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Ditopic hydridoborates and hydridoboranes: bridging ligands in coordination polymers and versatile hydroboration reagents[†]

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Single crystals of the *meta*- and *para*-phenylene-bridged ditopic trihydridoborates (Li(THF)₂)₂[*m*-C₆H₄(BH₃)₂] and (Li(THF)₂)₂[*p*-C₆H₄(BH₃)₂] have been prepared and investigated by X-ray crystallography. The compounds turned out to be coordination polymers in which each trihydridoborate substituent is connected with one trihydridoborate substituent of a neighbouring monomer *via* two bridging Li(THF)₂⁺ ions. (Li(THF)₂)₂[*m*-C₆H₄(BH₃)₂] and (Li(THF)₂)₂[*p*-C₆H₄(BH₃)₂] suffer from poor solubility in all common non-protic solvents. Thus, a more soluble derivative of (Li(THF)₂)₂[*p*-C₆H₄(BH₃)₂], equipped with *n*-hexyl groups at the positions 2 and 5 of the phenylene ring, has been used for all further investigations (*i.e.*, compound Li₂[**6**]). Treatment of Li₂[**6**] with Me₃SiCl in the presence of excess N(Me)₂Et leads to the abstraction of one hydride ion per boron atom under formation of the ditopic amine-borane adduct *p*-C₆H₂(*n*-hexyl)₂(BH₂-N(Me)₂Et)₂ (**7**). The compound turned out to be an efficient hydroboration reagent both for internal olefins (*i.e.*, 1,5-cyclooctadiene) and terminal alkynes (*i.e.*, *tert*-butyl acetylene) to give *p*-C₆H₂(*n*-hexyl)₂(9-BBN)₂ (**8**; 9-BBN = 9-borabicyclo[3.3.1]nonyl) and *p*-C₆H₂(*n*-hexyl)₂(B(C(H)=C(H)tBu)₂)₂ (**9**), respectively.

Introduction

For 50 years organoboranes have been used as versatile reagents in organic synthesis.¹ More recently, they have also found widespread applications as homogeneous (co)catalysts^{2–5} and anion sensors.^{6,7} One of the latest advances is the incorporation of boron into extended π -electron systems, which leads to materials with highly useful optoelectronic properties.^{8,9}

In many of these cases the hydroboration reaction plays a crucial role: not only in the course of multistep organic transformations when the organoborane is only a reaction intermediate,¹ but also as a powerful tool for the preparation of sophisticated boron-containing frameworks when the organoborane is the actual target molecule.¹⁰⁻¹⁷ Considerable effort has therefore been devoted to the development of organyl(hydrido)boranes with optimised reactivity, *e.g.*, improved regioselectivity (*cf.* 9-borabicyclo[3.3.1]nonane¹⁸) or applicability in asymmetric synthesis (*cf.* diisopinocampheylborane¹⁹). However, compared to the wealth of information that has been gathered on monotopic organyl(hydrido)boranes, their oligotopic congeners, *i.e.*, electron-precise compounds containing more than one R_2B -H group, have so far largely been neglected – with the remarkable excep-

tion of a number of polystyrene-supported borane complexes that were reported by Jäkle et al.14 This lack of oligotopic organyl(hydrido)boranes is surprising, because they could be relevant in various fields of chemistry as illustrated by the following examples: (i) A borane reagent or catalyst that possesses two boryl groups for cooperative substrate activation/orientation can give enhanced reactivity/chemoselectivity.²⁰⁻²⁴ (ii) When a monoorganylborane like MesBH₂ (Mes = mesityl) is used in the hydroboration polymerisation of dialkynes,^{10,11,25} the first hydroboration event (MesBH₂ + HC \equiv CR \rightarrow MesB(H)R'; R': C(H) = C(H)R) occurs under significantly different electronic and steric conditions than the second addition reaction (MesB(H)R'+ $HC \equiv CR \rightarrow MesBR'_{2}$). This factor, which has a negative impact on the polydispersity of the material obtained, can be largely eliminated by employing an appropriate ditopic hydridoborane with two spatially separated, but chemically related, B-H functionalities.

Given this background, we have recently begun to systematically investigate the chemistry of oligotopic hydridoborates and -boranes and to explore promising applications of this class of compounds. For example, starting from the ferrocenylene-bridged hydridoborate Li₂[**I**] (Fig. 1), the corresponding hydridoborane $Fe(C_5H_4BH_2)_2$ has been liberated by hydride abstraction with Me₃SiCl and trapped as N(Me)₂Et- or SMe₂-adduct **II** (Fig. 1).¹⁵ In the absence of Lewis basic donors, $Fe(C_5H_4BH_2)_2$ undergoes a condensation reaction with liberation of B₂H₆ and formation of the polymeric borane **III** (Fig. 1).¹⁵

Contrary to $Fe(C_5H_4BH_2)_2$, the ditopic borane 9,10-dihydro-9,10-diboraanthracene is stable not only as the base adduct,

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Fig. 1 The ditopic trihydridoborate $Li_2[I]$, the ditopic dihydridoborane II, and the oligotopic boranes III and IV.

but also in pure form and exists as a unique B–H–B-bridged coordination polymer in the solid state (*cf.* **IV**, Fig. 1).^{16,17} Polymer **IV** has already been successfully employed for the preparation of boron-doped conjugated π -electron systems *via* hydroboration reactions.^{16,17}

Compound IV can be viewed as an *ortho*-phenylene-bridged ditopic hydridoborane. The purpose of this paper is to report on related *meta*- and *para*-phenylene-bridged species; as in the case of the ferrocenylene derivatives $\text{Li}_2[\mathbf{I}]$ and \mathbf{II} , the corresponding hydridoborates will be included into the discussion.

