratabenzene

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We recently reported that treatment of several transition metal halides with potassium diphenylphosphidoboratabenzene (K-DPB) affords phosphorus-bound σ complexes, whereas otherwise identical reactions of potassium diphenylamidoboratabenzene (K-DAB) do not provide the corresponding nitrogen-bound σ complexes.^{1–3} Earlier investigations of aminoboranes and phosphinoboranes have clearly established that nitrogen is more prone than phosphorus to participate in π -bonding with boron (1 \leftrightarrow 2).⁴ It therefore seemed likely that the dichotomy in



reactivity between K-DPB and K-DAB has its origin in a dichotomy in bonding. In this communication we furnish support for this hypothesis in the form of structural studies that reveal that the phosphorus lone pair of K-DPB engages in little, if any, π -bonding with boron, whereas the nitrogen atom of K-DAB adopts a geometry that permits a π interaction. This is, to the best of our knowledge, the first crystallographic comparison of P–B versus N–B π -bonding between two molecules that differ only in the group 15 atom.^{4,5}

X-ray quality crystals of K-DPB·(18-crown-6)·(toluene)_{1/2} (3) were obtained upon cooling a saturated solution of K-DPB in toluene/18-crown-6 to –35 °C (Figure 1a, Table 1a).⁶ The phosphorus atom of K-DPB·(18-crown-6)·(toluene)_{1/2} is pyramidal, with \angle B–P–C12 = 106.2(3)°, \angle B–P–C6 = 102.5(3)°, and \angle C12–P–C6 = 101.4(2)° (Σ = 310°). The C6–P–B–C1 torsion angle of –66.2(5)° and the P–B bond

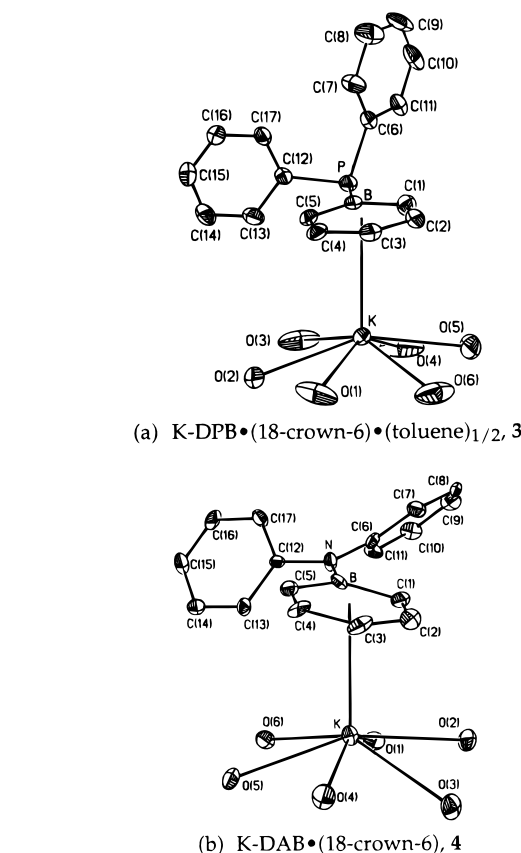


Figure 1. ORTEP illustrations, with thermal ellipsoids drawn at the 35% probability level, of (a) K-DPB·(18-crown-6)·(toluene)_{1/2} (3) [the toluene has been omitted from the ORTEP] and (b) K-DAB·(18-crown-6) (4).

Table 1. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for (a) K-DPB·(18-crown-6)·(toluene)_{1/2} (3) and (b) K-DAB·(18-crown-6) (4)

(a) K-DPB·(18-crown-6)·(toluene) _{1/2} , 3			
B–P–C(12)	106.2(3)	C(6)–P–B–C(1)	–66.2(5)
B–P–C(6)	102.5(3)	C(6)–P–C(12)–C(17)	16.0(5)
C(12)–P–C(6)	101.4(2)	C(12)–P–C(6)–C(11)	–112.7(4)
C(1)–B–P	117.9(4)	C(12)–P–B–C(1)	–172.2(4)
C(1)–B–C(5)	115.4(5)	B–P–C(12)–C(13)	–62.3(5)
C(5)–B–P	126.7(4)	B–P–C(6)–C(11)	137.7(4)
P–B	1.968(7)		
P–C(12)	1.835(5)		
P–C(6)	1.840(6)		
(b) K-DAB·(18-crown-6), 4			
B–N–C(12)	120.2(6)	C(6)–N–C(12)–C(17)	–42.3(9)
B–N–C(6)	122.7(6)	C(6)–N–B–C(1)	–21.9(10)
C(12)–N–C(6)	117.0(5)	C(12)–N–C(6)–C(11)	–39.6(9)
C(1)–B–N	122.9(7)	C(12)–N–B–C(1)	162.7(6)
C(1)–B–C(5)	113.2(7)	B–N–C(12)–C(13)	–47.9(9)
C(5)–B–N	123.8(7)	B–N–C(6)–C(11)	144.9(7)
N–B	1.510(10)		
N–C(12)	1.431(8)		
N–C(6)	1.399(8)		

distance of 1.968(7) Å⁷ are inconsistent with the presence of significant π -bonding between phosphorus and boron.

