A novel diaminoborate ligand system derived from 1,8-diaminonaphthalene and 9-BBN: preparation of titanium and zirconium complexes and crystal structure of the titanium complex

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1,8-Diaminonaphthalene reacts selectively with 1 equiv. of 9-BBN to form a bridging amine–aminoborane, and with 2 equiv. of 9-BBN to form a non-bridging bis(aminoborane); these aminoboranes give rise to a novel diaminoborate (4e,1−) ligand system by reactions with dimethylamides of titanium and zirconium.

The search for new ligand systems, and especially ones that could replace the (6e,1−) cyclopentadienyl type ligands, is a major area of research in current inorganic and organometallic chemistry. Most progress has been achieved with ligands based on nitrogen donors like trispyrazolylborate,[1] benzamidinate,[2] silyl amide,[3] boryl amide[4] and others.[5] A major aspect in designing of such ligands, other than their electronic character, is their steric effects on the metal environment. In this report we describe a novel boron nitrogen ligand derived *via* two routes from 1,8-diaminonaphthalene and 9-BBN, and its complexes with titanium and zirconium.

Aniline was reported to react with 9-borabicyclo[3.3.1]-nonane (9-BBN) to form the corresponding *B*-phenylamino-9-BBN with evolution of hydrogen gas.[6] We found that 1,8-diaminonaphthalene can react with 9-BBN, with evolution of hydrogen gas, to form two isolable products, depending on the molar ratio of the reactants: addition of exactly 1 equiv. of 9-BBN to 1,8-diaminonaphthalene results in highly selective formation of an amine–aminoborane, HL^1, whereas addition of 2 equiv. of 9-BBN to 1,8-diaminonaphthalene yields a bis(aminoborane), L^2, quantitatively. Adding 1 equiv. of 9-BBN to isolated HL^1 produces L^2 in high yield as well (Scheme 1). When stored and handled under dry nitrogen at room temperature, HL^1 and L^2 are stable for months.

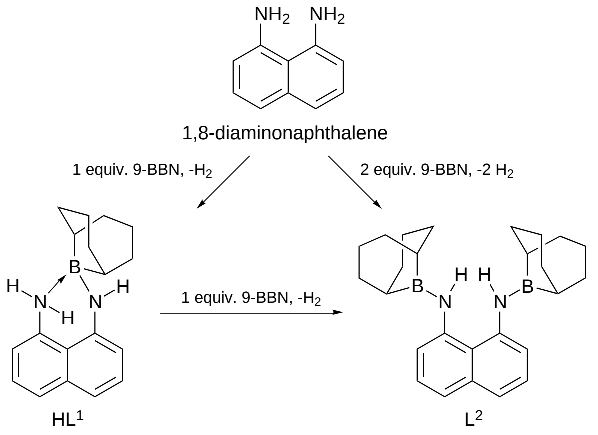
^1H, ^{13}C and ^{11}B NMR indicate that HL^1 is *pseudo*-C_{2v}-symmetrical on the NMR timescale, with the boron atom bridging between the two nitrogen atoms.‡ The three N–H protons appear as a sharp singlet in the ^1H NMR spectrum even at −50 °C. These data are consistent with a fast dynamic process in which the bridging 9-BBN unit is rocking between the two faces of the naphthalene ring, while the three N–H protons rapidly equilibrate between the two nitrogen atoms.

On the other hand, the two boron atoms in L^2 are three-coordinate according to ^{11}B NMR spectroscopy, *i.e.* they are not bridging between the two nitrogen atoms. Three peaks for six aromatic protons indicate a symmetrical naphthalene system. Two peaks for four bridgehead carbons of the two 9-BBN units indicate a high barrier to rotation of the 9-BBN groups around the B–N bonds attributed to p_π–p_π interactions.§

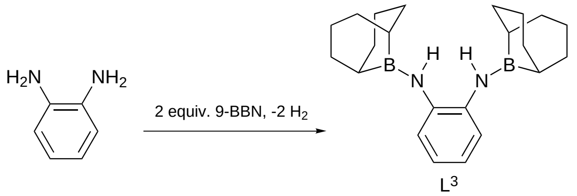
Interestingly, related aromatic diamines do not exhibit the same high selectivity in formation of an amine–aminoborane. Thus, reaction between 1,2-phenylenediamine and 2 equiv. of 9-BBN gave a bis(aminoborane), L^3, quantitatively, whose spectral properties are analogous to those of L^2 (Scheme 2).¶ However, reaction between 1,2-phenylenediamine and 1 equiv. of 9-BBN gave an inseparable mixture of products.

