

Letter

One-Step Conversion of Potassium Organotrifluoroborates to Metal Organoborohydrides

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Supporting Information



ABSTRACT: This letter describes the one-step conversion of heteroatom-substituted potassium organotrifluoroborates (KRBF₃) to metal monoorganoborohydrides (MRBH₃) using alkali metal aluminum hydrides. The method tolerates a variety of functional groups, expanding MRBH₃ diversity. Hydride removal with Me₃SiCl in the presence of dimethylaminopyridine (DMAP) affords the organoborane·DMAP (RBH₂·DMAP) adducts.

Metal organoborohydrides (MBR_nH_(4-n), abbreviated MOBs) have been the subject of research for over 60 years, beginning with the pioneering work of Schlesinger.¹ This work dramatically expanded under Brown, who demonstrated the tuning effects of organic substituents on the reactivity of compounds containing *B*-H bonds as hydride donors and reducing agents.² Modification of the steric,³ stereochemical,⁴ hydrophobic,⁵ and electronic⁶ influences of organic substituents permits creation of MOBs with reactivity ranging from milder than NaBH₄, with the creation of sodium cyanoborohydride⁷ and sodium triacetoxyborohydride,⁸ to much stronger than LiAlH₄, with the invention of "Super Hydride" LiBEt₃H.⁹ Others, including Singaram,¹⁰ Paetzold,¹¹ Soderquist,¹² and Noth,¹³ furthered this work. The recent explosion of frustrated Lewis pair chemistry takes advantage of the hydride donation ability of organoborohydrides¹⁴ with the first examples of metal-free catalytic hydrogenation.

In addition to their widespread use as hydride donors, MOBs have been employed as synthetic building blocks for the creation of chiral tetracoordinate boron centers,¹⁵ CBN hydrogen storage compounds,¹⁶ optoelectronic materials,¹⁷ boron-containing polymers,¹⁸ and ligands for *d*- and *f*-block metals.¹⁹ Not only can MOBs serve in these roles, they also act as four-coordinate "protected boranes" ($R_nBH_{(3-n)}$) which can be generated *in situ* upon addition of Bronsted or Lewis acids.²⁰ Therefore, we envisioned that not only would a new method enabling the creation of highly substituted MRBH₃s expand the chemistry of four-coordinate organoborohydrides, it would also

facilitate the creation of new three-coordinate organoboranes (RBH₂), a process recently used to prepare frustrated Lewis pairs with $-BH_2$ Lewis acidic sites.²¹

Despite the widespread application of MOBs in organoboron research, most prior work has focused on metal triorganoborohydride compounds (MR₃BH), with limited examples of metal diorgano-²² and monoorganoborohydrides (MR₂BH₂ and MRBH₃, respectively). The $-BH_3$ unit is notable for its isoelectronic and isoelectronic relationship with the methyl group. With the exception of N-heterocyclic carbene–borane adducts, MRBH₃s synthesized and isolated to date are mostly limited to alkyl, aryl, silyl,²³ carbonyl,²⁴ and fluoro²⁵ substituents, with only a handful of examples of heteroatom is not connected directly to boron.²⁶ The relative absence of diverse, highly functionalized R groups in MRBH₃s in the literature may be due to their limited synthetic access.

Three general methods of generating MRBH₃s exist: (1) addition of binary or complex metal hydrides to organoboranes²⁷ or organohaloboranes²⁸ (Scheme 1), (2) addition of organolithium or organomagnesium compounds to borane– Lewis base adducts (e.g., BH₃·THF), and (3) addition of a complex metal aluminohydride to a boronic ester or boronic acid.²⁹ Of these routes, method 3 appears to be the most

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Scheme 1. Synthetic Methods for the Preparation of MRBH₃



convenient, general, and functional group tolerant, yet all three routes rely on air- or water-sensitive sources of boron. Therefore, we envisioned that KRBF₃s could serve as ideal substrates for the creation of a diverse family of heteroatom-substituted MRBH₃s and sought to discover the conditions with the greatest functional group tolerance capable of this conversion.