Results and discussion

Meta- and para-phenylene-bridged ditopic hydridoborates

At the first stage, we aimed for the synthesis of the parent systems $\text{Li}_2[m-2]$ and $\text{Li}_2[p-2]$ (Scheme 1).

In order to prepare Li₂[*m*-2], *m*-bis(dibromoboryl)benzene (1)²⁶ was first converted *via* ether cleavage into *m*bis(dialkoxyboryl)benzenes, which could subsequently be transformed into the hydridoborate by means of Li[AlH₄]. For the synthesis of Li₂[*p*-2] we found it convenient to start from literature-known *p*-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)benzene²⁷ (3; *cf.* the ESI† for an X-ray crystal structure determination of 3); Li[AlH₄] was again employed as the hydride transfer reagent. Even though we were fortunate to obtain a few single crystals of Li₂[*m*-2] and Li₂[*p*-2] suitable for X-ray crystallography, it soon became evident that facile access to more soluble derivatives of Li₂[*m*-2] and Li₂[*p*-2] is mandatory for further progress (see below).

Li₂[*m*-2] crystallises from THF–Et₂O with 4 equiv. of THF ((Li(THF)₂)₂[*m*-2]; Fig. 2 top and Table 1). The crystal lattice of (Li(THF)₂)₂[*m*-2] consists of zigzag coordination polymer strands that are held together by interactions between two Li⁺ ions and two negatively charged trihydridoborate moieties. A C_2 -axis runs through the carbon atoms C(1) and C(4) and an inversion centre is located at the midpoint of each B₂Li₂ ring. The *meta*-phenylene rings within each polymer chain as well as the phenylene bridges of different chains adopt crystallographically imposed coplanar conformations. The distances between the Li⁺



Scheme 1 Synthesis of the *meta*- and *para*-phenylene-bridged ditopic trihydridoborates Li₂[*m*-2] and Li₂[*p*-2]. (i) Toluene, reflux, 1 h. (ii) THF, rt. (iii) Et₂O, 0 °C \rightarrow rt. (iv) THF–Et₂O, rt, 12 h.

ions and the boron atoms amount to $B(1)\cdots Li(1) = 2.469(4)$ Å and $B(1)\cdots Li(1A) = 2.537(4)$ Å. Using Edelstein's²⁸ correlation of metal-boron distances as a measure of the denticity of a trihydridoborate group, values of 1.6 ± 0.1 Å and 1.36 ± 0.06 Å are estimated for the ionic radii of bidentate and tridentate trihydridoborate ligands, respectively. Thus, $B \cdots Li$ distances of about 2.50 Å and 2.26 Å can be expected for $RBH_3-\eta^2$ -Li and

Table 1 Crystallographic data for (Li(THF)₂)₂[m-2] and (Li(THF)₂)₂[p-2]

	$(Li(THF)_2)_2[m-2]$	$(Li(THF)_2)_2[p-2]$
Formula	$C_{11}H_{21}BLiO_2$	$C_{11}H_{21}BLiO_2$
fw	203.03	203.03
Colour, shape	colourless, block	colourless, block
T/K	173(2)	173(2)
Cryst. syst.	Monoclinic	Triclinic
Space group	C2/c	$P\bar{1}$
a/Å	14.456(2)	8.8448(8)
b/Å	11.0059(11)	9.0494(8)
c/Å	16.369(2)	9.1349(9)
α (°)	90	73.851(7)
β (°)	106.218(11)	68.733(7)
γ (°)	90	66.814(7)
$V/Å^3$	2500.7(5)	618.47(10)
Ζ	8	1
$D_{\rm c}/{\rm g~cm^{-3}}$	1.079	1.090
F(000)	888	222
μ/mm^{-1}	0.068	0.069
Cryst. size/mm	$0.52 \times 0.45 \times 0.38$	$0.37 \times 0.33 \times 0.32$
Reflections collected	5116	14793
Indep. reflns (R_{int})	2300 (0.0209)	2176 (0.0470)
Data/restraints/params	2300/0/158	2176/0/147
GOOF on F^2	1.052	1.075
$R_1, \mathrm{w}R_2 \ (I > 2\sigma(I))$	0.0642, 0.1711	0.0679, 0.1865
R_1 , w R_2 (all data)	0.0759, 0.1808	0.0755, 0.1927
Largest diff peak and	0.539 and -0.303	0.687 and -0.404
hole/e Å ⁻³		



