Ligand Design

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A σ-Donor with a Planar Six-π-Electron $B_2N_2C_2$ Framework: Anionic N-Heterocyclic Carbene or Heterocyclic Terphenyl Anion? **

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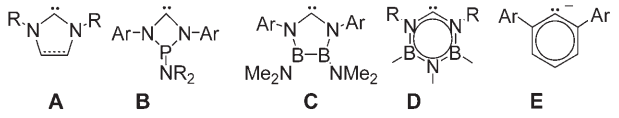
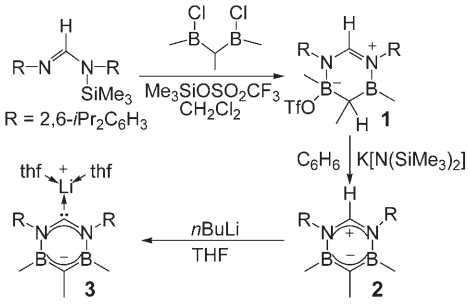
Dedicated to Professor Tristram Chivers

The remarkable success of N-heterocyclic carbenes[1] (NHCs) as ligands in main-group and especially in transition-metal chemistry and catalysis[2] has prompted the synthesis and characterization of numerous representatives of this class of compounds. Derivatives with a five-membered framework (**A**) have been investigated most extensively. However, four-, six-, and seven-membered carbenes have also been reported. Emerging trends in carbene ligand design involve the replacement of one or both intraannular nitrogen atoms with elements such as carbon, phosphorus, and sulphur,[3] and the replacement of the carbon backbone with heteroelements (**B**–**D**).[4] In this way, the steric and electronic properties of the ligand can be effectively tuned. Although NHCs are traditionally neutral ligands, a few anionic derivatives have been prepared in which the charge is localized on an adjoining borate or cyclopentadienyl moiety.[5] Herein we report the synthesis of an anionic NHC (**3**) that has a six-π-electron system in which the charge is localized on the ring framework. This compound has the potential to coordinate in either σ (η^1) or π (η^6) fashion.



The reaction of the corresponding trimethylsilyl formamidinate[4c] with 1,1-bis(methylchloroboryl)ethane[6] in the presence of trimethylsilyl triflate (Scheme 1) yielded the zwitterionic ring compound **1**. Crystallographic analysis (Figure 1) revealed an iminium borate structure with the triflate group coordinated to one of the boron atoms.[7] The $B_2N_2C_2$ ring in **1** has a half-boat conformation with the sp^3-hybridized carbon C(2) situated outside the slightly twisted $B_2N_2C(1)$ plane. The B–C and B–N bonds to borate center B(1) are longer than the corresponding bonds to borane center B(2), and the two N–C(1) bonds within the ring are not equal. The ^{11}B NMR spectrum of **1** in benzene displayed only one signal at $\delta = 40.7$ ppm, which corresponds to a three-coordinated boron and indicates that the triflate dissociates in solution to form an ion pair. The ^1H and ^{13}C spectra are in agreement with C_s symmetry.



Scheme 1. Synthesis of derivatives **1**–**3**.

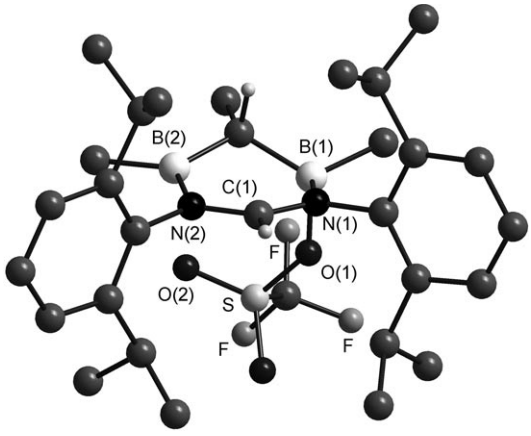


Figure 1. Molecular structure of **1**. Hydrogen atoms on the organic substituents have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N(1)–C(1) 1.298(2), N(2)–C(1) 1.345(2), N(1)–B(1) 1.595(3), N(2)–B(2) 1.475(3), C(2)–B(1) 1.603(3), C(2)–B(2) 1.550(3), O(1)–B(1) 1.626(3); N(1)-C(1)-N(2) 125.74(17), C(1)-N(1)-B(1) 121.48(16), C(1)-N(2)-B(2) 122.23(16), B(1)-C(2)-B(2) 113.66(16).