Potassium organotrifluoroborates (KRBF₃s) serve as attractive organoboron starting materials due to their ease of synthesis, hydrolytic stability, and late-stage functionalization compatibility.³⁰ The work of Molander and others has rapidly expanded this chemistry, with application primarily as masked boronic acids in Suzuki–Miyaura coupling. Others have demonstrated the utility of KRBF₃s as reagents for allyl and crotylborations and for the generation of organohaloboranes (RBF₂ and RBCl₂),³¹ BN heterocycles,³² and chiral borane Lewis acid synthesis.³³ To the best of our knowledge, this is the first general method for the conversion of KRBF₃s to MRBH₃s and is broadly tolerant of a wide variety of heteroatom-containing functional groups.

We began screening hydride reagents in various solvents on model compound 1a, discovering that LiAlH₄ in THF was capable of converting the B-F bond to the desired B-H bond³⁴ (Table 1). Variation of stoichiometry revealed that only 1.1 equiv of LiAlH₄ is needed for the quantitative conversion in 1 h.³⁵ Due to the limited solubility of KRBF₃s in other LiAlH₄compatible solvents, THF was the only solvent that facilitated this conversion. Unfortunately, we were only able to isolate the THF adduct of the LiRBH₃ compound 1b•THF, which was insoluble in any solvent after concentration in vacuo. The milder $Li(t-BuO)_2AlH$ accomplished the desired conversion, but also yielded the same LiRBH3. THF adduct 1b. THF. After an exhaustive screening of hydride sources and additives, we found that 1.1 equiv of NaAlH₄ in THF accomplished quantitative conversion at 22 °C in 18 h, yielding compound 1c. While using NaAlH₄ overcomes the problems of the lithium salts, it is problematic because the MRBH₃ products contain a mixture of sodium and potassium cations. Therefore, we attempted the reaction with 1.1 equiv of KAlH₄, which yielded compounds 1d-12d (except 9d) that contain only potassium cations. The sodium and potassium MRBH₃s do not suffer from the solubility problems of the lithium salts, with moderate solubility in THF, MeCN, and DMSO.

By screening a variety of KRBF₃ substrates, we demonstrated that this new method is compatible with benzyl, aryl, styryl, amino, chloroaryl, bromoaryl, trifluoromethyl, thioether, acetal, ether, and amide functional groups (Scheme 2). Purification of the new MRBH₃s is straightforward, with filtration through Celite providing the desired products in moderate to good yields.³⁶ Furthermore, this method yields sodium and potassium organoborohydrides, in contrast to almost every other example

Table 1. Optimization of Conditions for H/F Exchange on $1a^a$

ĺ	BF ₃ K hyd	ride sourc solvent	xe→ ()	`BH₃M b c	M = Li M = Na	
1a			1b-d		a M = K	
entry	hydride	equiv	solvent	time (h)	product	
1	LiAlH ₄	4	THF	24	1b•THF	
2	LiAlH ₄	2	THF	24	1b•THF	
3	LiAlH ₄	1.1	THF	24	1b•THF	
4	LiAlH ₄	1.1	THF	1	1b•THF	
5	LiAlH ₄	4	Et ₂ O	24	-	
6	LiAlH ₄	4	1,4-dioxane	24	incomplete	
7	Li(Ot-Bu) ₃ AlH	3.1	THF	24	1b•THF	
8	NaAlH ₄	4	THF	24	1c	
9	NaAlH ₄	1.1	THF	18	1c	
10	KAlH ₄	1.1	THF	18	1d	
11	LiH	4	THF	24	-	
12	NaH	4	THF	24	-	
13	CaH_2	4	THF	24	-	
14	1. TMSCl	4	THF	24	-	
	2. LiH	4				
15	1. TMSCl	4	THF	24	-	
	2. NaH	4				
16	1. TMSCl	4	THF	24	-	
	2. CaH ₂	4				
17	Me ₂ SiHCl ^b	6	MeCN	24	-	
^{<i>a</i>} Progress monitored by ¹¹ B NMR. ^{<i>b</i>} Reaction run at 60 $^{\circ}$ C						

Scheme 2. Sodium Organoborohydrides Synthesized Using New Method



^a1.5 equiv NaAlH₄ used. ^b1.0 equiv KAlH₄ used. ^c1.5 equiv KAlH₄ used. ^dFW for compound was based on a 1:1 ratio of Na:K.

of $MRBH_3$ compounds in the literature, where the metal is lithium or a transition metal.

