The replacement of C=C double bonds in organic molecules by isotopic covalent B=N units is not only interesting from a fundamental point of view, but also opens up the exploration of a vast hybrid organic–inorganic chemical space. While the typical B=N double bond (1.39 Å) is only marginally longer than a C=C double bond (1.34 Å, Figure 1), the intrinsic strong polarization of B=N bonds imparts very different electronic properties and stability to the resulting molecules and materials, which can be exploited for new applications in materials science, catalysis, and medicinal chemistry.

Since the landmark synthesis of borazine by Stock and Pohland in 1926 (Figure 1, I),[1] new synthetic methodologies have enabled access to an ever-increasing variety of B=N/C=C-isoteric compounds and materials, including boron nitride[2] and borocarbonitride (B,C,N) nanomaterials,[3] hybrid organic–inorganic BN-doped conjugated polymers,[4] (poly)aromatic compounds,[5] and aromatic small molecules.[6]

However, well-defined acyclic conjugated BN chains, such as poly(aminoboranes) (III) or BN-based cumulenes (IV), remain difficult to access. The intuitive synthetic routes to III via the polymerization of inaminoborane (RB=N=NR’)[7] or the dehydrocoupling of amine borane (H2RB·NH2R) precursors[8] or the dehydrocoupling of amine borane (H2RB·NH2R) precursors[8] or the dehydrocoupling of amine borane (H2RB·NH2R) precursors[8] are in practice marred by the formation of cyclic oligomers such as I and II. The most efficient access to higher oligo(aminoboranes) is by B=N coupling of chloroborane and silylamine precursors via CSI(Me3) elimination.[9] The group of Helten has used this methodology to synthesize the first well-defined oligo(aminoboranes) (V) by polycondensation of 1,3-bis(trimethylsilyl)-1,3,2-diazaborolidine precursors with dichloro(organo)boranes (Scheme 1a).[10] Our group has also reported the coupling of two Cl2BN(SiMe3)2 molecules at [(C5H5)Ru(CO)2]Na with elimination of NaCl and ClSiMe3, yielding the (N-aminoboryl)aminoborane complex VI (Scheme 1b).[11]

We have recently reported the synthesis of the boranediyl A-frame complexes 2-X3 from the twofold oxidative addition of dialhoborane precursors (X=BY, Y=Cl, Br; B=alkyl, aryl, amino) to the bis(dimethylphosphino)methane (dpmm)-bridged Pt2 complex I (Scheme 2a).[12] Inspired also by the metal-template coupling of two BN units at ruthenium in complex VI (Scheme 1b),[12] we now report the use of the Pt2(dpmm) scaffold as a template for the coupling of B=N units derived from the coupling of dihalo(silylamine)boranes with A-frame complexes 2-X3.

By contrast, the analogous reaction with Br2BN(SiMe3)2 leads to a PtII ligand. In contrast, the analogous reaction with Br2BN(SiMe3)2 leads to cyclization of the BNBN unit, forming a unique 1,3,2,4-diazadiboretidin-2-yl elimination from the tBu-derivative leads to cyclization of the BNBN unit, forming a unique 1,3,2,4-diazadiboretidin-2-yl elimination.

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proceeds via a same intermediate (fwmh = 1480 Hz, Pt(B)) and 32 ppm (fwmh = 470 Hz, N2BCl). The conversion of 4** to 4** is evidenced more clearly by changes in the 31P{1H} spectrum, which shows two new 1:1 multiplets with higher pickup (4**). 11B NMR spectroscopic monitoring of

$\text{Pt} = \text{Cl}$ and $\text{SiMe}_3$ to form complex 6. The A-frame structure itself is more strongly distorted from the ideal A-frame than in 2-B**NMe2, as evident in the much shorter Pt-Br distance (6 3.2397(3); 2-B**NMe2 3.3003(4) Å) and larger P1/P1-P2/P2 torsion angles (6 -12.29(5), -23.83(5)°; 2-B**NMe2 4.96(7), 15.62(8)°).[13] Furthermore, the B1-N1 and B2-N2 bond lengths of 1.396(7) and 1.388(8) Å are within the range of partial double bonds, whereas the central N1-B2 bond is significantly shorter (1.237(8) Å), corresponding to a partial triple bond.[9] While the linear BNBN motif can be viewed formally as a 1-boryl-2-(amino)iminoborane, the delocalization of the π electron density apparent in the B-N bond lengths makes it structurally more akin to an all-BN isostere of a butatriene. Unlike butatriene, however, which is fully planar, the B1 and N2 planes form an angle of ca. 24°, which could result from the steric repulsion between the SiMe3 groups and the dmpm ligands.

The electronic structure of 6 was further investigated using DFT and intrinsic bond orbital (IBO)[20] calculations. The BNBN motif in the optimized structure of 6, obtained at the M06[21]-D3[22] level of theory, shows a larger deviation from linearity (B1-N1-B2 161.3°, N1-B2-N2 171.3(3)°). Similar results were obtained with other density functionals (see details in the SI). In order to investigate the origin of this deviation, we performed computations on four truncated model systems, in which the PMe3 and SiMe3 groups were successively replaced with PH3 and SiH4 or H, respectively (see Figure S19 in the SI). In all of these cases, the BNBN

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\text{Scheme 4. Reaction of complex 1 with Br}_{2}N(SiMe)_{3}. \text{Isolated yield in parentheses.}
\]

**Scheme 5. Proposed mechanism of formation of 3** and 6 via the common intermediate Int-X**\[\text{NMe}_{2}\]**. 

XSiMe3 elimination (reaction rate constant $k_4$) to form an η1-(N-aminoboryl)aminoboryl complex analogous to 3**, or by the oxidative addition of the second B−X bond of the silylamine(halo)boryl ligand to platinum to form the (silyl-aminoboryl)aminoboryl A-frame complex 2-X**NMe2(SiMe3) (reaction rate constant $k_5$). For $R = \text{SiMe}_3$, the latter then undergoes twofold XSiMe3 elimination with a second equivalent of X,BN(SiMe)3 to form complex 6. The selectivity of the reaction is therefore determined by the relative values of the reaction rate constants $k_4$ and $k_5$; for $R = \text{Cl}$ the rate of B−N coupling outperforms that of oxidative addition of B−Cl to Pt, leading to the exclusive formation of 3**, the opposite being the case for $X = \text{Br}$, leading to the exclusive formation of 6.