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Deprotonation of **1** with an equimolar amount of K[N(SiMe$_3$)$_2$] cleanly yielded the 1,5-diaza-2,4-diborine **2**. Few carbaborazines have been described, and a derivative with this framework has not been reported; however, its stability and properties have been the object of theoretical calculations.[8] At −40 °C, the ^{13}C NMR spectrum features signals corresponding to the ring carbon atoms adjacent to nitrogen and boron at $\delta = 146.8$ and 119.2 ppm, respectively, in the typical range for benzene derivatives.

The X-ray structural determination of **2** (Figure 2) confirmed the proposed structure, which contains a planar $B_2N_2C_2$ ring with equivalent pairs of B–N, B–C, and N–C

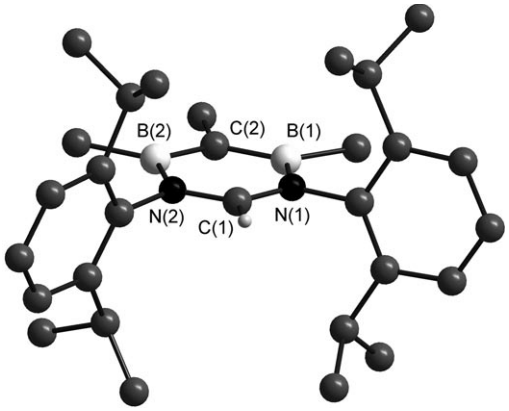

Figure 2. Molecular structure of **2**. Hydrogen atoms on the organic substituents have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N(1)–C(1) 1.3264(17), N(2)–C(1) 1.3274(17), N(1)–B(1) 1.5027(19), N(2)–B(2) 1.4980(19), C(2)–B(1) 1.477(2), C(2)–B(2) 1.479(2); N(1)-C(1)-N(2) 122.83(12).

bond lengths.[7] The endocyclic N–C bond lengths (ca. 1.33 Å) are intermediate between the two values observed in **1** and practically identical to those observed in the cationic precursors to carbenes **B**–**D**.[4] The B–N bond lengths in **2** (1.50 Å) are similar to those observed in **C** and significantly longer than those in borazines (1.42–1.44 Å).[9] The intraannular B–C and N–C bonds (1.48 and 1.33 Å, respectively) are shorter than the corresponding bonds observed in the regioisomers 1,3-diaza-2,4-diborine and 1,4-diaza-2,3-diborine (ca. 1.53 and 1.38–1.40 Å, respectively).[10] The B–N bond lengths in the latter derivatives are equal with those in borazines. As proposed by Bertrand and co-workers for the cationic precursor to **D**,[4d] the six π electrons in **2** appear to be distributed over two allyl-like fragments (B_2C^- and N_2C^+) to form a zwitterionic structure, rather than delocalized over the entire ring framework.

Deprotonation of **2** with *n*BuLi produced the lithium salt **3**, which was stable in the solid state under an inert atmosphere but decomposed slowly in tetrahydrofuran (thf) through deprotonation of the solvent and reformation of the starting material. The crystallographic determination (Figure 3) revealed that **3** contains a planar $B_2N_2C_2$ ligand σ-coordinated to the lithium ion.[7] The distorted trigonal planar coordination environment of lithium center is completed by two thf molecules, and the ring carbon atoms and

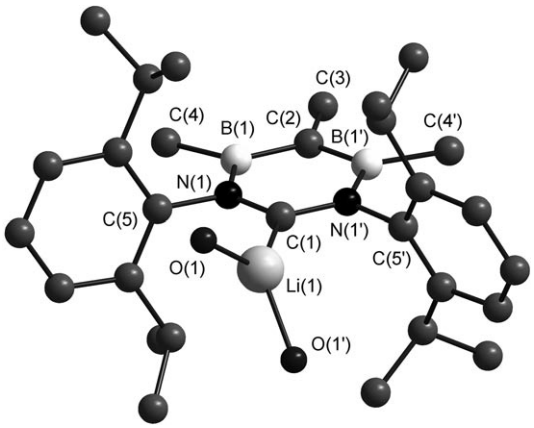

Figure 3. Molecular structure of **3**. Hydrogen atoms on the organic substituents and the carbon atoms in the thf molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–Li(1) 2.152(6), N(1)–C(1) 1.3627(19), N(1)–B(1) 1.495(3), C(2)–B(1) 1.475(3), N(1)–C(5) 1.450(2), C(4)–B(1) 1.599(3), C(2)–C(3) 1.518(4), O(1)–Li(1) 1.946(4); N(1)-C(1)-N(1′) 114.0(2), N(1)-C(1)-Li(1) 123.01(10), O(1)-Li(1)-C(1) 130.48(13), O(1)-Li(1)-O(1′) 99.0(3).

the lithium atom lie on a crystallographic C_2 axis. Consistent with other NHCs, deprotonation of **2** results in lengthening of the intraannular N–C bonds by approximately 0.03 Å to a value of 1.36 Å. The N(1)-C(1)-N(1′) angle in **3** (114.0°) is more acute than that in **2** (122.8°) and **1** (125.7°). This is a result of a lateral compression of the ring skeleton, which causes an increase of the C(1)···C(2) distance by 0.13 Å in **3** versus **2**. The overall geometry of **3** strongly resembles the structure of isoelectronic lithium terphenyl derivatives.[11] The planar six-π-electron σ-donating anion in **3** could therefore be seen as either an anionic NHC or a heterocyclic terphenyl anion (**E**).

