Supporting Information

Ditopic Hydridoborates and Hydridoboranes: Bridging Ligands in Coordination Polymers and Versatile Hydroboration Reagents

Daniel Franz, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner*

Content:

X-ray crystal structure analyses of 3, 4, 5, and $(Li(thf)_2)_2$[6]

Experimental Details. Data were collected on a STOE IPDS II two-circle diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). An empirical absorption correction was performed for **4** using the MULABS[1] option in PLATON[2]. The structures were solved by direct methods using the program SHELXS[3] and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97[4].

Compound **3** crystallises with two crystallographically independent half-molecules in the asymmetric unit (**3$_A$**, **3$_B$**). In **5**, three atoms of an *n*-hexyl chain are disordered over two sites with a site occupation factor of 0.69(1) for the major occupied site. The disordered atoms in **5** were refined isotropically. The crystals of **5** degraded upon cooling and had therefore to be measured at 293 K, which, together with the disorder, explains the poor figures of merit.

CCDC reference numbers: 793266 (**3**), 793267 (**4**), 793268 (**5**), and 793269 ($(Li(thf)_2)_2$[**6**]).

[1] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33-38. [2] A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7-13. [3] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467-473. [4] G. M. Sheldrick, *SHELXL-97. A Program for the Refinement of Crystal Structures*, Universität Göttingen, 1997.

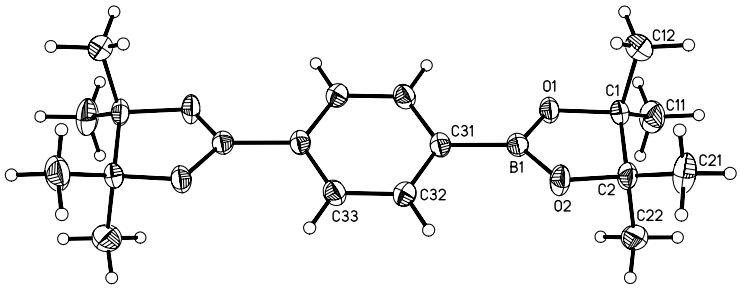

Figure 1S: Molecular structure and numbering scheme of compound **3$_A$**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−O(1) 1.368(2), B(1)−O(2) 1.367(2), B(1)−C(31) 1.567(2); O(1)−B(1)−O(2) 113.9(1), O(1)−B(1)−C(31) 122.5(1), O(2)−B(1)−C(31) 123.6(1); O(2)−B(1)−C(31)−C(32) −16.6(2). *Note*: Compound **3** crystallises with two crystallographically independent half-molecules in the asymmetric unit (**3$_A$**, **3$_B$**). Since all key structure parameters of **3$_A$** and **3$_B$** are very similar, only the data of **3$_A$** are given here.

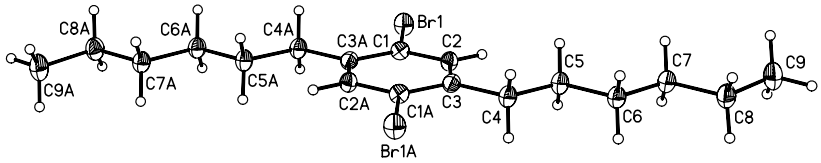

Figure 2S: Molecular structure and numbering scheme of compound **4**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond length (Å), bond angles (deg), and torsion angle (deg): Br(1)−C(1) 1.901(2); Br(1)−C(1)−C(2) 117.2(1), Br(1)−C(1)−C(3A) 119.8(1), C(2)−C(1)−C(3A) 122.9(2); C(2)−C(3)−C(4)−C(5) 0.1(2). Symmetry transformation used to generate equivalent atoms: A: −x, −y, −z+1.

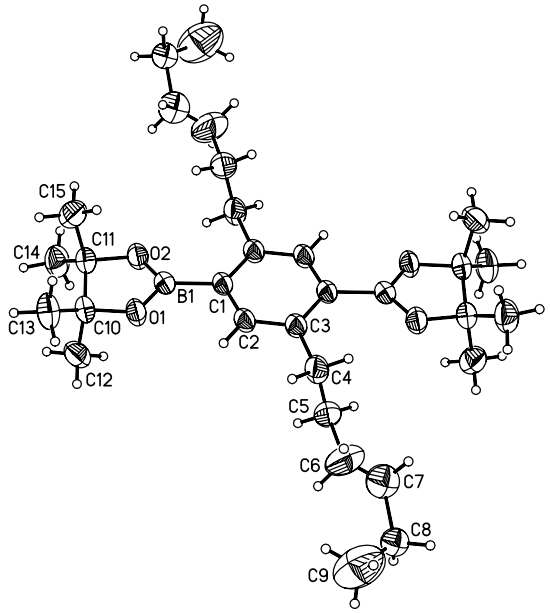

Figure 3S: Molecular structure and numbering scheme of compound **5**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−O(1) 1.362(3), B(1)−O(2) 1.349(4), B(1)−C(1) 1.571(4); O(1)−B(1)−O(2) 112.8(2), O(1)−B(1)−C(1) 120.4(2), O(2)−B(1)−C(1) 126.8(2); O(1)−B(1)−C(1)−C(2) 8.7(4), C(2)−C(3)−C(4)−C(5) 92.8(4).