Fig. 2 Molecular structures of $(\text{Li}(\text{THF})_2)_2[m-2]$ (top) and $(\text{Li}(\text{THF})_2)_2[p-2]$ (bottom) in the solid state; hydrogen atoms attached to carbon have been omitted for clarity. Selected bond lengths (Å), atom \cdots atom distances (Å), and angles (deg): $(Li(THF)_2)_2[m-2]$: B(1)–C(2) 1.616(3), B(1) \cdots Li(1) 2.469(4), B(1) \cdots Li(1A) 2.537(4), Li(1) \cdots Li(1A) 3.138(7); B(1) \cdots Li(1) \cdots B(1A) 102.4(1), Li(1) \cdots B(1) \cdots Li(1A) 77.6(1). Symmetry transformation used to generate equivalent atoms: A: -x+1, -y+1, -z+1. ($Li(THF)_2)_2[p-2]$: B(1)–C(1) 1.622(3), B(1) \cdots Li(1) 2.504(4), B(1) \cdots Li(1A) 2.522(4), Li(1) \cdots Li(1A) 3.182(7); B(1) \cdots Li(1A) 78.6(1). Symmetry transformation used to generate equivalent atoms: A: -x+1, -y+1, -z+1.

RBH₃- η^3 -Li coordination modes, respectively (ionic radii of Li⁺ = 0.90 Å (c. n. 6), 0.73 (c. n. 4)²⁹). This leads to the conclusion that each Li⁺ ion in (Li(THF)₂)₂[*m*-2] is η^2 -coordinated to one RBH₃⁻ ligand, whereas the binding mode to the other RBH₃⁻ unit is intermediate between η^2 and η^1 . The coordination sphere of each Li⁺ ion is completed by two THF ligands.

The solid-state structure of $(\text{Li}(\text{THF})_2)_2[\textbf{p-2}]$ (Fig. 2 bottom and Table 1) closely resembles that of $(\text{Li}(\text{THF})_2)_2[\textbf{m-2}]$, apart from the fact that, because of the *para*-phenylene linker, the polymer backbone is now straighter. Each hydridoborate unit in $(\text{Li}(\text{THF})_2)_2[\textbf{p-2}]$ acts as an η^2 -ligand towards two Li⁺ ions $(B(1)\cdots Li(1) 2.504(4) \text{ Å}, B(1)\cdots Li(1\text{A}) 2.522(4) \text{ Å}).$

The polymeric nature of $(\text{Li}(\text{THF})_2)_2[m-2]$ and $(\text{Li}(\text{THF})_2)_2[p-2]$ forms a striking contrast to the solid-state structure of the ferrocenylene-bridged hydridoborate Li₂[I] (Fig. 1). Li₂[I] has been crystallised as Et₂O adduct and its crystal lattice consists of

discrete dimeric entities.¹⁵ The anionic constituents of these dimers adopt *syn*-conformations as indicated in Fig. 1 and are bridged by four Li⁺ counterions *via* B–H–Li interactions.

Solubilised *para*-phenylene-bridged ditopic hydridoborates and hydridoboranes

With regard to the preparation of soluble 2-type molecules, we focused on the *para*-derivatives, because the doubly *n*-hexyl-substituted congener 5 (Scheme 2) of our previously employed starting material 3 (Scheme 1) is literature-known.³⁰ Compound 5 had been synthesised by esterification of the corresponding boronic acid with pinacol; the boronic acid, in turn, is accessible *via* lithium-halogen exchange between 1,4-dibromo-2,5-di-*n*-hexylbenzene (4)^{31,32} and *n*-BuLi, followed by addition of trimethyl borate and acidic aqueous workup.³³ However,



Scheme 2 Synthesis of the solubilised ditopic trihydridoborate Li₂[6] and the corresponding amine-borane adduct 7 (Bpin: 4,4,5,5-tetra-methyl-1,3,2-dioxaborolyl; [Pd]: Pd₂dba₃·CHCl₃/P(Me)*t*Bu₂). (i) Toluene, 90 °C, 4 d. (ii) Et₂O, 0 °C \rightarrow rt, 2 h. (iii) THF, -196 °C \rightarrow rt, 12 h.

we find it more convenient to synthesise **5** in one step *via* a transition metal-mediated borylation reaction starting from **4** (Scheme 2), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin), NEt₃ and Pd₂dba₃·CHCl₃/P(Me)*t*Bu₂ as the catalyst (dba: dibenzylideneacetone; yield of **5**: 67%; *cf.* the ESI† for X-ray crystal structure determinations of **4** and **5**).³⁴