Additionally, we discovered that the attenuated reducing power of NaAlH₄ and KAlH₄ compared to LiAlH₄ imparts greater functional group tolerance to this method, permitting synthesis of MRBH₃s with greater structural diversity than would have been possible with LiAlH₄. For example, amides are readily reduced by LiAlH₄, but react only slowly with NaAlH₄ and KAlH₄. Using our conditions, we can synthesize amidesubstituted **12c** and **12d**. To the best of our knowledge, these are the first examples of amide-substituted borohydrides where the carbonyl is not attached directly to boron. Curiously, NaAlH₄ exhibited broader functional group tolerance than KAlH₄, as we were unable to synthesize dioxolane substituted **9d** using KAlH₄ and experienced greater difficulty obtaining pure product with more sensitive functional groups such as styryl and amido derivatives **3d** and **12d**, respectively. Furthermore, KAlH₄ is not commercially available, making NaAlH₄ a more convenient reagent if obtaining a mixed alakali metal salt is not problematic.

The barrier to F/H exchange appears to be enthalpic and driven by favorable entropy. Conversion of BF₃ and AlH₃ to BH₃ and AlF₃ [eq 1] is endothermic, but exergonic in the gas phase, $\Delta H^{\circ}_{298} = +42.89 \text{ kJ mol}^{-1} \text{ or } +14.30 \text{ kJ mol}^{-1} \text{ per bond; } \Delta G^{\circ}_{298} = -11.31 \text{ kJ mol}^{-1} \text{ or } -3.77 \text{ kJ mol}^{-1} \text{ per bond.}^{37}$

$$BF_3 + AIH_3 \to BH_3 + AIF_3 \tag{1}$$

With the new organoborohydrides in hand, we sought to use them as starting materials for the preparation of heteroatomsubstituted boranes. Reaction of **4b** and **10b** with 1.0 equiv Me_3SiCl THF in the presence of DMAP afforded the organoborane·DMAP adducts **4e·DMAP** and **10e·DMAP**, respectively (Scheme 3). X-ray quality crystals **4e·DMAP** and **10e·DMAP**³⁸ were obtained from slow diffusion of pentane into concentrated solutions in dichloromethane.

Scheme 3. Conversion of Sodium Organoborohydrides into Organoborane DMAP Adducts



The unit cell of **4e·DMAP** contains one symmetry independent formula unit, in the monoclinic space group $P2_1/n$, whereas the unit cell of **10e·DMAP** contains two symmetry independent formula units in the orthorhombic space group *Pbca*. In both cases, boron appears to be sp³ hybridized, with $C(1)-B(1)-N(1) = 109.1(1)^{\circ}$ for **4e·DMAP** and $C(1)-B(1)-N(1) = 110.8(1)^{\circ}$ for **10e·DMAP**. The B(1)-C(1)distances of 1.615(2) Å and 1.609(3) Å for **4e·DMAP** and **10e· DMAP**, respectively, are consistent with a formal C–B single bond.³⁹

In **4e·DMAP** the nitrogen of the dimethylaminophenyl fragment appears to be mostly sp³ hybridized, with C(8)– $N(1)-C(7) = 111.4(1)^{\circ}$ and a C(3)–C(4)–N(1)-C(7) torsion angle of $-46.2(2)^{\circ}$, which suggests little π -donation into the phenyl ring. In contrast, The oxygen of the methoxy group in **10e·DMAP** appears to be mostly sp² hybridized, with C(7)–O(1)–C(4) = 117.2(1)^{\circ}, and is close to coplanar with

the phenyl ring, with a C(7)–O(1)–C(4)–C(3) torsion angle of $-7.3(2)^{\circ}$, consistent with π -donation into the phenyl ring.