The solid-state structure of 6 (Figure 2) confirmed the formation of the pseudo-merohedrally twinned crystals (B1-N1-B2 173.8(6), N1-B2-N2 171.3(3)°). While the Pt−B bond lengths of 2.028(6) and 2.021(6) Å are similar to those in complex 2-B**NMe2 (2.028(10), 2.042(9) Å), the A-frame structure itself is more strongly distorted from the ideal A-frame than in 2-B**NMe2, as evident in the much shorter Pt−B distance (6 3.2397(3); 2-B**NMe2 3.3003(4) Å) and larger P1/P1-P2/P2 torsion angles (6 -12.29(5), -23.83(5)°; 2-B**NMe2 4.96(7), 15.62(8)°).[13] Furthermore, the B1-N1 and B2-N2 bond lengths of 1.396(7) and 1.388(8) Å are within the range of partial double bonds, whereas the central N1-B2 bond is significantly shorter (1.237(8) Å), corresponding to a partial triple bond.[9] While the linear BNBN motif can be viewed formally as a 1-boryl-2-(amino)iminoborane, the delocalization of the π electron density apparent in the B−N bond lengths makes it structurally more akin to an all-BN isostere of a butatriene. Unlike butatriene, however, which is fully planar, the B1 and N2 planes form an angle of ca. 24°, which could result from the steric repulsion between the SiMe3 groups and the dmpm ligands.

The electronic structure of 6 was further investigated using DFT and intrinsic bond orbital (IBO)[20] calculations. The BNBN motif in the optimized structure of 6, obtained at the M06[21]-D3[22]- cc-pVQZ[23],aug-cc-pVQZ-PP[24] level of theory, shows a larger deviation from linearity (B1-N1-B2 161.3°, N1-B2-N2 176.2°) than that of the solid-state structure. Similar results were obtained with other density functionals (see details in the SI). In order to investigate the origin of this deviation, we performed computations on four truncated model systems, in which the PMe3 and SiMe3 groups were successively replaced with PH3 and SiH4 or H, respectively (see Figure S19 in the SI). In all of these cases, the BNBN
moiety was found to be linear (B1-N1-B2 and N1-B2-N2 178.8–180.0°). The distortion from linearity therefore seems to arise from the steric repulsion between the PMe2 and SiMe3 substituents, although the additional influence of crystal packing forces in the solid-state structure cannot be discounted. Furthermore, the calculated Mayer bond orders (MBOs)20 of the BNBN motif in 4 (B1–N1: 1.38, N1–B2: 2.11, B2–N2: 1.32) are very similar to those obtained for the parent H4BNBNH4 system (B1–N1: 1.51, N1–B2: 2.13, B2–N2: 1.43), these values suggesting strong cumulenic character in both cases. Indeed, inspection of the IBOs of 6 (Figure 3a) reveals that IBO-1 and IBO-3, which are orthogonal to the B2 and B1 atoms, are partially delocalized to the neighboring B2 and B1 atoms, evidencing deviation from the 1-boryl-2-(Pt1-B1-Pt2) plane, reveals that IBO-1 and IBO-3, which are orthogonal to the parent H2BNBNH2 system (B1

inspection of the canonical Kohn–Sham molecular orbitals (amino)iminoborane picture. This view is also supported by b) and B1 atoms, evidencing deviation from the 1-boryl-2-(Pt1-B1-Pt2) plane, are partially delocalized to the neighboring B2 and B1 atoms, from deviation from the 1-boryl-2-(amino)iminoborane picture. This view is also supported by inspection of the canonical Kohn–Sham molecular orbitals (MOs) of 6 and H2BNBNH2 (Figure 3b and S20 in the SI), where π electron delocalization over the entire BNBN unit is observed. The description of 6 as a BNBN analogue of butatriene is, therefore, fully supported by quantum chemical investigations.

To conclude, we have shown that the [μ-(dmpm)Pt2] framework acts as an effective template for the coupling of B–N units obtained by the intermolecular B–N coupling of dihalo(silylaminoboranes via halosilane elimination. For Cl2BNR(SiMe3) precursors BN chain growth occurs at a side-on Pt2 complex, whereas for Br2BN(SiMe3)2 an A-frame Pt6 complex bridged by a linear BNBN unit is formed. Structural and computational analyses confirm a cumulenic motif isosteric with butatriene.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: 1,3,2,4-diazaboretidin-2-yi ligand · A-frame complex · B–N coupling · butatriene analogue · isosterism

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The \([\mu\text{-dmpm}]\text{Pt}_2\) template promotes the coupling of B=N units derived from dihalo(silylamino)borane precursors by B–N bond formation through intermolecular halosilane elimination. For Cl\(_2\)BNR(SiMe\(_3\)) \(\eta^1\)-(N-amino-boryl)aminoboryl and \(\eta^1\)-1,3,2,4-diazaboretidin-2-yl Pt\(_2\) complexes are obtained, whereas for Br\(_2\)BN(SiMe\(_3\))\(_2\) an A-frame complex bridged by the first BNBN analogue of a butatriene is formed, as confirmed by structural and theoretical analyses.