

1,6-Bis(2,4,6-tri-*tert*-butylphenyl)-1,6-dibora-2,5-diaza-hexa-1,5-diene, the first compound containing two B≡N triple bonds

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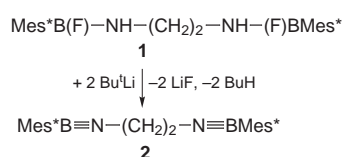
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The elimination of hydrogen fluoride from *N,N'*-bis[(2,4,6-tri-*tert*-butylphenyl)fluoroboryl]ethylenediamine **1** gives the title compound **2** as a thermally very stable moiety; water is easily added across the B≡N triple bonds.

Iminoboranes R–B≡N–R'¹ and aminoiminoboranes R₂N–B≡N–R'² are now quite well known species,³ particularly due to the work of Paetzold¹ and Nöth.² Iminoboranes are kinetically stabilized species and their thermal and hydrolytic stability is dependent upon the steric requirement of the substituents and their resistance against intramolecular chemical attack from the thermodynamically unstable (BN) triple bond. In the past we have studied systematically the stabilization of these moieties by the 2,4,6-tri-*tert*-butylphenyl (supermesityl, Mes*) group.^{4,5} If iminoboranes carrying the supermesityl group have the methyl group as the other substituent, their stability against dimerization is retained up to 100 °C. While if the other substituent is ethyl, benzyl, phenyl, *tert*-butyl or trimethylsilyl these iminoboranes will not dimerize, but upon heating will rearrange to give the corresponding benzo[1]borolanes at temperatures between 170 and 350 °C.

Our attempts to prepare a bis(imino)borane by HF-elimination from Mes*BF–NHNH–FBMes*⁶ upon treatment with Bu^tLi, MeLi or MN(SiMe₃)₂ (M = Li, Na) failed. Apparently the two supermesityl groups are too large to permit the necessary approach considering the short bond lengths in the corresponding bis(imino)borane.

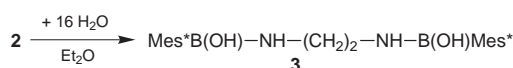
By using an ethylene bridge as a spacer to avoid excessive steric interference we have now prepared the first bis(imino)borane, containing two isolated B≡N triple bonds (Scheme 1).†



Scheme 1

The bis(imino)borane **2** is thermally stable up to its melting point of 311 °C. It neither dimerizes or oligomerizes nor reacts in an intramolecular fashion to give a benzo[1]borolane derivative. Heating above its melting point, however, delivers several decomposition products, which we could not identify until now. The ¹¹B NMR signal for **2** is at δ 5.9 (for Mes*B≡NMe, δ 5.3⁵) and the IR spectrum shows ν (¹¹BN) = 2020 and ν (¹⁰BN) = 2066 cm^{−1}, typical for iminoboranes.⁵

Compound **2** reacts readily with water to yield the corresponding *N,N'*-bis[(2,4,6-tri-*tert*-butylphenyl)hydroxyboryl]ethylenediamine derivative **3** (Scheme 2).‡



Scheme 2

We are grateful to the Fonds der Chemischen Industrie for financial support of this work.

Notes and references

† Preparative details and selected spectroscopic data for **1** and **2**: All reactions under dry nitrogen. Mes*BF₂ was obtained as described.⁴

1: to 1.2 g (0.02 mol) ethylenediamine dissolved in 100 ml hexane, 17 ml of a solution (23% in hexane) of BuLi (0.04 mol) were added with stirring. The mixture was refluxed for 2 h and then cooled to −15 °C. To the stirred suspension was added 11.8 g (0.04 mol) Mes*BF₂ dissolved in 80 ml hexane and the reaction mixture warmed to ambient temperature and then refluxed (2 h). The solvent was removed under reduced pressure and volatile byproducts removed at 160 °C (0.01 Torr). Sublimation in a three-bulb tube yielded 6.9 g (57%) of yellowish **1**, subl.p 240 °C (0.01 Torr) (air bath temp.). After short path resublimation the mp was 208 °C. C₃₈H₆₄B₂F₂N₂ (608.61): satisfactory analytical results. EIMS: *m/z* (%) = 608 (4) [M]⁺, 551 (3) [M – CMe₃]⁺, 57 (100).

