Experimental Section

8: Compound **7** (30.3 g, 0.1 mol) was added to a stirred solution of sodium cyclopentadienide (0.1 mol) in THF (600 mL) at 0°C under nitrogen atmosphere. After the mixture was stirred at 0°C for 15 min, solids were formed and removed by suction filtration through a celite pad. The solids and celite were washed with ethyl acetate/hexane (1/4), and the filtrate was concentrated under vacuum. The residual solids were purified by recrystallization from CH_2Cl_2/hexane (1/2) to give **8** as green plates (14.0 g, 63% yield). M.p. 145–147°C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.29$ (s, 6H; NCH_3), 6.26 (dt, $J = 5.0$, 1.7, 1H), 6.45 (ddm, $J = 5.0$, 3.1 Hz, 1H), 6.54 (ddm, $J = 5.0$, 3.1 Hz, 1H), 6.58 (ddm, $J = 4.6$, 2.9 Hz, 1H), 6.67 (dm, $J = 5.0$ Hz, 1H), 6.73 (dm, $J = 4.6$ Hz, 1H), 6.89 (dm, $J = 2.9$ Hz, 1H), 6.99 (d, $J = 12.4$ Hz, 1H), 7.00 (d, $J = 14.4$ Hz, 1H), 7.19 (dd, $J = 14.4$, 12.4 Hz, 1H), 7.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, −30°C): $\delta = 40.7$, 48.0, 114.0, 117.7, 118.9, 119.7, 121.4, 124.5, 129.2, 130.9, 131.4, 134.5, 141.2, 142.3, 147.6; IR (KBr): $\tilde{\nu} = 1623$, 1580, 1359, 1055 cm^{-1}; elemental analysis calcd for $C_{16}H_{17}N$: C 86.06, H 7.69, N 6.27; found: C 85.97, H 7.72, N 5.99.

4: A solution of **8** (1.00 g, 4.48 mmol) in 2,6-lutidine (200 mL) was refluxed under nitrogen atmosphere for 90 min. The solvent was removed under vacuum. The dark-colored solids were suspended in hexane (50 mL), and insoluble black solids were removed by filtration. The filtrate was concentrated with an evaporator, and the residue was purified by chromatography on silica gel with hexane as eluent to provide **4** as a dark red solid (16.5 mg, 2% yield). An analytical sample of **4** as red-purple leaflets was obtained by recrystallization from methanol/water (7/1). M.p. 139–140°C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.58$ (d, $J = 11.6$ Hz, 2H; H-4,6), 7.37 (t, $J = 4.0$ Hz, 2H; H-2, 8), 7.59 (dd, $J = 4.0$, 1.6 Hz, 2H; H-3,7), 7.71 (dd, $J = 4.0$, 1.6 Hz, 2H; H-1,9), 7.94 (t, $J = 11.6$ Hz, 1H; H-5), 8.64 (s, 1H; H-10); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 113.7$ (C-5), 128.9 (C-2,8), 129.5 (C-8a, 9a), 133.3 (C-3a, 6a), 138.4 (C-3, 7), 139.4 (C-1, 9), 140.0 (C-4, 6), 141.2 (C-10); IR (KBr): $\tilde{\nu} = 1589$, 1413, 1396, 1192, 774, 749 cm^{-1}; MS (70 eV): m/z (%): 179 ($M^+ + 1$, 15), 178 (M^+, 100), 177 (26), 152 (31), 76 (21); UV/Vis (n-hexane): λ_{max} (ε) = 213 (15100), 218 (15000), 222 (15200), 238sh (11000), 248sh (7840), 273sh (7760), 283 (9770), 290sh (8320), 329sh (38900), 344 (112000), 446 (1070), 468sh (933), 498sh (812), 531 (851), 608 (186), 631 (186), 649 (194), 663 (224), 677 (257), 692sh (355), 701 (407), 718 (427), 737 (437), 750 (746), 767 (1290), 800sh (36), 818sh nm (12); elemental analysis calcd for $C_{14}H_{10}$: C 94.35, H 5.65; found: C 94.19, H 5.80.