Compound 5 reacts cleanly with 2.5 equiv. of Li[AlH₄] to give the lithium trihydridoborate Li₂[6] (Scheme 2) as evidenced by a quartet at -26.2 ppm in the ¹¹B NMR spectrum of the reaction product (${}^{1}J_{BH} = 75$ Hz). The corresponding hydrogen substituents give rise to a 1:1:1:1 quartet at 1.02 ppm in the ¹H NMR spectrum. In the IR spectrum, characteristic B-H stretches are observed at \tilde{v} = 2252, 2190 cm⁻¹ (cf. Li[PhBH₃]: δ (¹¹B) = -26.4 $({}^{1}J_{BH} = 76 \text{ Hz}); \tilde{v}(B-H) = 2241, 2189 \text{ cm}^{-1}).{}^{35} \text{ X-ray quality crystals}$ of $(Li(THF)_2)_2[6]$ were grown from Et₂O-THF. Apart from the *n*hexyl tethers, the polymeric solid-state structure of $(Li(THF)_2)_2$ [6] is virtually identical to that of (Li(THF)₂)₂[**p-2**] (cf. the ESI⁺ for detailed information). The only major difference lies in the fact that not all repeat units are symmetry related, but that two crystallographically independent molecules, (Li(THF)₂)₂[6]_A and $(Li(THF)_2)_2[6]_B$, alternate along the polymer strand. As a result, adjacent para-phenylene rings include dihedral angles of 7.0°, whereas they are coplanar in $(Li(THF)_2)_2[p-2]$. Contrary to 4, the n-hexyl sidechains do not adopt an all-s-trans conformation but are coiled in $(Li(THF)_2)_2[6]$.

Treatment of Li₂[6] with excess Me₃SiCl/N(Me)₂Et in THF resulted in the replacement of one hydride ion per trihydridoborate moiety by a neutral N(Me)₂Et donor. The resulting ditopic amineborane adduct **7** (Scheme 2) is characterised by an ¹¹B NMR signal at -3.2 ppm, which, compared to Li₂[6], is deshielded by more than 20 ppm (*cf.* (C₅H₅)Fe(C₅H₄BH₂–N(Me)₂Et): δ (¹¹B) = -3.4). In line with the lower local symmetry about the boron atom in **7** as opposed to Li₂[6], the ¹¹B resonance is significantly broadened

Table 2Crystallographic data for 7 and 8

	7	8
Formula	$C_{26}H_{54}B_2N_2$	$C_{34}H_{56}B_2$
fw	416.33	486.41
Colour, shape	colourless, plate	colourless, plate
T/K	173(2)	173(2)
Cryst. syst.	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	10.3561(10)	12.5723(11)
b/Å	10.8699(6)	9.5902(6)
c/Å	12.2614(10)	13.5233(11)
α (°)	90	90
β (°)	94.386(7)	108.187(6)
γ (°)	90	90
V/Å ³	1376.22(19)	1549.1(2)
Ζ	2	2
$D_{\rm c}/{\rm g~cm^{-3}}$	1.005	1.043
F(000)	468	540
μ/mm^{-1}	0.056	0.057
Cryst. size/mm	$0.32 \times 0.28 \times 0.13$	$0.36 \times 0.33 \times 0.23$
Reflections collected	13090	10470
Indep. reflns (R_{int})	2800 (0.0479)	2727 (0.0647)
Data/restraints/params	2800/6/163	2727/8/162
GOOF on F^2	1.029	1.070
$R_1, WR_2 (I > 2\sigma(I))$	0.0495, 0.1231	0.0579, 0.1540
R_1 , w R_2 (all data)	0.0653, 0.1302	0.0795, 0.1646
Largest diff peak and hole/e $Å^{-3}$	0.264 and -0.234	0.259 and -0.271

such that ${}^{1}J_{BH}$ coupling could not be resolved. The result of an X-ray crystal structure analysis of 7 is shown in Fig. 3 (*cf.* Table 2 for key crystallographic data).

In the solid state, the molecule possesses a centre of inversion in the middle of the benzene ring. Both the N(1)–B(1) vector and the C(5)–C(4) vector are almost orthogonal to the phenylene plane (torsion angles: C(2)–C(1)–B(1)–N(1) = 84.4(1)°, C(2)– C(3)–C(4)–C(5) = -91.5(1)°). The B(1)–N(1) bond length of 1.651(2) Å possesses a similar value to that of the B–N bond in the related monotopic borane adduct (C₅H₅)Fe(C₅H₄BH₂–N(Me)₂Et) (1.655(7) Å).¹²

Hydroboration of 1,5-cyclooctadiene and *tert*-butyl acetylene with 7

The reactivity of 7 was tested both with an internal alkene (1,5-cyclooctadiene) and with a terminal alkyne (*tert*-butyl acetylene).

The 9-borabicyclo[3.3.1]nonyl (9-BBN) derivative 8 (Scheme 3) formed in almost quantitative yield after a solution of 1,5cyclooctadiene and 7 (2:1) in benzene had been heated to 60 °C for 18 h (NMR spectroscopic control). Repeated recrystallisation of the crude product from hexane gave an analytically pure sample. The ¹¹B NMR shift of 8 (86 ppm) is characteristic of threecoordinate triorganylboranes.36 A comparison of the alkyl region of the ¹H and ¹³C NMR spectra of 8 with the corresponding data of other 9-BBN derivatives³⁶ indicates the successful generation of the 9-BBN cage. Moreover, the proton integral ratios of 8 unequivocally prove the presence of two 9-borabicyclo[3.3.1]nonyl substituents per para-phenylene bridge. The following results of this hydroboration experiment are noteworthy: (i) compound 7 can be used as hydroboration reagent even though the boron atom bears a rather strongly Lewis basic N(Me)₂Et donor, (ii) the reaction product 8 is a free borane (already prior to workup)