The Li–C bond length and the chemical shift of the carbon atom connected to lithium center can be considered when comparing **3** to a lithium NHC complex and a lithium terphenyl. The Li(1)–C(1) bond measures 2.152(6) Å, which is typical for lithium NHC complexes. In representatives of this class, the substitution of the lithium center and the charge of the NHC ligand have little influence on the length of the Li–C bond (2.124(4)–2.197(4) Å).[12] Conversely, the length of the Li–C bond in trigonal-planar, three-coordinate terphenyl lithium derivatives falls within a narrow range (2.074(16)–2.128(4) Å).[13] The ^{13}C NMR signal corresponding to the carbene carbon atom could not be located in the spectrum of **3**. However, the potassium analogue, obtained by deprotonation of **2** with benzyl potassium, displayed a signal for the carbene carbon atom at 239.1 ppm, which is significantly downfield shifted relative to the ipso carbon atom in terphenyl lithium derivatives (175–201 ppm)[13] and the carbene carbon atom in NHC–Li (189–198 ppm)[12] and NHC–K complexes[14] (199–208 ppm). It is uncertain if this signal belongs to the free anionic carbene or the potassium-coordinated ligand. To our knowledge, potassium terphenyl derivatives have not been reported.

A density functional theory treatment of the simplified structures **I**–**III** showed an increase in the energy of both the

highest occupied molecular orbitals (HOMOs; σ) and the lowest unoccupied molecular orbitals (LUMOs; π) in the order of **I** to **II** to **III**, which indicates that the σ-donating ability decreases in the order **III** > **II** ≫ **I** and the π-accepting ability decreases in the reverse order (Figure 4). NHCs are generally considered to be excellent σ donors and poor

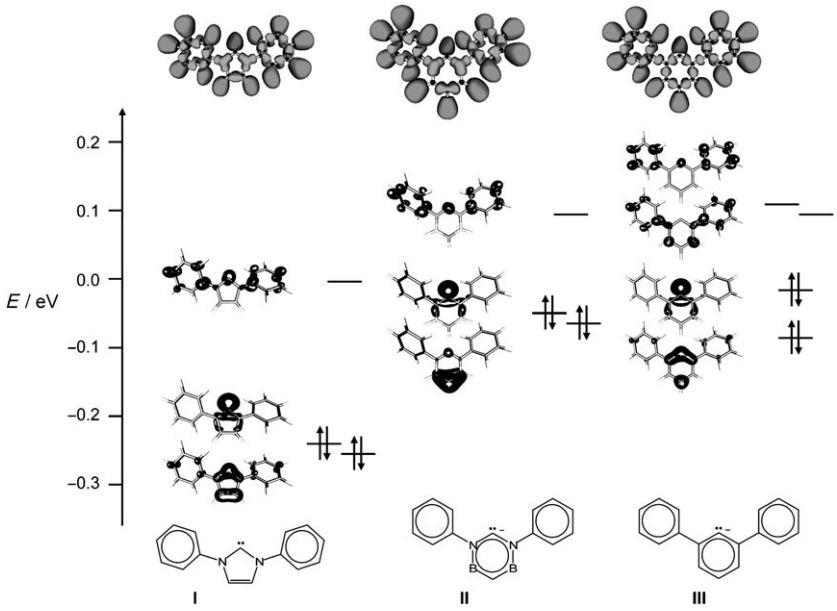

Figure 4. Frontier molecular orbitals and ELF diagrams for systems I–III.

π acceptors. Analysis of the electron localization function (ELF)[15] for the compounds in question gives occupancies of 2.28, 2.35, and 2.45 electrons for the carbon lone-pair basins in **III**, **II**, and **I**, respectively. Hence, the ELF analysis suggests that NHC **I** is a better σ donor than is predicted by the orbital energies alone. The same is implied by the trends in Mulliken atomic charges, which show that the carbene carbon atom in NHC **I** bears slightly more negative charge (−0.20) than that in **II** (−0.15) or **III** (−0.14). To fully resolve the issue of relative σ-donating ability of the studied systems, we performed charge decomposition analyses (CDA)[16] for complexes of **I**–**III** with Li^+ and CuCl. The results show that the σ-donating ability of ligands **I**–**III** follows the trend in orbital energies for the Li^+ complexes (total donation of σ electrons is 0.484, 0.566, and 0.622 for **I**, **II**, and **III**, respectively), but within the CuCl series ligand **II** has similar σ-donating ability to **I** (total donation of 0.236 and 0.233 electrons, respectively) and **III** has slightly less (0.206 electrons). Hence, the computational data indicate that the new anionic carbene **II** has similar or even greater σ-donating ability, depending on the metal fragment, than the traditional ligand **I**.