The geometries of the DMAP fragments of both 4e DMAP and 10e·DMAP are similar to other structures of DMAPborane adducts. The nitrogen of the dimethylamino fragments appear to be sp² hybridized with C(14)-N(3)-C(12) = $120.8(1)^{\circ}$ and $C(14)-N(2)-C(10) = 120.9(1)^{\circ}$, respectively, and are close to coplanar with torsion angles C(15)-N(3)- $C(11)-C(11) = -3.3(2)^{\circ}$ and C(14)-N(2)-C(10)-C(11) = $-1.7(2)^{\circ}$, respectively, consistent with π -donation into the pyridine ring. The B(1)-N(1) distances of 1.594(2) Å and 1.597(2) Å for 4e·DMAP and 10e·DMAP, respectively, are similar to the range observed for other DMAP-borane adducts.⁴⁰ Interestingly, in 10e DMAP, the B-H exhibits an intermolecular close contact of H(2)B-H(2) = 2.49(2) Å, which may be evidence of an electrostatic interaction between the hydridic B-H and an aromatic C-H, and is observed in other borohydride crystal structures.⁴¹

In summary, we have discovered a convenient method for the conversion of potassium organotrifluoroborates to alkali metal monoorganoborohydrides that is tolerant of a wide range of functional groups, which expands the chemical space of this class of compounds. We then demonstrated the conversion of two MRBH₃s to heteroatom-substituted organoborane DMAP adducts. With synthetic access to diversely substituted MRBH₃s now available, our laboratory seeks to systematically study the effects of various organic substituents on the reactivity of B-*H* bonds and quantify the substituent effects on hydricity. These new MRBH₃s may find use as reducing agents, ligands, and building blocks for the synthesis of organoboron-based molecules and materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01373.

Experimental procedures and characterization data (PDF)

Accession Codes

CCDC 1833625 contains 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.

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Notes

The authors declare no competing financial interest.

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REFERENCES

 Wartik, T.; Schlesinger, H. I. J. Am. Chem. Soc. 1953, 75, 835–839.
 For a review of hydride reducing agents, see: Brown, H. C.; Krishnamurthy, S. Tetrahedron 1979, 35, 567–607.

(3) (a) Lathem, A. P.; Treich, N. R.; Heiden, Z. M. Isr. J. Chem. 2015, 55, 226–234. (b) Brown, H. C.; Cha, J. S.; Nazer, B. J. Org. Chem. 1985, 50, 549–553. (c) Brown, H. C.; Krishnamurthy, S. J. Am. Chem. Soc. 1972, 94, 7159–7161.

(4) (a) Brown, H. C.; Zweifel, G. J. Am. Chem. Soc. **1961**, 83, 486–487. (b) Brown, H. C.; Singaram, B.; Cole, T. E. J. Am. Chem. Soc. **1985**, 107, 460–464. (c) Brown, H. C.; Cho, B. T.; Park, W. S. J. Org. Chem. **1987**, 52, 4020–4024.

(5) (a) Biscoe, R. B.; Breslow, R. J. Am. Chem. Soc. 2003, 125, 12718–12719. (b) Biscoe, R. B.; Uyeda, C.; Breslow, R. Org. Lett. 2004, 6, 4331–4334.

(6) Heiden, Z. M.; Lathem, A. P. Organometallics 2015, 34, 1818–1827.

(7) (a) Borch, R. F.; Durst, H. D. J. Am. Chem. Soc. **1969**, 91, 3996–3997. (b) Borch, R. F.; Bernstein, M. D.; Durst, H. D. J. Am. Chem. Soc. **1971**, 93, 2897–2904.

(8) For a review of sodium triacetoxybrohydride chemistry, see: Gribble, G. W. Chem. Soc. Rev. **1998**, 27, 395–404.

(9) (a) Brown, H. C.; Kim, S. C.; Krishnamurthy, S. J. Org. Chem. 1980, 45, 1–12. (b) Krishnamurthy, S.; Brown, H. C. J. Org. Chem. 1983, 48, 3085–3091.

(10) (a) Fisher, G. B.; Harrison, J.; Fuller, J. C.; Goralski, C. T.; Singaram, B. Tetrahedron Lett. **1992**, 33, 4533–4536. (b) Singaram, B.; Jackson, T. C.; Harrison, J. Synlett **1996**, 1996, 383–384. (c) Collins, C.; Fisher, G. B.; Reem, A.; Goralski, C. T.; Singaram, B. Tetrahedron Lett. **1997**, 38, 529–532. (d) For a review of aminoborohydride chemistry, see: Pasumansky, L.; Goralski, C. T.; Singaram, B. Org. Process Res. Dev. **2006**, 10, 959–970.