(6) Crystal data for K-DPB·(18-crown-6)·(toluene)_{1/2} (3): colorless parallelepiped (0.18 × 0.15 × 0.15 mm), monoclinic, $P2_1/c$, a = 13.363(1) Å, b = 13.672(1) Å, c = 19.055(1) Å, β = 108.903(1)°, V = 3293.6(4) Å³, Z = 4, and ρ_{calc} = 1.230 g/cm³, T = –86(2) °C. Graphite monochromated Mo $K\alpha$ radiation. Solution was done by Patterson methods. Full-matrix least-squares refinement on F^2 yielded R_1 = 0.0643; wR_2 = 0.1206 for data with $I > 2\sigma(I)$. The asymmetric unit contains a half molecule of toluene, disordered about a center of symmetry located in the center of the ring, which was refined as a half molecule of xylene with 1/4 occupancy for the methyl carbons.

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(1) Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 8176–8177.

(2) Similarly, under conditions in which K-DPB undergoes clean P -methylation, K-DAB does not undergo N -methylation. Qiao, S. Unpublished results.

(3) DPB is the only boratabenzene that has been observed to bind to a metal in a σ , rather than a π , mode. For leading references to π -bound boratabenzene complexes, see: (a) Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199–236. (b) Herberich, G. E. In *Comprehensive Organometallic Chemistry II, Vol. 1*, Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Chapter 5.

(4) (a) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343–379. (b) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449–460.

(5) Based on a search of the Cambridge Crystallographic Data Base. Because ring-related conformational constraints can be the primary determinant of the structure of cyclic systems, they were not included in this search.

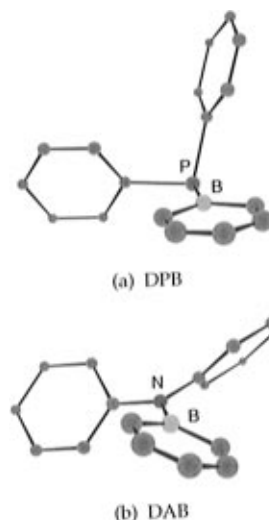
Table 2. ^1H and ^{13}C NMR Chemical Shifts (δ) of $[\text{C}_5\text{H}_5\text{B-X}]^-$

X	H _{ortho}	H _{para}	C _{ortho}	C _{para}
H	6.57	6.21	128	112
PPh ₂	6.50	6.20	128	113
Me	6.47	6.18	127	108
NPh ₂	5.99	5.72	119	106
OEt	5.67	5.67	115	104
NMe ₂	5.65	5.50	110	100

Herberich has established that π donation by boron-bound substituents of boratabenzenes results in upfield shifts of the ortho and para resonances in the ^1H and ^{13}C NMR spectra.⁸ The NMR chemical shifts observed for K-DPB (Table 2, X = PPh₂) therefore suggest that, in solution, as in the solid state, there is little or no interaction between the phosphorus lone pair and the adjacent boron atom.

K-DAB, the nitrogen analogue of K-DPB, was prepared from borabenzene- PMe_3 ¹⁰ by treatment with KNPh₂. Crystallization by diffusion of hexane into a toluene/18-crown-6 solution of K-DAB yielded a light-yellow crystal of K-DAB·(18-crown-6) (**4**; Figure 1b, Table 1b).¹¹ In contrast to the pyramidal geometry of the phosphorus atom in K-DPB, the nitrogen atom in K-DAB·(18-crown-6) adopts a trigonal planar structure ($\angle\text{B-N-C12} = 120.2(6)^\circ$, $\angle\text{B-N-C6} = 122.7(6)^\circ$, and $\angle\text{C12-N-C6} = 117.0(5)^\circ$; $\Sigma = 360^\circ$).¹² As illustrated in Figure 1b, the nitrogen "lone pair" is oriented such that it can interact with the boron atom,¹³ in preference to the carbon atoms, although some distortion from planarity is evident. This distortion, as well as the comparatively long N-B bond distance of 1.510(10) Å,¹⁴ is likely due to the steric bulk of the phenyl groups. The ^1H and ^{13}C NMR chemical shifts of K-DAB suggest the presence of significant π -bonding between the boron and the nitrogen, although the overlap is not as strong as in the NMe₂-substituted boratabenzene (Table 2).