Fig. 3 Molecular structure of **7** in the solid state; hydrogen atoms attached to carbons have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), angles (deg), and torsion angles (deg): B(1)–N(1) 1.651(2), B(1)–C(1) 1.624(2); N(1)–B(1)–C(1) 112.0(1), C(3)–C(4)–C(5) 114.2(1); C(2)–C(1)–B(1)–N(1) 84.4(1), C(1)–B(1)–N(1)–C(12) –57.6(1), C(2)–C(3)–C(4)–C(5) –91.5(1).

and not an amine adduct, and (iii) the assembly of the bulky 9-BBN framework is not sterically prevented by the ortho-nhexyl group. To gain further insight into the degree of steric crowding in 8, we have characterised the compound by X-ray crystallography (Fig. 4; Table 2). In the centrosymmetric molecule, the 9-BBN cage is rotated away from the *n*-hexyl substituent such as to minimise unfavourable intramolecular interactions (C(2)- $C(1)-B(1)-C(11) = -128.2(2)^{\circ}$; the shortest contact is established between one of the 9-BBN bridgehead hydrogen atoms and one α -CH₂ hydrogen atom and amounts to 2.156 Å). The sum of the bond angles about the boron atoms of **8** is 359.5° , thereby giving no indication for a sterically induced deviation from the ideal trigonal-planar configuration. All in all, we come to the conclusion that the solubilising *n*-hexyl sidechains are compatible even with large boryl substituents and therefore do not affect the suitability of 7 for extensive further derivatisation by hydroboration.

The reaction between 7 and *tert*-butyl acetylene also proceeded cleanly and gave 9 under similar reaction conditions as had been applied for the synthesis of 8 (Scheme 3). This time, an excess of the C–C-unsaturated component was employed (6.5 equiv.), because *tert*-butyl acetylene is highly volatile and unreacted starting material can easily be removed *in vacuo*. The successful hydroboration reaction is indicated in the proton NMR spectrum



Scheme 3 Synthesis of the hydroboration products 8 and 9. (i) Benzene, 60 $^{\circ}$ C, 18 h.



Fig. 4 Molecular structure of **8** in the solid state; hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), angles (deg), and torsion angles (deg): B(1)-C(1) 1.569(3), B(1)-C(11) 1.573(3), B(1)-C(15) 1.568(3); C(1)-B(1)-C(11) 126.6(2), C(1)-B(1)-C(15) 122.2(2), C(11)-B(1)-C(15) 110.7(2), C(3)-C(4)-C(5) 112.4(2); C(2)-C(1)-B(1)-C(11) -128.2(2), C(2)-C(3)-C(4)-C(5) 108.4(2).

by two doublets at $\delta({}^{1}\text{H}) = 6.96$ and 6.76 with a ${}^{3}J_{\text{HH}}$ coupling constant of 17.7 Hz, which fits to an *E*-olefin; the proton integral ratios point towards the introduction of four *tert*-butylvinyl substituents. The chemical shift value of the only ¹¹B resonance (65 ppm) testifies to the presence of the free borane rather than the N(Me)₂Et adduct (*cf.* (CH₂=CH)₃B: $\delta(^{11}\text{B}) = 56.4;^{37}$ Ph₃B: $\delta(^{11}\text{B}) = 60.2^{38}$).

Conclusions

This paper reports on rare examples of ditopic trihydridoborates and dihydridoboranes, *i.e.*, $(Li(THF)_2)_2[m-C_6H_4(BH_3)_2]$, $(Li(THF)_2)_2[p-C_6H_4(BH_3)_2]$, $(Li(THF)_2)_2[p-C_6H_2(n-hexyl)_2(BH_3)_2]$ and $p-C_6H_2(n-hexyl)_2(BH_2-N(Me)_2Et)_2$. The hydridoborate salts not only serve as precursors for the corresponding boranes, but are also potentially useful ligands for the generation of organic/inorganic hybrid compounds. Especially the solubilised dianion $[p-C_6H_2(n-hexyl)_2(BH_3)_2]^2$ holds great promise in this respect, because it can act as a bridging ligand in coordination polymers (*cf.* the polymeric solid-state structure of $(Li(THF)_2)_2[p-C_6H_2(n-hexyl)_2(BH_3)_2]$).

As a proof of principle, we have shown that the amine-borane adduct $p-C_6H_2(n-hexyl)_2(BH_2-N(Me)_2Et)_2$ is an efficient hydroboration reagent both for internal olefins (*i.e.*, 1,5-cyclooctadiene) and terminal alkynes (*i.e.*, *tert*-butyl acetylene). The *n*-hexyl sidechains not only have a solubilising effect, but at the same time serve the purpose of increasing the regioselectivity of the hydroboration reaction.

We are currently exploring the potential of ditopic hydroboration reagents like $p-C_6H_2(n-hexyl)_2(BH_2-N(Me)_2Et)_2$ for the preparation of novel Lewis acidic organocatalysts, and for the synthesis of boron-doped extended π -systems *via* hydroboration polymerisation protocols.

