Lewis-base adducts of 9,10-dihydro-9,10-diboraanthracene: ditopic hydroboration reagents and a B–N analogue of triptycene

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The dimethyl sulfide, pyridazine, or pyrazolide adducts of 9,10-dihydro-9,10-diboraanthracene are potent hydroboration reagents for terminal alkynes; the 1,2-diazene derivatives possess a paddle-wheel structure and are stabilised towards hydrolysis.

Hydroboration of carbon–carbon triple bonds is a powerful tool for the preparation of boron-doped π -conjugated organic macromolecules.^{1–4} For the following reasons, such compounds have promising potential as electron transporters and luminophores in organic light-emitting devices (OLEDs).^{5–7} (1) Due to the isoelectronic relationship between three-coordinate boron atoms and carbocations, the incorporation of boron into conjugated π -systems leads to similar electronic states as oxidative doping, but gives neutral materials. (2) In the presence of suitable σ -donors Do, the formation of B–Do adducts results in a shortening of the average π -conjugation length accompanied by a change in the electronic spectrum of the polymer. This is a highly useful effect, which can be exploited for the development of molecular switches and sensors.

While a broad variety of (hetero)aromatic diynes has already been employed in hydroboration polymerisation reactions, the choice of the boron component was long restricted mainly to mesitylborane, (MesBH₂)₂.^{1,2} Both for preparative reasons and in an attempt to improve the optoelectronic properties of the macromolecules, our group has recently introduced 9,10-dihydro-9,10-diboraanthracene as novel ditopic hydroboration reagent (**1**, Fig. 1).³ **1** possesses a unique B–H–B bridged polymeric structure [**1**]_n in the solid state and is therefore insoluble in all common non-donor solvents.³ Nevertheless, the hydroboration polymerisation of [**1**]_n with dialkynes was possible in THF under heterogeneous conditions and gave extended π -systems (e.g., **2**; Fig. 1) showing an intense photoluminescence.³

In order to facilitate further development of this class of compounds, it would, however, be desirable to have soluble, highly crystalline low molecular weight derivatives of **1** that can easily be purified and used for further transformations in a

Fig. 1 The B–H–B bridged polymer [**1**]_n and the photoluminescent boron-doped π -conjugated system **2** prepared by hydroboration polymerisation of 1,4-diethynyl-2,5-bis(hexyloxy)benzene with [**1**]_n (THF, rt).

homogeneous liquid phase. All these requirements are met by the dimethyl sulfide (DMS) adduct **3** (Scheme 1), which is readily available when saturated solutions of **1** in dry DMS are cooled to $-78\text{ }^{\circ}\text{C}$. The ¹¹B NMR spectrum of **3** in C₆D₆ (DMS) solution shows one resonance at 28.1 ppm (1.9 ppm), testifying to the presence of four-coordinate boron atoms.⁸ The better shielded boron nuclei in neat DMS compared to C₆D₆ indicate a dynamic B–S association/dissociation equilibrium in the latter solvent. Yet the presence of only two equivalents of the Lewis base is still sufficient to prevent precipitation of polymeric [**1**]_n. An X-ray crystal structure analysis of **3** is in line with the proposed diadduct structure (Fig. 2). The two DMS ligands are attached in a *syn* fashion to the 9,10-dihydro-9,10-diboraanthracene and the methyl groups are pointing away from the centre of the molecule. Consequently, the sulfur lone pairs closely approach each other (S(1)⋯S(2) = 3.943(1) Å). As in the parent compound [**1**]_n, the borane backbone of **3** adopts a folded boat conformation with a dihedral angle between the two aryl rings of $\varphi = 157^{\circ}$ ([**1**]_n: $\varphi = 134^{\circ}$; in the corresponding pyridine diadduct, the pyridine ligands coordinate in an *anti* fashion and φ equals 180°).³ Hydroboration of *tert*-butylacetylene with **3** in C₆D₆ proceeds rapidly and gives essentially quantitative yields (Scheme 1). An NMR spectroscopic investigation (¹H, ¹¹B) of the solution prior to workup revealed that the vinylborane product was still coordinated by DMS. However, the ligands can easily be removed under reduced pressure to give donor-free **4**, which is identical to a sample prepared with [**1**]_n (¹H NMR spectroscopy;³ combustion analysis).