HL^1 reacted cleanly with tetrakis(dimethylamino)titanium in an amine elimination reaction giving $[TiL^1(NMe_2)_3]$ **1** and dimethylamine. **1** was isolated in high yield as an orange crystalline solid upon evaporation of the solvent and recrystallisation from diethyl ether–pentane at −35 °C. Tetrakis(dimethylamino)zirconium reacted similarly yielding $[ZrL^1(NMe_2)_3]$ **2** as a white crystalline solid after a similar work-up (Scheme 3, route a). **1** and **2** exhibit almost identical NMR spectra that indicate that, in solution, L^1 is a (4e,1−) symmetrical chelating diaminoborate-type ligand.‖

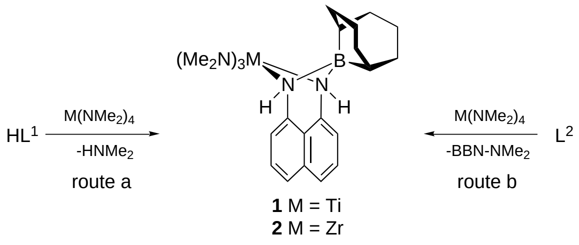
The X-ray crystal structure of the titanium complex **1** showed that the chelating diaminoborate ligand effectively blocks one face of the metal (Fig. 1).** The main structural feature is an almost perfectly symmetrical Ti–N–B–N four-membered ring, having B–N and Ti–N bond lengths of 1.60 and 2.29 Å, respectively, and N–B–N and N–Ti–N bond angles of 94.4 and 61.4°, respectively.



Scheme 1



Scheme 2



Scheme 3

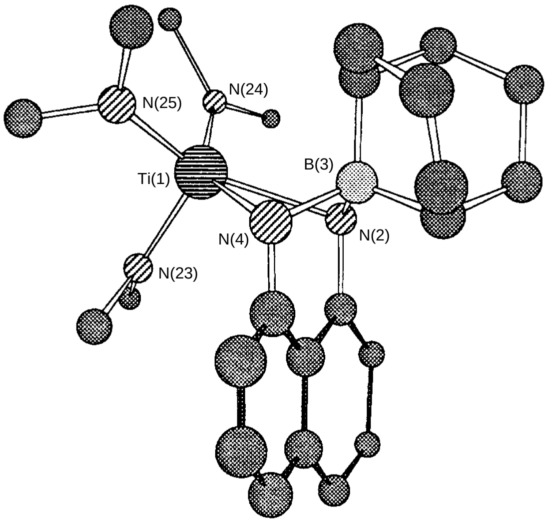


Fig. 1 Molecular structure of [TiL^1(NMe$_2$)$_3$] **1**. Hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Ti(1)–N(2) 2.302(3), Ti(1)–N(4) 2.282(4), Ti(1)–N(23) 1.874(3), Ti(1)–N(24) 1.927(5), Ti(1)–N(25) 1.912(3), B(3)–N(2) 1.586(7), B(3)–N(4) 1.604(5); N(2)–Ti(1)–N(4) 61.4(1), N(2)–B(3)–N(4) 94.4(4), Ti(1)–N(2)–B(3) 88.0(2), Ti(1)–N(4)–B(3) 88.3(3).

Several reports describing systems that include M–N–B–N four-membered rings have appeared (M = Ge, Sn, Ti, Zr, Cr).[7] However, in those cases the N–B–N unit either forms a (4e,2−) ligand, or it is a part of a larger heterocyclic system. The system we describe herein is the first case of a (4e,1−) diaminoborate ligand system, to the best of our knowledge. Unlike other (4e,1−) ligands, such as benzamidinate or acetylacetonate, the diaminoborate ligand consists of tetrahedral atoms rather than trigonal-planar atoms close to the metal centre. Since tetrahedral atoms are inherently more sterically demanding than trigonal-planar atoms, close control of the metal environment can be achieved by proper substitutions in this ligand system.

The *N*,*N*′-bis(trimethylsilyl) derivative of 1,8-diaminonaphthalene acts as a (4e,2−) ligand.[8] Considering the B–Si diagonal relationship one may expect that L^2 would act as a chelating (4e,2−) bis(borylamide) ligand[4] by double deprotonation. However, this was not the case. Instead, L^2 reacted cleanly with tetrakis(dimethylamino)-titanium and -zirconium to yield the diaminoborate complexes **1** and **2**, respectively, accompanied by 9-BBN–NMe$_2$ as a by-product[9] (Scheme 3, route b). The driving force for this unprecedented transformation is, apparently, the stability of the boron-bridged structure, in the 1,8-diaminonaphthalene skeleton.