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Nonorthogonal Dilithium-1,3-biborataallenes Containing Planar-Tetracoordinate Carbon Atoms[**]

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Dieter Schweikart, Christian Balzereit,
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Orthogonality ($\Theta = 90°$) of the planes of the terminal atoms of the allene skeleton and their neighbors, here referred to as "terminal planes", is a characteristic feature of allenes. Strong deviation from this orthogonality has been observed up to now only for an allene skeleton as part of a highly strained six-membered ring.[1] Almost orthogonal ($\Theta = 92°$)[2] terminal planes have also been found for the heteroallene **1** of the ion pair $\mathbf{1} \cdot Li \cdot 3Et_2O$ (Scheme 1),[2] where **1** contains four sterically demanding aryl substituents. Here we present contaction triples of **2a**, which is isoelectronic with **1**, and of related tetraaryl-1,3-diboratallenes **2b–d** and show their planes

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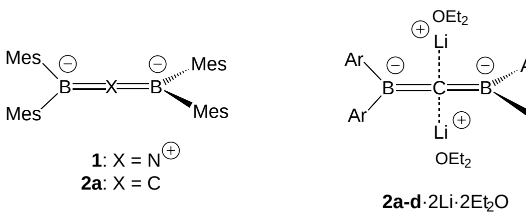
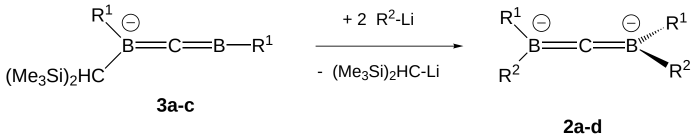


Scheme 1. Isoelectronic heteroallenes **1** and **2a** as well as contact-ion triples of the 1,3-diborataallenes **2a–d** (substituent key see Scheme 2).

deviate by up to 36° from orthogonality. The central carbon atoms in **2a–d**·2Li·2Et$_2$O are planar-tetracoordinate.[3–7]

The 1,3-diborataallenes **2a–d** were prepared analogously to **2e**[8] from anions **3a–c** and two equivalents of aryllithium compounds (Scheme 2). The NMR chemical shifts of the carbon atoms of their skeletons (Table 1) lie in the range characteristic for allenes. Figure 1 shows the crystal structures of **2b**·2Li·2Et$_2$O and **2d**·2Li·2Et$_2$O.[9] In Table 1 relevant experimental structure data of **2a–d** are compared to those calculated at the B3LYP level[10] for tetraphenyl- and tetra(*o*-methylphenyl)-1,3-diborataallenes, **2f** and **2g**, as well as for the unsubstituted 1,3-diborataallene **2h**.



Scheme 2. Syntheses of 1,3-diborataallenes **2a–d** from 1-bora-3-borata-allenes **3a–c** and aryllithium compounds LiR^2. Substituent key: **a**: R^1 = R^2 = 2,4,6-trimethylphenyl (mesityl, Mes); **b**: R^1 = R^2 = 2,3,5,6-tetramethylphenyl (duryl, Dur); **c**: R^1 = R^2 = 2,6-dimethyl-4-*tert*-butylphenyl; **d**: R^1 = Dur, R^2 = 2,4,5-trimethylphenyl; **e**: R^1 = Mes, R^2 = *tert*-butyl.

The 1,3-diborataallenes **2a–d** form contact-ion triples each with two lithium cations which, in addition, are coordinated to one molecule of Et$_2$O. The atoms of the skeleton B=C=B are arranged almost linear (176–179°). The terminal planes C$_i$-B1-C$_i$ and C$_i$-B3-C$_i$ in **2a–d**·2Li·2Et$_2$O form angles of Θ = 125, 119, 126, and 97°, respectively, with each other, and thus, deviate considerably from orthogonality in **2a–c**·2Li·2Et$_2$O. The central carbon atoms of all four contact-ion triples **2a–d**·2Li·2Et$_2$O are surrounded by two boron atoms and two lithium ions in a planar arrangement. With Li-C-B angles close to 90°, they are—like Al$_4$C anions[11]—rare examples of species in which planar-tetracoordinate carbon atoms form angles of comparable size with all their neighbors.

The heteroallenes **2a–c** that deviate strongly from orthogonality have short nonbonding distances (334–347 pm, see

Table 1. Selected NMR and structural data of contact-ion triples of **2a–e** (exp) and **2f–h** (calcd).