The nature of **1** as a ditopic Lewis acid suggests applications as inverse chelator of bidentate Lewis bases.⁹ In the context of main-chain boron-doped polymers **2**, this approach offers several interesting perspectives: (1) since cooperative binding is possible, switching of optoelectronic polymer properties should be more efficient with bidentate than with monodentate donor molecules; (2) the four-coordination of the boron atoms

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Scheme 1 Polymeric $[1]_n$ can be transformed into soluble **3**, a convenient ditopic hydroboration reagent (*cf.* **4**). Paddle-wheel shaped adducts (**5**, **6**, and Li[**7**]) are formed, when **3** is treated with 1,2-diazenes. (a) DMS, rt; (b) + 5 *t*BuCCH, C₆H₆, rt; (c) + 1 C₄H₂N₂R₂, C₆H₆, rt; (d) + 1 Li[C₃H₂N₂(SiMe₃)], C₆H₆/THF, rt.

Fig. 2 Molecular structure and numbering scheme of compound **3**; displacement ellipsoids are drawn at the 50% probability level; protons attached to carbon atoms are omitted for clarity. Selected (average) bond lengths [Å], atom···atom distances [Å], bond angles [°], and dihedral angles [°]: B–C = 1.607(3), B–S = 2.031(2), B–H = 1.19(2), B(1)···B(2) = 3.069(3), S(1)···S(2) = 3.943(1); C–B–C = 115.0(2), C–B–S = 105.3(2), B–S–C = 103.9(1), C–S–C = 98.7(1); Ar(C(11))//Ar(C(21)) = 157.0, B(1)C(1)C(11)//B(2)C(2)C(12) = 33.8.

helps to stabilise the polymer chain with respect to oxidation or hydrolysis, *e.g.*, during chain length determination by gel permeation chromatography or dynamic light scattering measurements; (3) the use of charged Lewis basic additives facilitates a polymer analysis by ESI or MALDI-TOF mass spectrometry. Given this background, we have treated the DMS adduct **3** with pyridazine and obtained the soluble compound **5** (Scheme 1), which is a B–N analogue of triptycene.¹⁰ The ¹¹B NMR spectrum of **5** shows one resonance at 5.3 ppm; the ¹H as well as the ¹³C NMR spectrum is characterised by only two signals for the phenylene rings and two signals for the pyridazine fragment (proton integral ratio = 2 : 1). All these spectroscopic features are in accordance with a highly symmetric molecular framework. Repeated attempts to grow X-ray quality crystals of **5** failed. We therefore replaced pyridazine by benzo[*d*]pyridazine (Scheme 1) and confirmed the proposed molecular structure of the reaction product **6** by X-ray diffraction (details are given in the ESI†). Apart from the two neutral 1,2-diazines mentioned above, 4-trimethylsilylpyrazolide has also been added to a solution of **3** in order to synthesise the anionic species [**7**][−] (Scheme 1). In contrast to **5** and **6**, which showed no molecular ion peaks in the ESI^{+/−} mass spectrum (THF), the ESI[−]-MS of Li[**7**] in THF features exclusively one peak at *m/z* = 315.2 ([**7**][−]). This result strongly suggests that decoration of **2**-type polymers with 4-trimethylsilylpyrazolide may indeed path the way to their (so far impractical) mass spectrometric characterisation. The X-ray crystal structure analysis of Li(thf)₄[**7**][−]·THF reveals a monomeric paddle-wheel framework for [**7**][−] (Fig. 3) with an average B–N bond length