(11) Groteklaes, M.; Paetzold, P. Chem. Ber. 1988, 121, 809-810.

(12) Medina, J. R.; Cruz, G.; Cabrera, C. R.; Soderquist, J. A. J. Org. Chem. 2003, 68, 4631–4642.

(13) (a) Biffar, W.; Noth, H.; Sedlak, D. Organometallics **1983**, *2*, 579–585. (b) Knizek, J.; Noth, H. J. Organomet. Chem. **2000**, 614-615, 168–187.

(14) (a) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124–1126. (b) . For reviews of catalytic hydrogenation using FLPs, see: (c) Paradies, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 3552–3557. (d) Stephan, D. W.; Erker, G. Frustrated Lewis Pair Mediated Hydrogenations. In *Frustrated Lewis Pairs I*; Erker, G., Stephan, D. W., Eds.; Springer: Berlin, 2013; Vol. 332, pp 85–110.

(15) (a) Vedrenne, P.; Le Guen, V.; Toupet, L.; Le Gall, T.; Mioskowski, C. J. Am. Chem. Soc. **1999**, *121*, 1090–1091. (b) Imamoto, T.; Morishita, H. J. Am. Chem. Soc. **2000**, *122*, 6329–6330.

(16) (a) Chen, G.; Zakharov, L. N.; Bowden, M. E.; Karkamkar, A. J.;
Whittemore, S. M.; Garner, E. B., III; Mikulas, T. C.; Dixon, D. A.;
Autrey, T.; Liu, S.-Y. *J. Am. Chem. Soc.* 2015, *137*, 134–137.
(b) Campbell, P. G.; Ishibashi, J. S. A.; Zakharov, L. N.; Liu, S.-Y. *Aust. J. Chem.* 2014, *67*, 521–524.

(17) For a review of boranes and borohydrides in conjugated materials, see: Lorbach, A.; Hubner, A.; Wagner, M. *Dalton Trans.* **2012**, *41*, 6048–6063.

(18) (a) Franz, D.; Bolte, M.; Lerner, H.-M.; Wagner, M. Dalton Trans. **2011**, 40, 2433–2440. (b) Scheibitz, M.; Li, H.; Schnorr, J.; Perucha, A. J.; Bolte, M.; Lerner, H. – W.; Jakle, F.; Wagner, M. J. Am. Chem. Soc. **2009**, 131, 16319–16329.

(19) (a) Welling, U.; Paetzold, P.; Englert, U. *Inorg. Chim. Acta* **1995**, 231, 175–180. (b) Knizek, J.; Noth, H.; Schmidt-Amelunxen, M. *Eur. J. Inorg. Chem.* **2011**, 2011, 5548–5557. (c) Yu, Y.; Brennessel, W. W.; Holland, P. L. *Organometallics* **2007**, 26, 3217–3226. (d) Chen, X.;

Lim, S.; Plecnik, C. E.; Liu, S.; Du, B.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2005**, *44*, 6052–6061. (e) Arnold, N.; Mozo, S.; Paul, U.; Radius, U.; Braunschweig, H. *Organometallics* **2015**, *34*, 5709–5715.

(20) Cole, T. E.; Bakshi, R. K.; Srebnik, M.; Singaram, B.; Brown, H. C. Organometallics **1986**, *5*, 2303–2307.

(21) Chernichenko, K.; Kotai, B.; Papai, I.; Zhivonitko, V.; Nieger, M.; Leskela, M.; Repo, T. Angew. Chem., Int. Ed. **2015**, *54*, 1749–1753.

(22) Brown, H. C.; Rangaishenvi, M. V.; Racherla, U. S. J. Org. Chem. 1987, 52, 728-730.

(23) Paetzold, P.; Geret, L.; Bose, R. J. Organomet. Chem. 1990, 385, 1–11.

(24) Pitchumony, T. S.; Spingler, B.; Motterlini, R.; Alberto, R. Org. Biomol. Chem. 2010, 8, 4849–4854.

(25) Schnurr, A.; Samigullin, K.; Breunig, J. M.; Bolte, M.; Lerner, H. – W.; Wagner, M. Organometallics **2011**, 30, 2838–2843.