	$\delta(^{13}C)$ (CB_2)	$\delta^{11}B$	Θ [°]	Li-C-Li [°]	B-C-B [°]	$H_3C\cdots CH_3$[a] [pm]
2a·2Li·2Et$_2$O	205	26	124.9	174.9	179.4	346 346
2b·2Li·2Et$_2$O	206	28	119.0	176.2	177.2	334.1 337.2
2c·2Li·2Et$_2$O	205	27	125.8	177.1	179.2	347.3 342.4
2d·2Li·2Et$_2$O	215	27	96.7	174.5	176.3	373.7[b] 383.5[b]
2e·2Li·2Et$_2$O	180	32	97	120.1	168.4	585.1 401.9[c]
2f·2Li·2Me$_2$O	–	–	95.5	177.5	180.0	–
2f·2Li	–	–	114.4	179.8	180.0	–
2g·2Li	–	–	133.9	180.0	180.0	381.3
2h·2Li	–	–	89.7	150.4	180.0	–

[a] Distance between *o*-methyl carbon atoms (see Figure 1 top). [b] Distance $H_3C\cdots C_o$-H between *o*-methyl carbon atoms and *o*-carbon atoms (see Figure 1 bottom). [c] Distance between methyl carbon atoms of *tert*-butyl groups at different boron atoms.

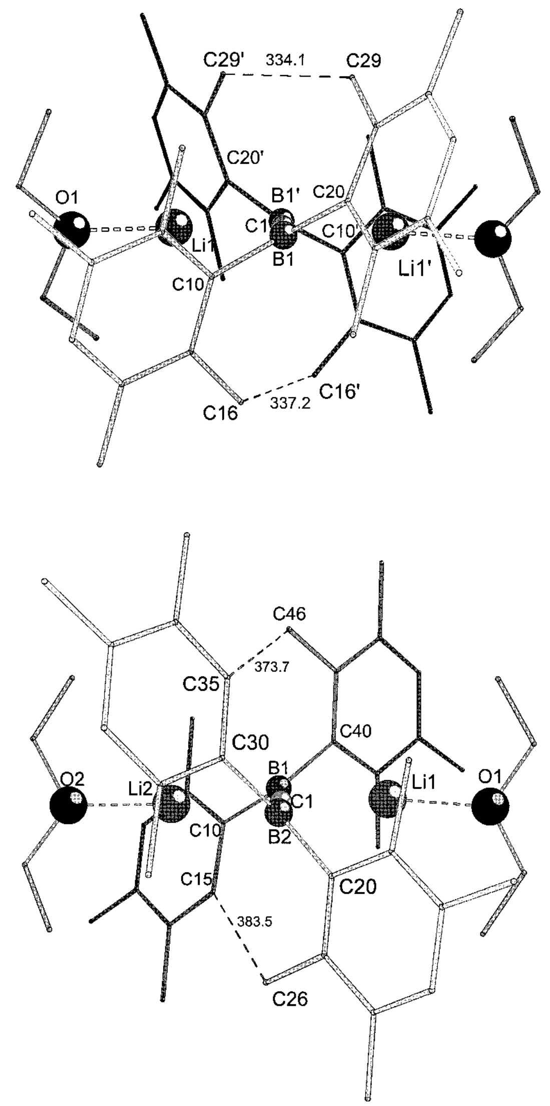
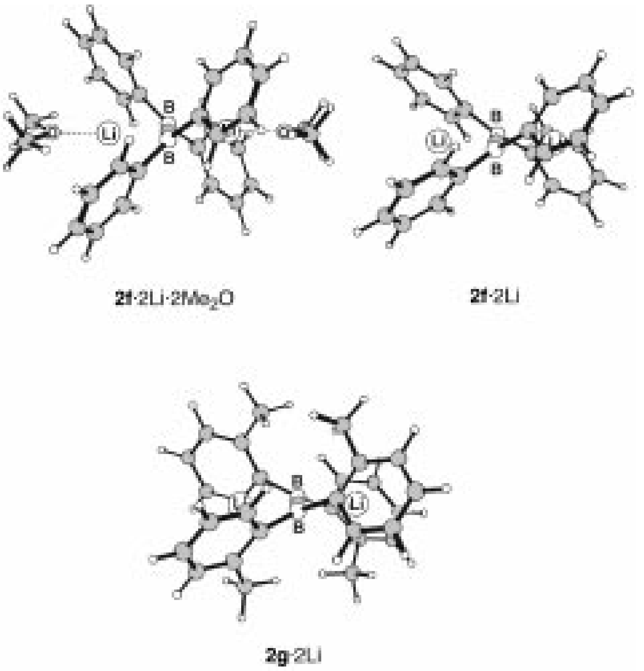