Experimental

General Considerations

All reactions were carried out under an N2 atmosphere in carefully dried solvents using Schlenk tube techniques or a glove box. NMR: Bruker Avance 300 and Avance 400. Chemical shift values $({}^{1}H, {}^{13}C{}^{1}H)$ are reported in parts per million relative to SiMe₄ and were referenced to residual solvent signals. ¹¹B{¹H} NMR spectra are referenced to external BF₃·Et₂O. J values are given in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, br = broad, n.r. = not resolved, n.o. = signal not observed. Elemental analyses were performed by the Microanalytical Laboratory of the University of Frankfurt or the Mikroanalytisches Labor Pascher, Remagen, Germany. Reagents purchased from commercial sources were used as received unless otherwise noted. m-Bis(dibromoboryl)benzene,²⁶ p-bis(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)benzene,27 and 1,4-dibromo-2,5-di-n-hexylbenzene^{31,32} were prepared according to previously reported procedures.

Synthesis of Li₂[m-2]

m-Bis(dibromoboryl)benzene 1 (6.47 g, 15.50 mmol) was dissolved in toluene (30 mL) and Et₂O (10 ml), and the mixture was heated at reflux temperature for 1 h. All volatiles were driven off *in vacuo*, the residue was redissolved in THF (30 mL)/*t*BuOMe (30 mL) and the solution was stirred at rt until the ¹¹B{¹H} NMR spectrum indicated full conversion to *m*-bis(dialkoxyboryl)benzene. After drying *in vacuo*, a fraction of the product (0.67 g) was treated with Et₂O (4 mL) and the resulting mixture was cooled to 0 °C. A solution (1 M) of Li[AlH₄] in Et₂O (10.0 mL, 10.0 mmol) was added slowly *via* syringe under vigorous stirring, whereupon a colourless solid formed. The mixture was allowed to warm to rt and the solid was isolated by filtration and washed with Et_2O (20 mL). $Li_2[m-2]$ was extracted into warm THF (17 mL). X-ray quality crystals of $(Li(THF)_2)_2[m-2]$ were grown by gas-phase diffusion of Et_2O into the extract over a period of 14 d.

Synthesis of Li₂[p-2]

In a Schlenk tube, a solution of *p*-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)benzene (0.079 g, 0.24 mmol) in THF (3 mL) was carefully layered first with THF (8 mL) and then with a solution (0.3 M) of Li[AlH₄] in Et₂O (4.2 mL, 1.3 mmol). After 1 h, a colourless solid began to precipitate; after the vessel had been left standing at rt for 12 h, the supernatant was separated from the solid phase *via* syringe. The solid was washed with Et₂O (10 mL) and dried *in vacuo*. After the addition of neat N, N, N', N'tetramethylethylenediamine (6 mL; dried over solid *n*-BuLi) crystalline material was identified among the microcrystalline precipitate and single crystals for X-ray diffraction analysis could be selected manually ((Li(THF)₂)₂[**p**-2]).

Synthesis of 5

A tube-shaped glass vessel equipped with a Teflon Young's tap and a magnetic stirrer bar was charged in a glove box with Pd₂dba₃·CHCl₃ (0.304 g, 0.29 mmol). The solid was dissolved in toluene (20 mL) and a solution of P(Me)tBu₂ (0.195 g, 1.22 mmol) in toluene (20 mL) was added with stirring via syringe at 0 °C. The mixture was allowed to warm to rt and stirring was continued for 2 h. The resulting pale orange solution was frozen at -196 °C. NEt₃ (18.5 mL, 13.4 g, 132 mmol) was vacuum-transferred from Na/K alloy into the reaction flask. The mixture was again warmed to rt and freshly sublimed 1,4-dibromo-2,5-di-n-hexylbenzene (12.25 g, 30.30 mmol), toluene (12 mL), and HBpin (12.0 mL, 10.6 g, 82.7 mmol) were added in this order. The mixture was cooled to -78 °C, the glass vessel was depressurised to approximately 250 torr, sealed by closing the Young's tap, and heated in an oil bath at 90 °C for 4 d. The glass tube was cooled to rt and a saturated aqueous NH₄Cl solution (100 mL) was added carefully with stirring (*Caution*: H_2 gas is evolved). The organic phase was separated and the aqueous phase extracted with Et₂O $(2 \times 100 \text{ mL})$. The combined organic phases were dried over Na₂SO₄. After filtration, the filtrate was evaporated to dryness under reduced pressure and the pale brown residue recrystallised from hot MeOH. The obtained off-white solid was dissolved in hexane and separated from small amounts of an insoluble black material by filtration. Removal of all volatiles from the filtrate in vacuo gave analytically pure 5. Yield: 10.10 g, 67% (Found: C, 72.52; H, 10.63. Calc. for C₃₀H₅₂B₂O₄ [498.34]: C, 72.31; H, 10.52). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an Et₂O solution of 5.