A computational study (HF/6-31G*¹⁵) of the DPB and DAB anions provided minima (Figure 2) that are in good agreement

**Figure 2.** HF/6-31G*-minimized conformations of (a) DPB and (b) DAB.

with the crystal structures (Figure 1),¹⁶ suggesting that the observed solid-state conformations are not simply a consequence of packing forces. Single-point energy calculations reveal that the energy of the borabenzene HOMO of DAB in the minimized conformation is 10.6 kcal/mol higher than in the rotamer in which the nitrogen lone pair lies in the nodal plane of the borabenzene ring; the corresponding value for DPB is 4.3 kcal/mol.¹⁷ These calculations are consistent with greater borabenzene-heteroatom interaction for nitrogen than for phosphorus.

In summary, this work provides the first direct crystallographic comparison of P-B versus N-B π -bonding for two molecules that differ only in the group 15 atom. The data clearly indicate that the nitrogen of K-DAB engages in significantly greater π -bonding with boron than does the phosphorus of K-DPB. The difference in bonding between these two species correlates with their divergent chemical reactivity.

Acknowledgment. We thank the reviewers for their suggestions, and we thank Dr. William M. Davis and Mr. Aaron L. Odom for their helpful insights into crystal structure solution and refinement. Support has been provided by the American Cancer Society, the Camille and Henry Dreyfus Foundation, the National Science Foundation (Young Investigator Award, with funding from DuPont, Merck, Pfizer, Pharmacia & Upjohn, Procter & Gamble, and Rohm & Haas), and the Research Corp. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. This paper is dedicated to Professor Gerhard E. Herberich on the occasion of his 60th birthday.

Supporting Information Available: Experimental procedures, compound characterization data, crystal structure data, and coordinates from the computational study (25 pages). See any current masthead page for ordering and Internet access instructions.

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(15) Gaussian 94, Revision D.4: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

(16) Frequency calculations established that these structures are minima.

(17) Because of the sterically hindered nature of DAB and DPB, the energies of these rotamers, relative to the respective minima, do not provide a suitable basis for comparison (steric effects cannot be factored out).

(7) Typical length for a P-B single bond: 1.90–2.00 Å (ref 4).

(8) Herberich, G. E.; Schmidt, B.; Englert, U. *Organometallics* **1995**, *14*, 471–480.

(9) (a) X = H: Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 8480–8481. (b) X = PPh₂ and OEt: Qiao, S.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 6329–6330. (c) X = Me: Herberich, G. E.; Becker, H. J.; Carsten, K.; Engelke, C.; Koch, W. *Chem. Ber.* **1976**, *109*, 2382–2388. (d) X = NPh₂: this work. (e) X = NMe₂: Herberich, G. E.; Schmidt, B.; Englert, U.; Wagner, T. *Organometallics* **1993**, *12*, 2891–2893.

(10) Hoic, D. A.; Wolf, J. R.; Davis, W. M.; Fu, G. C. *Organometallics* **1996**, *15*, 1315–1318.

(11) Crystal data for K-DAB·(18-crown-6) (**4**): light-yellow irregular block (0.24 × 0.18 × 0.08 mm), orthorhombic, $Pna2_1$, $a = 17.289(6)$ Å, $b = 15.269(7)$ Å, $c = 10.929(4)$ Å, $V = 2885(2)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.261$ g/cm³, $T = -135(2)$ °C. Solution was done by direct methods. Full-matrix least-squares refinement on F^2 yielded $R_1 = 0.0690$, $wR^2 = 0.1184$ for data with $I > 2\sigma(I)$. Unlike K-DPB·(18-crown-6)·(toluene)_{1/2}, the crystal of K-DAB·(18-crown-6) does not have a half molecule of toluene in the lattice. A crystal of K-DAB grown by cooling a saturated toluene/18-crown-6 solution to -35 °C (the conditions used for growth of the K-DPB·(18-crown-6)·(toluene)_{1/2} crystal) had the same cell constants as those described above.

(12) The nitrogen of triphenylamine is trigonal planar in the solid state: Sobolev, A. N.; Belsky, V. K.; Romm, I. P.; Chernikova, N. Y.; Guryanova, E. N. *Acta Crystallogr.* **1985**, *C41*, 967–971.

(13) Herberich has established that π bonding between nitrogen and boron occurs in dialkylamidoboratabenzenes (ref 9e). See also: Ashe, A. J., III; Kampf, J. W.; Muller, C.; Schneider, M. *Organometallics* **1996**, *15*, 387–393.

(14) A B-N bond distance of 1.45 Å has been observed in each dimethylamidoboratabenzene that has been crystallographically characterized: (a) Reference 9e. (b) Herberich, G. E.; Englert, U.; Schmidt, M. U.; Standt, R. *Organometallics* **1996**, *15*, 2707–2712.