Figure 1. Crystal structures of **2b**·2Li·2Et$_2$O (top) and **2d**·2Li·2Et$_2$O (bottom). Selected bond lengths [pm] and angles [°] (completing Table 1). **2b**·2Li·2Et$_2$O: C1-B1 146.5(1), B1-C10 164.9(2), B1-C20 166.6(2), C1-Li1 206.1(2), B1-Li1 253.0(3), B1-Li1′ 252.5(3), O-Li1 193.9(2), C10-Li1 248.1(3), C20-Li1 276.3(3); C1-B1-C10 119.3(1), C1-B1-C20 127.1 (1), C10-B1-C20 113.4(1); **2d**·2Li·2Et$_2$O: C1-B1 145.8(7), C1-B2 146.8(7), B1-C10 162.0(8), B1-C40 162.9(7), B2-C20 162.9(7), B2-C30 161.7(6), C1-Li1 199.8(11), C1-Li2 205.2(11), B1-Li1 244.0(13), B1-Li2 243.8(10), B2-Li1 257.7(12), B2-Li2 253.6(14), O1-Li1 189.9(11), O2-Li2 190.3(10), C20-Li1 294(1), C40-Li1 256(2), C10-Li2 249(1), C30-Li2 275(1); C1-B1-C10 121.6(4), C1-B1-C40 122.8(4), C10-B1-C40 115.6(4), C1-B2-C20 124.6(4), C1-B2-C30 118.4(4), C20-B2-C30 117.0(4).

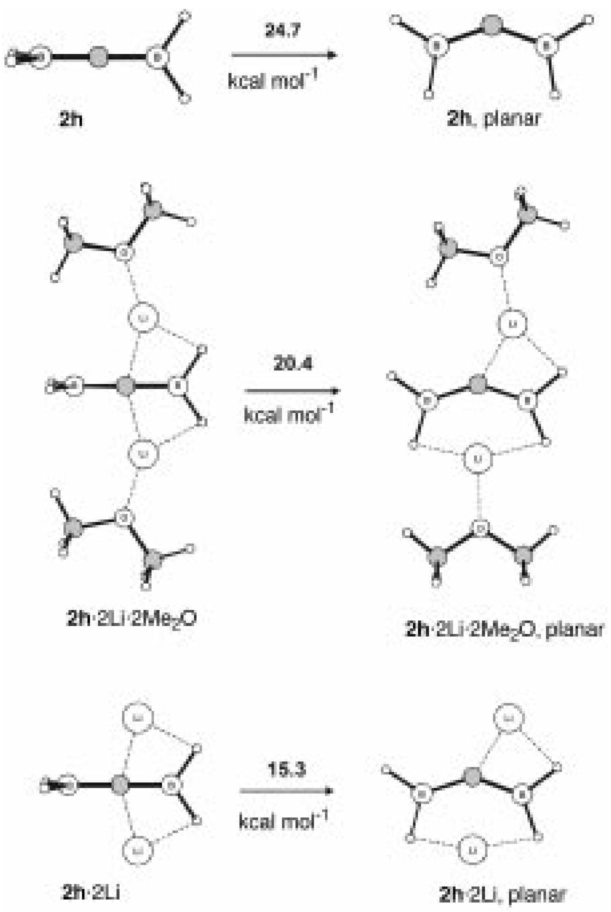
Table 1) between carbon atoms of *ortho*-methyl groups of aryl substituents, which are bound to different boron atoms and coordinated to different lithium ions (**2b**: C29···C29′ and C16···C16′). These distances are considerably shorter than the sum of the van der Waals radii of two methyl groups (400 pm).[12] Figure 1 reveals that these nonbonding distances would become even shorter, if the angle between the terminal planes decreased to approach 90°. The terminal planes of **2d**·2Li·2Et$_2$O deviate only by 7° from orthogonality. This can be explained by the lack of steric hindrance because two of the aryl groups of **2d**·2Li·2Et$_2$O bear only a hydrogen atom at an *ortho*-carbon atom. The distances of these *ortho*-carbon atoms to the carbon atoms of *ortho*-methyl groups of duryl substituents are considerably longer (374 and 384 pm) than those between *ortho*-methyl groups in **2a**–**c**·2Li·2Et$_2$O. Thus, steric hindrance plays an important role in the deviation from orthogonality in **2a**–**c**·2Li·2Et$_2$O. However, four aryl substituents each with two *ortho*-methyl groups *alone* are not sufficient to create strong distortions, as seen by the angle of $\Theta = 92°$ for **1**.[2] Evidently, interactions of the aryl rings with the lithium cations, which are absent in the solvent-separated ion pair **1**·Li·3Et$_2$O, play a decisive role in contact-ion triples **2a**–**c**·2Li$_2$·2Et$_2$O.