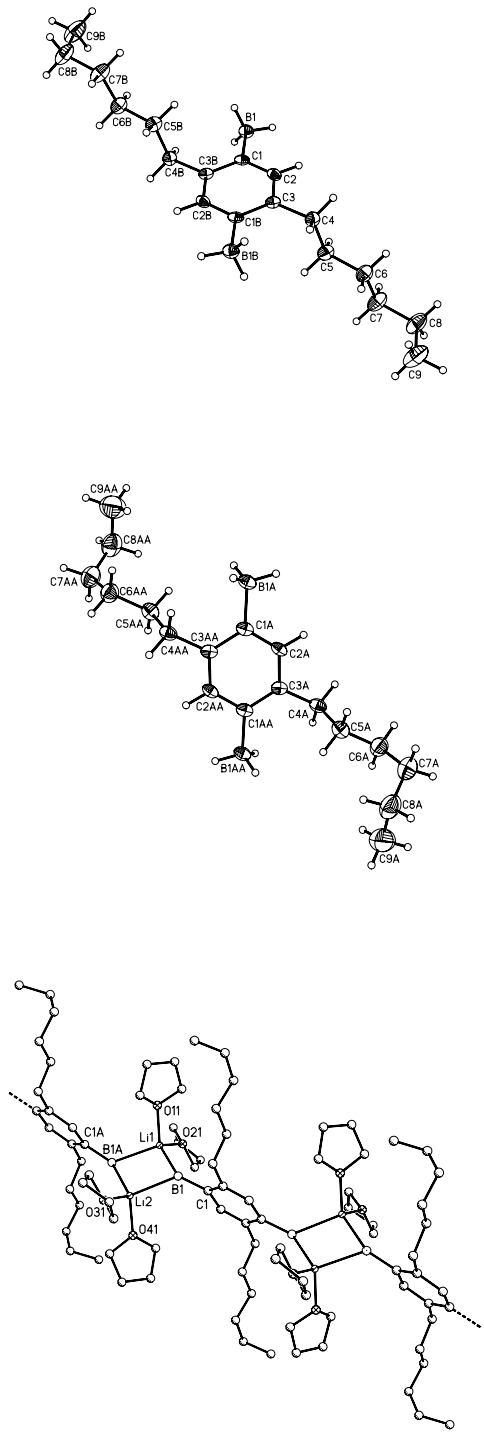

Figure 4S: Molecular structure of $(Li(thf)_2)_2$[**6**]; hydrogen atoms attached to carbon have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), atom···atom distances (Å), angles (deg), and dihedral angle (deg): B(1)−C(1) = 1.615(2), B(1A)−C(1A) = 1.618(2), B(1)···Li(1) 2.448(1), B(1)···Li(2) 2.516(4), B(1A)···Li(1) 2.492(5), B(1A)···Li(2) 2.443(1), Li(1)···Li(2) 3.135(4); B(1)···Li(1)···B(1A) 101.5(1), B(1)···Li(2)···B(1A) 101.0(1), Li(1)···B(1)···Li(2) 78.3(1), Li(1)···B(1A)···Li(2) 78.9(1); C(1)C(2)C(3)//C(1A)C(2A)C(3A) 7.0.

Table 1S: Crystallographic Data for **3** and **4**.

	3	**4**
formula	$C_{18}H_{28}B_2O_4$	$C_{18}H_{28}Br_2$
fw	330.02	404.22
colour, shape	colourless, block	colourless, plate
temp (K)	173(2)	173(2)
cryst. syst.	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.3824(8)	6.6943(6)
b (Å)	9.8427(9)	7.8948(8)
c (Å)	12.8041(12)	9.8024(9)
α (deg)	102.329(7)	109.190(7)
β (deg)	96.038(8)	99.292(7)
γ (deg)	110.013(7)	108.450(7)
V (Å^3)	951.26(15)	443.27(7)
Z	2	1
$D_{calcd.}$ (g cm^{-3})	1.152	1.514
F(000)	356	206
μ (mm^{-1})	0.077	4.563
cryst. size (mm)	0.25 × 0.24 × 0.22	0.25 × 0.25 × 0.13
reflections collected	14687	7617
indep. reflns (R_{int})	3545 (0.0378)	1798 (0.0594)
data/restraints/params	3545 /0/218	1798/0/92
GOOF on F^2	1.024	1.077
*R*1, w*R*2 ($I > 2\sigma(I)$)	0.0385, 0.0928	0.0243, 0.0592
*R*1, w*R*2 (all data)	0.0494, 0.0973	0.0257, 0.0597
Largest diff peak and hole (eÅ^{-3})	0.234 and −0.156	0.383 and −0.545

Table 2S: Crystallographic Data for **5** and $(Li(thf)_2)_2$[**6**].

	5	$(Li(thf)_2)_2$[**6**]
formula	$C_{30}H_{52}B_2O_4$	$C_{34}H_{66}B_2Li_2O_4$
fw	498.34	574.37
colour, shape	colourless, block	colourless, needle
temp (K)	293(2)	173(2)
cryst. syst.	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.6693(9)	9.2666(10)
b (Å)	9.4074(10)	14.2673(15)
c (Å)	11.9721(13)	15.9830(19)
α (deg)	76.715(8)	67.763(8)
β (deg)	86.255(9)	76.707(9)
γ (deg)	73.941(8)	75.464(9)
V (Å^3)	807.84(16)	1871.7(4)
Z	1	2
$D_{calcd.}$ (g cm^{-3})	1.024	1.019
F(000)	274	636
μ (mm^{-1})	0.064	0.062
cryst. size (mm)	0.51 × 0.48 × 0.39	0.32 × 0.14 × 0.13
reflections collected	13355	11646
indep. reflns (R_{int})	2851 (0.0754)	6579 (0.0788)
data/restraints/params	2851/0/163	6579/0/381
GOOF on F^2	1.112	0.829
*R*1, w*R*2 ($I > 2\sigma(I)$)	0.0841, 0.2535	0.0572, 0.0961
*R*1, w*R*2 (all data)	0.1003, 0.2677	0.1275, 0.1117
Largest diff peak and hole (eÅ^{-3})	0.368 and −0.284	0.233 and −0.196