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COMMUNICATION

9-H-9-Borafluorene dimethyl sulfide adduct: a product of a unique ring-contraction reaction and a useful hydroboration reagent[†]

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The dimethyl sulfide adduct 2(DMS) is a crystalline storage form of the unstable hydroboration reagent 9-*H*-9-borafluorene (2); 2(DMS) is available by the addition of DMS to either *in situ* generated [2]₂ or 1,2-(2,2'-biphenylylene)diborane(6) (7).

The incorporation of three-coordinate boron atoms into conjugated π -electron frameworks leads to changes in the electronic structure which often bring about enhanced luminescence and charge-transport properties.¹

A convenient way to assemble extended π systems bearing boron atoms at preselected positions is offered by the hydroboration of (hetero)aromatic (di)alkynes with arylboranes. Since reagents of the type $\operatorname{Ar}_n \operatorname{BH}_{(3-n)}(n = 1, 2)$ tend to undergo substituent redistribution, the use of arylboranes in hydroboration reactions was long restricted mainly to $\operatorname{MesBH}_2^{2,3}$ and $\operatorname{TripBH}_2^4$ (Mes = mesityl; $\operatorname{Trip} = 2,4,6$ triisopropylphenyl). In these cases, ligand scrambling is unfavourable for steric reasons.

We have recently shown that 9,10-dihydro-9,10-diboraanthracene (1; Fig. 1) is also stable towards dismutation and at the same time a powerful hydroboration reagent for various alkynes, which are selectively transformed into luminescent vinylboranes.^{5,6}

Compound 1 can either be isolated as a B–H–B bridged coordination polymer $[1]_n^5$ (Fig. 1) or as a monomeric dimethyl sulfide diadduct $1(DMS)_2^{.7,8}$ In contrast, the superficially related 9-H-9-borafluorene 2 (Fig. 1) is not an easily isolable species.⁹ After its formation from 9-Br-9-borafluorene and Et₃SiH, the compound first exists as a C_1 -symmetric dimer [2]₂, featuring one B–H–B three-centre, two-electron bond together with a boron-bridging phenyl ring.⁹ In situ generated [2]₂ is a suitable hydroboration reagent for the introduction of



Fig. 1 The B–H–B bridged 9,10-dihydro-9,10-diboraanthracene polymer $[1]_n$, a simplified sketch of the 9-*H*-9-borafluorene dimer $[2]_2$ and the ring-opened boron-doped oligophenylene $[2]_5$ (each circle represents one o-C₆H₄ ring).

9-borafluorenyl moieties, but only during short periods of time, because it tends to undergo ring-opening oligomerisation to main-chain boron-doped oligophenylenes (*cf.* [**2**]₅; Fig. 1).⁹ Compounds like [**2**]₅ represent a new class of macromolecules offering numerous ways of modification. In conclusion, 9-*H*-9-borafluorene (**2**) can react *via* two different channels, both of them giving access to highly interesting π -conjugated materials.

Aiming at a systematic future development of this chemistry (Scheme 1), we now report on (i) a storable adduct 2(DMS) of the hydroboration reagent 2, (ii) the high-yield synthesis of 1,2-(2,2'-biphenylylene)diborane(6) (7) mimicking one oligomer repeat unit of $[2]_5$, and (iii) the interconversion of $7 \rightarrow 2(DMS)$, which sheds light on important aspects of the ring-opening polymerisation reaction.

Treatment of [2]₂, freshly prepared *in situ* from 9-Br-9borafluorene (3) and Et₃SiH,⁹ with excess DMS provides the stable, crystalline adduct 2(DMS) in essentially quantitative yield (Scheme 1). The ¹¹B NMR spectrum of 2(DMS) in C₆D₆ is characterised by a doublet at -7.1 ppm with a coupling constant of ¹J_{BH} = 103 Hz. In stark contrast, the corresponding signal of the 9,10-dihydro-9,10-diboraanthracene diadduct 1(DMS)₂ appears at significantly lower field

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[†] Electronic supplementary information (ESI) available: Synthesis and NMR-spectroscopic characterisation of 2(DMS), 4, 5, $(Li(Et_2O))_2[6]$, 7, $tBuC(H)=C(H)BC_{12}H_8$ and $tBuC(H)_2-C(H)(BC_{12}H_8)_2$; conversion of 7 into 2(DMS); single crystal X-ray structure analyses of 2(DMS), 4, 5, $(Li(Et_2O))_2[6]$ and 7. CCDC 837677, 837678, 837679, 837680 and 837681. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc14888e



Scheme 1 Synthesis of the 9-*H*-9-borafluorene adduct 2(DMS), the ditopic lithium trihydridoborate Li₂[6] and the 2,2'-biphenylylenebridged diborane(6) 7; DMS-induced ring-contraction reaction from 7 to 2(DMS) (DMS = dimethyl sulfide). (a) C_6H_6 , rt; (b) Et₂O, 0 °C to rt; (c) Et₂O, -78 °C to rt; (d) C_6D_6 , rt.

strengths ($\delta(^{11}B) = 28.1$; C_6D_6) and $^{1}J_{BH}$ is not resolved.⁷ If a sample of $1(DMS)_2$ is measured in neat DMS, the ^{11}B nuclei resonate at 1.9 ppm ($^{1}J_{BH} \approx 60$ Hz);⁷ a similar effect on the ^{11}B chemical shift value is absent in the case of 2(DMS). We therefore conclude that the B–S association/dissociation equilibrium lies more on the adduct side in 2(DMS) compared to $1(DMS)_2$. However, this statement cannot be related directly to the Lewis acidities or the antiaromatic character of free 1 and 2, because a diadduct is compared with a monoadduct. 2(DMS) crystallises from C_6H_6 with two crystallographically independent molecules in the asymmetric unit ($2(DMS)_A$, $2(DMS)_B$). Since all key metrical parameters of $2(DMS)_A$