¹H NMR (300.0 MHz, CDCl₃): δ = 7.52 (s, 2 H, ArH), 2.81 (m, 4 H, α-CH₂), 1.56–1.46 (m, 4 H, β-CH₂), 1.34 (s, 24 H, Bpin-CH₃), 1.34–1.25 (m, 12 H, γ-, δ-, ε-CH₂), 0.88 (m, 6 H, CH₃); ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ = 146.1 (ArC-2,5), 136.5 (ArC-3,6), 83.3 (Bpin-CCH₃), 35.5 (α-CH₂), 33.8 (CH₂), 31.8 (CH₂), 29.6 (CH₂), 24.8 (Bpin-CH₃), 22.7 (ε-CH₂), 14.2 (CH₃), n.o. (ArC-1,4); ¹¹B{¹H} NMR (96.3 MHz, CDCl₃): δ = 31.9 ($h_{1/2}$ = 550 Hz).

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Synthesis of Li₂[6]

A solution of 5 (2.78 g, 5.58 mmol) in Et₂O (40 mL) was cooled to 0 °C. A solution (1 M) of Li[AlH₄] (14.0 mL, 14.0 mmol) in Et₂O was added dropwise under vigorous stirring over a period of 40 min, whereupon a colourless precipitate formed. Stirring was continued for 45 min at 0 °C and for another 45 min at rt. The insolubles were collected on a frit and washed with Et₂O (20 mL). The solid was then transferred to a flask, treated with THF (35 mL), and the resulting suspension was stirred for 12 h at rt. After filtration, Li₂[6] was precipitated from the filtrate by dropwise addition of Et₂O (40 mL) over a period of 1 h. The precipitate was allowed to settle, the supernatant was removed via cannula, and Li₂[6] was dried in vacuo. Yield: 1.57 g, 65% (Found: C, 72.67; H, 11.59. Calc. for $C_{18}H_{34}B_2Li_2$ [285.93] × 2 C₄H₈O [72.11]: C, 72.60; H, 11.72). Concentration of the mother liquor under reduced pressure gave a second crop (0.38 g) of Li₂[6]. X-ray quality crystals of (Li(THF)₂)₂[6] were obtained by gasphase diffusion of Et₂O into a THF solution of Li₂[6].

IR: $\tilde{\nu}/cm^{-1} = 2252$, 2190 (BH). ¹H NMR (400.1 MHz, THFd₈): $\delta = 6.80$ (s, 2 H, ArH), 2.53 (m, 4 H, α-CH₂), 1.55 (m, 4 H, β-CH₂), 1.30 (m, 12 H, γ-, δ-, ε-CH₂), 0.88 (m, 6 H, CH₃), 1.02 (q, *J* = 75, BH); ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈): $\delta = 141.5$ (ArC-2,5), 136.8 (ArC-3,6), 37.8 (α-CH₂), 33.3 (CH₂), 32.8 (CH₂), 31.2 (CH₂), 23.7 (ε-CH₂), 14.5 (CH₃), n.o. (ArC-1,4); ¹¹B{¹H} NMR (128.4 MHz, THF-*d*₈): $\delta = -26.2$ (*h*_{1/2} = 30 Hz); ¹¹B NMR (128.4 MHz, THF-*d*₈): $\delta = -26.2$ (q, *J* = 75).

Synthesis of 7

A solution of N(Me)₂Et (3.2 mL, 2.2 g, 30.0 mmol) in THF (10 mL) was condensed from Na/K alloy onto solid (Li(THF))₂[**6**] (1.40 g, 3.25 mmol). After warming to rt, more THF (20 mL) was added *via* syringe, and the mixture was again frozen at -196 °C. Me₃SiCl (4.2 mL, 3.6 g, 33.1 mmol) was added by vacuum transfer from CaH₂, the reaction mixture was allowed to warm to rt and stirred overnight, whereupon a colourless suspension formed. All volatiles were removed *in vacuo* and the residue was stirred with Et₂O (25 mL)/pentane (5 mL) for 1.5 h at rt. After filtration, the filtrate was freed of solvents under reduced pressure to obtain analytically pure 7. Yield: 1.21 g, 90% (Found: C, 74.53; H, 12.78; N, 6.44. Calc. for C₂₆H₅₄B₂N₂ [416.33]: C, 75.01; H, 13.07; N, 6.73). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an Et₂O solution of 7 under reduced pressure without stirring.

¹H NMR (300.0 MHz, CDCl₃): δ = 7.16 (s, 2 H, ArH), 2.81 (q, *J* = 7.3, 4 H, NC*H*₂CH₃), 2.66 (m, 4 H, α -CH₂), 2.36 (s, 12 H, NCH₃), 1.46 (m, 4 H, β -CH₂), 1.29–1.12 (m, 12 H, γ -, δ -, ϵ -CH₂), 1.08 (t, *J* = 7.3, 6 H, NCH₂CH₃), 0.76 (m, 6 H, CH₃), n.o. (BH); ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ = 143.9 (ArC-2,5), 140.1 (ArC-3,6), 56.2 (NCH₂CH₃), 47.5 (NCH₃), 35.6 (α -CH₂), 33.1 (CH₂), 32.0 (CH₂), 29.9 (CH₂), 22.7 (ϵ -CH₂), 14.1 (CH₃), 8.3 (NCH₂CH₃), n.o. (ArC-1,4); ¹¹B{¹H} NMR (96.3 MHz, CDCl₃): δ = -3.2 (*h*_{1/2} = 370 Hz). ¹¹B NMR (96.3 MHz, CDCl₃): δ = -3.2 (*h*_{1/2} = 460 Hz).