Fig. 3 Molecular structure and numbering scheme of the anion [**7**][−]; displacement ellipsoids are drawn at the 50% probability level; protons attached to carbon atoms are omitted for clarity. Selected (average) bond lengths [Å], atom···atom distances [Å], bond angles [°], and dihedral angles [°]: B–C = 1.616(5), B–N = 1.605(4), B–H = 1.19(5), B(1)···B(2) = 2.734(6); C–B–C = 105.8(3), C–B–N = 103.2(3), B–N–N = 115.5(3); Ar(C(11))//Ar(C(21)) = 118.8, B(1)C(11)C(21)//B(2)C(12)C(22) = 84.6.

of 1.605(4) Å and an average B–N–N bond angle of 115.5(3)° (cf. **6**: B–N = 1.643(3) Å; B–N–N = 114.3(2)°). The folding of the 9,10-dihydro-9,10-diboraanthracene moiety in [7][−] (φ = 119°) is slightly more pronounced than in **6** (φ = 127°), but considerably more prominent than in **3** (φ = 157°).

Compound **3** is highly sensitive to air and moisture; in contrast, it takes several hours until the ¹H NMR spectra of solutions of **5** and Li[7] in wet THF show significant signs of decomposition. Both **5** and Li[7] are active hydroboration reagents towards *tert*-butylacetylene. The corresponding vinylboranes form as pyridazine/4-trimethylsilylpyrazolide adducts, which clearly indicates that the bridging of the two boron atoms by appropriate bidentate Lewis bases is not restricted to the parent compound **1**, but should also be possible for **2**-type polymers.

To summarise, in the context of main-chain boron-doped π -conjugated polymers we introduce the DMS adduct **3** of 9,10-dihydro-9,10-diboraanthracene **1** as a convenient ditopic hydroboration reagent for the transformation of alkynes into donor-free vinylboranes. Moreover, we show that various 1,2-diazenes can be used to bridge the boron atoms of 9,10-dihydro-9,10-diboraanthracene derivatives, which is of interest both for hydrolysis protection during polymer analysis and for the modulation of bulk physical polymer properties.

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Notes and references

- 1 N. Matsumi, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 1998, **120**, 5112.
- 2 N. Matsumi and Y. Chujo, *Polym. J.*, 2008, **40**, 77.
- 3 A. Lorbach, M. Bolte, H. Li, H.-W. Lerner, M. C. Holthausen, F. Jäkle and M. Wagner, *Angew. Chem., Int. Ed.*, 2009, **48**, 4584.
- 4 J. Chai, C. Wang, L. Jia, Y. Pang, M. Graham and S. Z. D. Cheng, *Synth. Met.*, 2009, **159**, 1443.
- 5 C. D. Entwistle and T. B. Marder, *Angew. Chem., Int. Ed.*, 2002, **41**, 2927.
- 6 F. Jäkle, *Coord. Chem. Rev.*, 2006, **250**, 1107.
- 7 M. Elbing and G. C. Bazan, *Angew. Chem., Int. Ed.*, 2008, **47**, 834.
- 8 H. Nöth and B. Wrackmeyer, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, in *NMR Basic Principles and Progress*, ed. P. Diehl, E. Fluck and R. Kosfeld, Springer, Berlin, 1978.
- 9 F. P. Gabbaï, A. Schier, J. Riede and M. J. Hynes, *Chem. Commun.*, 1998, 897.
- 10 Compound **5** is one of very few examples of molecules in which a pyridazine ring bridges two boron atoms *via* B–N bonds. For other examples see: (a) D. R. Martin, C. M. Merkel, J. U. Mondal and C. R. Rushing, Jr., *Inorg. Chim. Acta*, 1985, **99**, 81; (b) D. J. H. Emslie, W. E. Piers and M. Parvez, *Angew. Chem., Int. Ed.*, 2003, **42**, 1251; (c) C. A. Jaska, D. J. H. Emslie, M. J. D. Bosdet, W. E. Piers, T. S. Sorensen and M. Parvez, *J. Am. Chem. Soc.*, 2006, **128**, 10885.