This argumentation is supported by calculations at the B3LYP/6-31G(d) level for contact-ion triples of tetraphenyl-1,3-diborataallene **2f** with and without ether ligands at the lithium cations. A torsion angle of 95.5° is obtained for **2f**·2Li·2Me$_2$O, but a considerably larger angle of 114.4° for **2f**·2Li (Scheme 3). There are four short Li···C$_i$ distances (250.0 ± 0.6 pm) in **2f**·2Li, but two significantly longer ones (260.1 pm) and two very long distances (271.3 pm) in **2f**·2Li$_2$·2Me$_2$O. These differences can be explained by the well-known[13] decrease of the coordination ability of lithium cations versus π ligands by ether ligands. Since **2f**·2Li·2Me$_2$O without *ortho*-methyl substituents shows almost no deviation from orthogonality ($\Theta = 95.5°$), the strong deviations in contact-ion triples **2a**–**c**·2Li·2Et$_2$O must be due to steric hindrance; **2f**·Li$_2$ *without* coordinated ether molecules deviates considerably from orthogonality inspite of lacking steric hindrance. Adding steric hindrance to ether-free contact-ion triples of dilithium tetraaryl-1,3-diborataallenes leads to even stronger deviations from orthogonality: a torsion angle of 133.9° is calculated for **2g**·2Li (Scheme 3).



Scheme 3. Calculated structures for contact-ion triples from tetraphenyl- and tetra-(*o*-methylphenyl)-1,3-diborataallenes **2f** and **2g** and two lithium ions *without* (top right and bottom) and *with* dimethyl ether ligands (top left).

Calculations[10] also show that 1,3-diborataallenes are considerably easier to distort than isoelectronic allenes.[14] According to our calculations, planarization requires 43.6 kcal mol^{-1} for unsubstituted allene but only 24.7 kcal mol^{-1} for unsubstituted 1,3-diborataallene **2h**. Even smaller energies are calculated for the contact-ion triples **2h**·2Li·2Me$_2$O and **2h**·2Li: 20.4 and 15.3 kcal mol^{-1}, respectively (Scheme 4).[15]



Scheme 4. Energies for the planarization of unsubstituted 1,3-diborataallene **2h** (top) and its contact-ion triples with two lithium ions *without* (bottom) and *with* (center) dimethyl ether ligands.

In conclusion, the strong deviations from orthogonality in dilithium-1,3-diborataallenes **2a**–**c**·2Li·2Et$_2$O are due to the following effects: distortion towards planarity requires less energy in 1,3-diborataallene than in allene, and interaction of the lithium cations with the π electrons of the arylsubstituents leads to steric hindrance between *ortho*-methyl groups of aryl substituents bound to different boron atoms.