NMR data: ¹H (CDCl₃, SiMe₄, 250 MHz) δ 1.34 (s, 18H, CMe₃: 4), 1.43 (d, ⁶J_{HF} 1.1 Hz, 36H, CMe₃: 2/6), 3.22 (m, 4H, CH₂), 3.34 (br, d, ³J_{HF} 17.6 Hz, 2H, NH), 7.40 (s, 4H: 3/5); ¹³C (CDCl₃, TMS, 100.6 MHz) δ 31.3 (CMe₃: 4), 33.0 (d, ⁵J_{CF} 2.5 Hz, CMe₃: 2/6), 34.9 (CMe₃: 4), 37.5 (CMe₃: 2/6), 41.6 (d, ³J_{CF} 2.1 Hz, CH₂), 121.0 (3/5), 127.5 (br, 1), 149.8 (d, ⁵J_{CF} 0.6 Hz: 4), 153.6 (d, ³J_{CF} 2.1 Hz: 2/6); ¹¹B (CDCl₃, BF₃·OEt₂ ext., 80.25 MHz) δ 33.0; ¹⁹F (CDCl₃, C₆F₆ int., 188.3 MHz) δ 70.3.

2: to a suspension of 4.0 g (0.0066 mol) of **1** in 70 ml hexane, 9 ml of a 15% solution of Bu^tLi in pentane (0.0132 mol) was added dropwise with stirring at 0 °C. The pentane was distilled off and the reaction mixture refluxed for 2 h. The solution was filtered through a pressure funnel, the residue washed with three portions of hexane (20 ml each) and the solvent distilled off under reduced pressure. By short path sublimation in a high vacuum the remainder yields 1.5 g (41%) of colourless **2**; mp 311 °C, subl.p 180 °C (0.0001 Torr) (bath temp.). **2** is only sparingly soluble in organic solvents. C₃₈H₆₂B₂N₂ (568.55). Satisfactory elemental analyses were obtained. EIMS: *m/z* (%) = 568 (2) [M]⁺, 511 (5) [M – CMe₃]⁺, 284 (100) [M/2]⁺; FDMS: *m/z* (%) = 568 (100). NMR data: ¹H (CDCl₃, SiMe₄, 250 MHz) δ 1.33 (s, 18H, CMe₃: 4), 1.57 (s, 36H, CMe₃: 2/6), 3.73 (s, 4H, CH₂), 7.33 (s, 4H: 3/5); ¹³C (CDCl₃, SiMe₄, 100.6 MHz) δ 31.3 (CMe₃: 4), 31.9 (CMe₃: 2/6), 35.3 (CMe₃: 4), 36.7 (CMe₃: 2/6), 44.9 (CH₂), 114.0 (br, 1), 119.6 (3/5), 152.4 (4), 159.1 (2/6); ¹¹B (CDCl₃, BF₃·OEt₂ ext., 80.25 MHz) δ 5.9. IR: ν (¹¹BN) = 2020 cm^{−1}, ν (¹⁰BN) = 2066 cm^{−1} (in KBr).

‡ Preparative details and selected spectroscopic data for **3**: to a stirred suspension of 2.0 g (0.0035 mol) of **2**, suspended in 30 ml Et₂O was added 1 ml H₂O (0.055 mol, excess). The mixture was refluxed for 2 h and the liquids removed under reduced pressure leaving colourless **3**. Yield: 1.9 g (91%), mp 221 °C; **3** is fairly soluble in THF. C₃₈H₆₆B₂N₂O₂ (604.58). Satisfactory elemental analyses were obtained. EIMS: *m/z* (%) = 604 (1) [M]⁺, 547 (3) [M – CMe₃]⁺, 302 (15) [M/2]⁺, 257 (100) [Mes*BO – Me]⁺. NMR data: ¹H (THF-d₈, SiMe₄, 250 MHz) δ 1.28 (s, 18H, CMe₃: 4), 1.44 (s, 36H, CMe₃: 2/6), 3.22 (m, 4H, CH₂), 3.47 (m, br, 2H, NH), 6.46 (d, ⁴J_{HH} 1.5 Hz, 2H, OH), 7.31 (s, 4H: 3/5); ¹³C (THF-d₈, SiMe₄, 100.6 Hz) δ 31.8 (CMe₃: 4), 34.0 (CMe₃: 2/6), 35.4 (CMe₃: 4), 38.5 (CMe₃: 2/6), 43.2 (CH₂), 121.4 (3/5), 134.8 (br, 1), 148.7 (4), 153.5 (2/6); ¹¹B (THF-d₈, BF₃·OEt₂ ext., 80.25 MHz) δ 32.7. IR: ν(OH) = 3605 cm^{−1} (in KBr). No dehydration was observed up to the mp.

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