(26) Recent examples include: (a) Nitro: Belanger-Chabot, G.; Rahm, M.; Haiges, R.; Christe, K. O. *Angew. Chem., Int. Ed.* **2013**, *52*, 11002–11006. (b) Phosphane oxide: Breunig, J. M.; Lehmann, F.; Bolte, M.; Lerner, H.-M.; Wagner, M. *Organometallics* **2014**, *33*, 3163– 3172. (c) Bromo: Seven, O.; Bolte, M.; Lerner, H. – W.; Wagner, M. *Organometallics* **2014**, *33*, 1291–1299.

(27) Brown, H. C.; Singaram, B.; Mathew, C. P. J. Org. Chem. 1981, 46, 4541-4544.

(28) Wiberg, E.; Evans, J. E. F.; Noth, H. Z. Naturforsch., B: J. Chem. Sci. 1958, 13, 265-266.

(29) Singaram, B.; Cole, T. E.; Brown, H. C. Organometallics 1984, 3, 774–777.

(30) For reviews of potassium trifluoroborate chemistry, see: (a) Molander, G. A.; Sandrock, D. L. *Curr. Opin. Drug Discovery Devel.* 2009, 12, 811–823. (b) Darses, S.; Genet, J. – P. *Chem. Rev.* 2008, 108, 288–325.

(31) Kim, B. J.; Matteson, D. S. Angew. Chem., Int. Ed. 2004, 43, 3056–3058.

(32) (a) Abbey, E. R.; Lamm, A. N.; Baggett, A. W.; Zakharov, L. N.; Liu, S. – Y. J. Am. Chem. Soc. **2013**, 135, 12908–12913. (b) Molander,

G. A.; Wisniewski, S. R.; Amani, J. Org. Lett. 2014, 16, 5636-5639.

(33) Morrison, D. J.; Piers, W. E.; Parvez, M. Synlett 2004, 13, 2429-2433.

(34) Seyferth converted $Ph_3PCH_2BF_3$ to $PH_3CH_2BH_3$ using LiAlH₄: Seyferth, D.; Grim, S. O. J. Am. Chem. Soc. **1961**, 83, 1613–1616.

(35) Determined by ¹¹B NMR.

(36) If additional purification is needed, compounds are redissolved in THF and again filtered through Celite.

(37) (a) Calculated using the method in ref 30. (b) Thermodynamic data for BF₃, BH₃, and AlF₃ taken from: NIST-JANAF Thermochemical Tables. *J. Phys. Chem. Ref. Data, Monograph* 9; Chase, M.W., Jr., Ed.; American Institute of Physics, 1998. (c) Thermodynamic data for AlH₃ are taken from: Graetz, J.; Reilly, J.; Sandrock, G.; Johnson, J.; Zhou, W. M.; Wegrzyn, J.Aluminum Hydride, AlH₃, as a Hydrogen Storage Compound; Brookhaven National Laboratory Formal Report BNL-77336-2006, U.S. Dept. of Energy, 2006; pp 57–63.

(38) The crystal structure of **10c** has been previously reported: JELWOP: Shooter, J.; Allen, C. J.; Tinsley, C. W. K.; Zakharov, L. N.; Abbey, E. R. *Acta Crystallogr. E: Cryst. Commun.* **2017**, *73*, 1747–1750.

(39) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. J. Chem. Soc., Perkin Trans. 2 **1987**, 12, S1–S19.

(40) (a) N1–B1 distance = 1.630(3) Å in VOGJEI: Chu, J.; Han, X.; Kefalidis, C. E.; Zhou, J.; Maron, L.; Leng, X.; Chen, Y. *J. Am. Chem. Soc.* **2014**, *136*, 10894–10897. (b) N1–B1 distance = 1.594(3) Å in JUDQAA: Lesley, M. J. G.; Woodward, A.; Taylor, N. J.; Marder, T. B.; Cazenobe, I.; Ledoux, I.; Zyss, J.; Thornton, A.; Bruce, D. W.; Kakkar, A. K. *Chem. Mater.* **1998**, *10*, 1355–1365.

(41) H6-H2B distance = 2.49 Å in MITPIQ: Seven, O.; Bolte, M.; Lerner, H.-W.; Wagner, M. Organometallics **2014**, 33, 1291–1299.