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[9] Crystal structure determinations: $\mathbf{2a}\cdot 2\,\mathrm{Li}\cdot 2\,\mathrm{Et_2O}$: Owing to bad crystal quality and severe disorder of ether molecules the actual results of X-ray structure analyses are not yet satisfactory ($R = 0.12$). Thus, only a few preliminary geometrical data are included here. $\mathbf{2b}\cdot 2\,\mathrm{Li}\cdot 2\,\mathrm{Et_2O}$: A colorless crystal ($0.60 \times 0.45 \times 0.25$ mm) was investigated at 193 K on an IPDS area-detector system (Stoe) using $\mathrm{Mo_{K\alpha}}$ radiation. $\mathrm{C_{49}H_{72}B_2Li_2O_2}$, monoclinic, space group $C2/c$, $Z = 4$, $a = 2179.8(1)$, $b = 935.03(4)$, $c = 2199.4(1)$ pm, $\beta = 97.750(7)°$, $V = 4441.7 \times 10^{-30}\,\mathrm{m^3}$, $\rho_{\mathrm{calcd}} = 1.090\,\mathrm{Mg\,m^{-3}}$. A total of 16991 reflections were collected up to $\theta = 26°$, 4324 unique ($R_{\mathrm{int}} = 0.031$), 2972 with $I > 2\sigma(I)$. The structure was solved by direct methods and refined against all F^2 data by full-matrix least-squares methods with H atoms "riding" on calculated positions; $wR_2 = 0.1013$ for all reflections, $R = 0.0374$ for the observed ones. $\mathbf{2c}\cdot 2\,\mathrm{Li}\cdot 2\,\mathrm{Et_2O}\cdot 3\,\mathrm{toluene}$: A light-yellow crystal ($0.55 \times 0.30 \times 0.12$ mm) was investigated at 193 K on an IPDS area-detector system (Stoe) using $\mathrm{Mo_{K\alpha}}$ radiation. $\mathrm{C_{78}H_{112}B_2Li_2O_2}$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 1819.4(7)$, $b = 2645.7(4)$, $c = 1695.0(4)$ pm, $\beta = 117.4(4)°$, $V = 7242 \times 10^{-30}\,\mathrm{m^3}$, $\rho_{\mathrm{calcd}} = 1.025\,\mathrm{Mg\,m^{-3}}$. A total of 40229 reflections were collected up to $\theta = 24.1°$, 11144 unique ($R_{\mathrm{int}} = 0.114$), 3365 with $I > 2\sigma(I)$. The structure was solved by direct methods and refined against all F^2 data by full-matrix least-squares methods with H atoms "riding" on calculated positions; $wR_2 = 0.247$ for all reflections, $R = 0.0795$ for the observed ones. The modest quality may be attributed to the weak scattering power of the crystal and strong disorder of the three toluene molecules, which were refined using split-atom positions. $\mathbf{2d}\cdot 2\,\mathrm{Li}\cdot 2\,\mathrm{Et_2O}$: A light-yellow crystal ($0.30 \times 0.30 \times 0.20$ mm) was investigated at 193 K on an IPDS area-detector system (Stoe) using $\mathrm{Mo_{K\alpha}}$ radiation. $\mathrm{C_{47}H_{68}B_2Li_2O_2}$, orthorhombic, space group $Pca2_1$, $Z = 4$, $a = 1585.6(1)$, $b = 1553.2(1)$, $c = 1829.6(1)$ pm, $V = 4505.3 \times 10^{-30}\,\mathrm{m^3}$, $\rho_{\mathrm{calcd}} = 1.033\,\mathrm{Mg\,m^{-3}}$. A total of 24410 reflections were collected up to $\theta = 24.15°$, 7088 unique ($R_{\mathrm{int}} = 0.121$), 2893 with $I > 2\sigma(I)$. The structure was solved by direct methods and refined against all F^2 data by full-matrix least-squares methods with H atoms "riding" on calculated positions; $wR_2 = 0.1760$ for all reflections, $R = 0.0605$ für the observed ones. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156101 ($\mathbf{2b}\cdot 2\,\mathrm{Li}\cdot 2\,\mathrm{Et_2O}$), CCDC-156102 ($\mathbf{2c}\cdot 2\,\mathrm{Li}\cdot 2\,\mathrm{Et_2O}$), and CCDC-156103 ($\mathbf{2d}\cdot 2\,\mathrm{Li}\cdot 2\,\mathrm{Et_2O}$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] a) All geometries were optimized by using the B3LYP hybrid functional with a 6-31G(d) basis set. For the calculation of the structures and rotational barriers of the 1,3-diborataallenes **2h**, $\mathbf{2h}\cdot 2\,\mathrm{Li}$, and $\mathbf{2h}\cdot 2\,\mathrm{Li}\cdot 2\,\mathrm{OMe_2}$ it was necessary to augment the basis set with diffuse functions at the havier atoms 6-31+G(d). All structures were characterized to be local minima or transition states by calculating the vibrational frequencies. b) Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; d) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

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[15] Exact handling of the biradical singlet character of this species requires a multideterminant procedure. The rotational barriers of this work are based on open-shell B3LYP calculations which, according to reference [14], are sufficient to determine such barriers.