Proximity effects have a strong effect on chemical reactivity in 1,8-disubstituted naphthalenes.[10] We think that the selective formation of HL^1 and of the (4e,1−) metal complexes of L^1 (**1** and **2**) are a result of such effects. We are currently investigating these effects as well as the reactivity of the novel diaminoborate complexes.

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Footnotes

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‡ HL^1 was prepared on a 20 mmol scale by adding 1 equiv. of 9-BBN in hexanes to a solution of 1,8-diaminonaphthalene in ether under nitrogen, and stirring at room temp. until hydrogen evolution ceased (*ca*. 30 min). The light yellow solid that precipitated was washed with ether and dried to give pure HL^1 in *ca*. 95% yield: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 0.58 (br s, 2 H, CH), 1.60–2.20 (m, 12 H, 6 CH$_2$), 4.06 (s, 3 H, NH), 6.12 (d, 2 H, *J* 8 Hz), 7.08 (t, 2 H, *J* 8 Hz), 7.24 (d, 2 H, *J* 8 Hz). ^{13}C{^{1}H} NMR ([^{2}H$_8$]thf, 50.4 MHz) δ 24.4 (CH), 27.3 (CH$_2$), 33.2 (CH$_2$), 113.4 (CH), 120.6 (CH), 128.3 (CH). ^{11}B NMR (C$_6$D$_6$, 115.5 MHz) δ −1.7.

§ L^2 was prepared on a 10 mmol scale, by adding 2 equiv. of 9-BBN in hexanes to a solution of 1,8-diaminonaphthalene in ether under nitrogen, and stirring at room temp. until hydrogen evolution ceased (*ca*. 30 min). Removing the solvents under vacuum yielded white crystalline L^2 quantitatively: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 1.29–1.95 (m, 14 H), 6.92 (s, 2 H, NH), 7.04 (d, 2 H, *J* 8 Hz), 7.15 (t, 2 H, *J* 8 Hz), 7.44 (d, 2 H, *J* 8 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$ 50.4 MHz) δ 22.9 (CH), 28.1 (CH), 24.4 (CH$_2$), 33.8 (CH$_2$), 34.4 (CH$_2$), 126.2 (CH), 123.6 (CH), 126.3 (CH). ^{11}B NMR (C$_6$D$_6$, 115.5 MHz) δ 49.9.

¶ L^3: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 1.30–2.04 (m, 14 H), 5.67 (s, 2 H, NH), 7.02 (m, 2 H), 7.23 (m, 2 H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 50.4 MHz) δ 23.2, 28.0 (CH), 24.5, 34.0, 34.8 (CH$_2$), 125.3, 125.9 (CH); ^{11}B NMR (C$_6$D$_6$, 115.5 MHz) δ 51.6.

‖ [TiL^1(NMe$_2$)$_3$] **1**: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 0.63 (br s, 1 H, CH), 0.67 (br s, 1 H, CH), 1.75–2.20 (m, 12 H, 6 CH$_2$), 2.84 (s, 18 H), 4.11 (s, 2 H, NH), 6.39 (d, 2 H, *J* 7 Hz), 7.13 (t, 2 H, *J* 7 Hz), 7.20 (d, 2 H, *J* 7 Hz). ^{11}B NMR (C$_6$D$_6$, 115.5 MHz) δ −2.8. [ZrL^1(NMe$_2$)$_3$] **2**: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 0.69 (br s, 2 H, CH), 1.68–2.11 (m, 12 H, 6 CH$_2$), 2.69 (s, 18 H) 3.99 (s, 2 H, NH), 6.37 (d, 2 H, *J* 7 Hz), 7.08 (t, 2 H, *J* 7 Hz), 7.22 (d, 2 H, *J* 7 Hz). ^{11}B NMR (C$_6$D$_6$, 115.5 MHz) δ −4.4.

** *Crystal data* for C$_{24}$H$_{40}$BN$_5$Ti, *M* = 457.32, monoclinic, space group $P2_1/a$, *a* = 15.649(4), *b* = 18.949(2), *c* = 18.404(3) Å, β = 111.72(2)°, *U* = 5070(2) Å^3, *Z* = 8, D_c = 1.198 g cm^{-3}, λ(Mo-Kα) 0.71073 Å, $2\theta_{max}$ = 45.96°. Data were collected on an Enraf-Nonius CAD4 diffractometer using an orange crystal mounted in a sealed glass capillary at room temperature. Of a total of 6245 collected reflections, 6027 were unique (R_{int} = 0.0387). The structure was solved by direct methods. The final cycle of full-matrix least-squares refinement was based on 6027 observed reflections ($I > 0$) and 571 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.0995, R_w = 0.1391 for the entire data. GOF = 1.010. Residual electron densities: +0.20, −0.29 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/314.

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