Synthesis of 8

A glass tube equipped with a Teflon Young's tap and a magnetic stirrer bar was charged with 7 (0.44 g, 1.06 mmol) and 1.5-

cyclooctadiene (0.24 g, 2.22 mmol). Benzene (10 mL) was added, the mixture was frozen at -196 °C, the vessel was evacuated, the tap was closed, and the mixture was heated with stirring in an oil bath at 60 °C for 18 h. After cooling to rt, the vessel was flushed with N₂ and stored for 2 d. The benzene was removed by freeze-drying under dynamic vacuum. The solid residue was recrystallised twice from hexane (5 mL/4 mL) at -30 °C/0 °C in order to obtain an analytically pure sample. Yield: 0.23 g, 45% (Found: C, 83.89; H, 11.63. Calc. for C₃₄H₅₆B₂ [486.41]: C, 83.96; H, 11.60).

¹H NMR (300.0 MHz, C₆D₆): δ = 7.62 (s, 2 H, ArH), 2.89 (m, 4 H, α-CH₂), 2.22 (n.r., 4 H, BBNH-a), 2.07 (n.r., 20 H, BBNHb,c), 1.66 (m, 4 H, β-CH₂), 1.49 (n.r., 4 H, BBNH-c), 1.37 (m, 4 H, γ-CH₂), 1.24 (m, 8 H, δ-, ε-CH₂), 0.85 (m, 6 H, CH₃); ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ = 143.5 (ArC-2,5), 132.4 (ArC-3,6), 36.6 (α-CH₂), 35.0 (β-CH₂), 34.7 (BBNC-b), 33.0 (br, BBNC-a), 32.1 (CH₂), 30.0 (γ-CH₂), 23.7 (BBNC-c), 23.0 (CH₂), 14.2 (CH₃), n.o. (ArC-1,4); ¹¹B{¹H} NMR (96.3 MHz, C₆D₆): δ = 86 ($h_{1/2}$ = 1000 Hz).

Synthesis of 9

A glass tube equipped with a Teflon Young's tap and a magnetic stirrer bar was charged with 7 (0.41 g, 0.98 mmol) and *tert*-butyl acetylene (0.81 mL, 0.54 g, 6.57 mmol). Benzene (15 mL) was added, the mixture was frozen at -196 °C, the vessel was evacuated, the tap was closed, and the mixture was heated with stirring in an oil bath at 60 °C for 18 h. After cooling to rt, the vessel was flushed with N₂. Subsequently, all volatiles were removed *in vacuo* to obtain **9** as a colourless turbid oil. Purification of the crude product by recrystallisation failed due to its high solubility in all common non-coordinating solvents (including hexane at low temperature). Attempts at a purification by vacuum sublimation led to thermolysis with formation of tris(*tert*-butylvinyl)borane (NMR spectroscopic control). Chromatographic workup is precluded by the pronounced air and moisture sensitivity of the compound.

¹H NMR (300.0 MHz, C_6D_6): $\delta = 7.42$ (s, 2 H, ArH), 6.96 (d, 4 H, J = 17.7, C_2H_2), 6.76 (d, 4 H, J = 17.7, C_2H_2), 2.87 (m, 4 H, α -CH₂), 1.71 (m, 4 H, β -CH₂), 1.37–1.20 (m, 12 H, γ -, δ -, ϵ -CH₂), 0.99 (s, 36 H, C(CH₃)₃), 0.86 (m, 6 H, CH₃); ¹³C{¹H} NMR (75.5 MHz, C_6D_6): $\delta = 169.4$ (C_2H_2), 141.3 (ArC-2,5), 132.6 (ArC-3,6), 130.6 (br, C_2H_2), 37.0 (α -CH₂), 35.5 (C(CH₃)₃), 33.3 (CH₂), 32.2 (CH₂), 29.7 (CH₂), 28.9 (C(CH₃)₃), 23.0 (ϵ -CH₂), 14.3 (CH₃), n.o. (ArC-1,4); ¹¹B{¹H} NMR (96.3 MHz, C_6D_6): $\delta = 65$ ($h_{1/2} =$ 1500 Hz).

Crystal structure determinations of ((Li(THF)₂)₂[*m*-2]), ((Li(THF)₂)₂[*p*-2]), 7, and 8

Data were collected on a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using the program SHELXS³⁹ and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97.⁴⁰

In $(\text{Li}(\text{THF})_2)_2[m-2]$, two atoms of a THF ligand are disordered over two positions with a site occupation factor of 0.64(1) for the major occupied site. In $(\text{Li}(\text{THF})_2)_2[p-2]$, one atom of a THF ligand is disordered over two positions with a site occupation factor of 0.51(2) for the major occupied site. In 7, three atoms of an *n*-hexyl chain are disordered over two equally occupied positions. CCDC reference numbers: 793257 ((Li(THF)₂)₂[*m*-2]), 793258 ((Li(THF)₂)₂[*p*-2]), 793259 (7), and 793260 (8).

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