Fig. 2 Molecular structure and numbering scheme of $2(DMS)_A$; displacement ellipsoids are drawn at the 50% probability level; H atoms attached to carbon atoms are omitted for clarity. Selected bond length [Å], bond angles [°] and dihedral angle [°]: B(1)–S(1), 1.980(7); C(1)–B(1)–C(11), 100.7(6); C(1)–B(1)–S(1), 106.8(4); C(11)–B(1)–S(1), 108.6(5); Ar(C(1))//Ar(C(11)), 4.1.

and $2(DMS)_B$ are the same within the experimental error margins, only the structure of $2(DMS)_A$ is discussed here (Fig. 2). The molecule possesses a B–S bond length of 1.980(7) Å, which is shorter by 0.051 Å than the average B–S bond length in $1(DMS)_2$ (2.031(2) Å).⁷ Moreover, the tricyclic framework is planar in 2(DMS) (dihedral angle between the two *o*-phenylene rings: Ar(C(1))//Ar(C(11)) = 4.1°), but folded in $1(DMS)_2$ (23.0°)⁷.

2(DMS) is the aimed-for storage form of 9-*H*-9-borafluorene, because it shows no tendency towards ring-opening oligomerisation. The compound also acts as a highly useful hydroboration reagent. For example, we prepared $tBuC(H)=C(H)BC_{12}H_8^9$ as well as $tBuC(H)_2-C(H)(BC_{12}H_8)_2^9$ each of them in high yields, *via* the selective single or double hydroboration of $tBuC\equiv CH$ (BC₁₂H₈ = 9-borafluorenyl; *cf.* the ESI† for details). This means a major improvement compared to earlier attempts at the hydroboration of $tBuC\equiv CH$ with *in situ* generated [**2**]₂ which had always resulted in a mixture of both products.⁹

The key starting material for the synthesis of 7 as a repeatunit model of $[2]_5$ is the ditopic trihydridoborate Li₂[6], which, in turn, can be prepared from the boronic acid derivatives 4 or 5 and Li[AlH₄] (Scheme 1). Compound 4^{10} is literatureknown; the internal boronic acid anhydride 5 has been prepared using a protocol of IJpeij et al.¹⁰ for the synthesis of 2,2'-biphenyl diboronic acid. A quartet resonance at -28.3 ppm (${}^{1}J_{BH} = 77$ Hz) in the ${}^{11}B$ NMR spectrum of Li₂[6], together with a 1:1:1:1 quartet at $\delta(^{1}H) = 1.49$ (6 H) testify to the presence of two trihydridoborate substituents in the anion framework. According to an X-ray crystal structure analysis of the etherate (Li(Et₂O))₂[6], the crystal lattice consists of discrete C_2 -symmetric moieties, in contrast to the coordination polymer formed by $(\text{Li}(\text{thf})_2)_2[m-C_6H_4(BH_3)_2]^{11}$ in the solid state. The dihedral angle between the two $o-C_6H_4$ rings in (Li(Et₂O))₂[6] amounts to 68.1° and the trihydridoborate substituents are bridged by two $[Li(Et_2O)]^+$ cations.





Fig. 3 The molecular structure and numbering scheme of **7**; displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å], atom···atom distance [Å], bond angles [°] and dihedral angle [°]: B(1)–C(1), 1.555(2); B(2)–C(11), 1.557(2); B(1)···B(2), 1.755(2); C(1)–C(2)–C(12), 122.3(1); C(11)–C(12)–C(2), 122.1(1); Ar(C(1))//Ar(C(11)), 3.3.

Treatment of $(\text{Li}(\text{Et}_2\text{O}))_2[6]$ with excess Me₃SiCl in Et₂O resulted in the clean formation of 7 (70% yield).¹² A characteristic NMR feature of 7 is the ¹¹B resonance at 13.7 ppm, which is split into a doublet due to coupling with the terminal hydride substituent (${}^{1}J_{\text{BH}} = 120$ Hz; coupling to the bridging hydrogen atoms is not resolved). In the proton NMR spectrum, the boron-bonded hydrogen atoms give rise to a featureless signal at 1.30 ppm (2H, BH_{bridging}) and a quartet at 4.77 ppm (2H, ${}^{1}J_{\text{HB}} = 120$ Hz; BH_{terminal}). An X-ray crystal structure analysis of 7 revealed an almost planar 2,2'-biphenyl fragment, bridged by a (H)B(μ -H)₂B(H) moiety (Fig. 3).

The average B–C distance amounts to 1.556(2) Å; the B(1) \cdots B(2) distance is 1.755(2) Å (*cf.* B \cdots B = 1.76(1) Å in B₂H₆¹³ and 1.806(6) Å/1.800(4) Å in [**2**]₅⁹). The synthesis sequence outlined in Scheme 1 thus provides convenient access to a so far largely unexplored class of bridged organo-diboranes(6) in general and to the simplest [**2**]₅ repeat-unit model in particular.

Addition of excess DMS to 7 led to a ring-contraction reaction which gave the 9-*H*-9-borafluorene DMS adduct 2(DMS) on the one hand and $H_3B(DMS)$ on the other. Thus, the insertion of compounds $R_nBH_{(3-n)}$ (n = 0, 1) into 9-borafluorenes with formation of 7-type species is obviously reversible when appropriate Lewis bases are added.¹⁴ We therefore suggest that a careful adjustment of reaction conditions together with the appropriate choice of Lewis basic additives can render the substituent dismutation reaction of arylboranes a powerful tool for the preparation of rather unique organoborane frameworks.

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