In summary, experimental and theoretical evidence indicates that the anionic carbene in **3** bridges the gap between two classical ligands that have quite different properties: NHCs and terphenyl anions. Its facile synthesis from the formally zwitterionic diazadiborine **2** renders the novel system a promising anionic ligand, with which both σ (η^1) and π (η^3 or η^6) coordination modes are possible. Its coordinating ability towards transition metals is currently being investigated.

Experimental Section

All operations were carried out with exclusion of air and moisture. The NMR spectra were measured on a Bruker Avance DRX-400 spectrometer. All chemicals were prepared according to reported procedures or purchased from commercial sources. Computational details are presented in the Supporting Information.

1: 1,1-Bis(chloromethylboryl)ethane (345 mg, 2.3 mmol) was added slowly to a solution of *N*,*N*′-bis(2,6-diisopropylphenyl)trimethylsilylformamidine (1.0 g, 2.3 mmol) in dichloromethane (20 mL) at room temperature. The solution was stirred for one hour, trimethylsilyltriflate (0.5 g, 2.2 mmol) was added, and the solution was stirred for an additional 30 minutes. Volatile substances were removed in vacuo and the oily residue was recrystallized from hexane to yield **1** as a colorless, crystalline solid (0.82 g, 1.14 mmol, 61 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 0.21$ (s, 6H, BCH_3), 0.87 (q, 1H, B_2CHCH_3, $^3J_{H,H} = 7.0$ Hz), 1.14, 1.15 (d, 6H, $CH(CH_3)_2$, $^3J_{H,H} = 6.9$ Hz), 1.24, 1.25 (d, 6H, $CH(CH_3)_2$, $^3J_{H,H} = 6.8$ Hz), 1.32 (d, 3H, B_2CHCH_3, $^3J_{H,H} = 7.0$ Hz), 2.94 (sept., 2H, $CH(CH_3)_2$, $^3J_{H,H} = 6.9$ Hz), 3.24 (sept., 2H, $CH(CH_3)_2$, $^3J_{H,H} = 6.8$ Hz), 7.23, 7.27 (dd, 2H, *m*-C_6H_3, $^3J_{H,H} = 7.8$ Hz, $^4J_{H,H} = 1.5$ Hz), 7.37 (t, 2H, *p*-C_6H_3, $^3J_{H,H} = 7.8$ Hz), 7.57 ppm (s, 1H, $N_2C(H)$); ^{13}C NMR (100 MHz, CD_2Cl_2, −50 °C): $\delta =$ 0.8 (B_2CHCH_3), 4.5 (BCH_3), 9.9 (B_2CHCH_3), 24.1, 24.2, 25.6, 25.8 ($CH(CH_3)_2$), 28.5, 29.4 ($CH(CH_3)_2$), 124.2, 124.6 (*m*-C_6H_3), 128.9 (*p*-C_6H_3), 136.6 (*i*-C_6H_3), 144.0, 144.8 (*o*-C_6H_3), 160.9 ppm (N_2CH); ^{11}B NMR (128 MHz, C_6D_6, 25 °C): $\delta = 40.7$ ppm; MS (EI, 70 eV): *m*/*z* 443(8) [$M^+ - O_3SCF_3$], 427(100) [$M^+ - O_3SCF_3 - CH_3$]; HRMS (EI, 70 eV): found *m*/*z* 443.3727 [$M^+ - O_3SCF_3$], calcd for $H_{45}C_{29}N_2{}^{11}B_2$ *m* = 443.3769.

2: A mixture of **1** (1.0 g, 1.69 mmol) and K[$N(SiMe_3)_2$] (0.36 g, 1.8 mmol) was stirred in toluene (30 mL) for 1 h at room temperature and then filtered. Volatile substances were removed in vacuo to leave behind **2** as a crystalline, colorless solid (0.64 g, 1.45 mmol, 86 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 0.26$ (s, 6H, BCH_3), 1.12, 1.18 (d, 12H, $CH(CH_3)_2$, $^3J_{H,H} = 6.8$ Hz), 2.06 (s, 3H, B_2CHCH_3), 2.75 (sept., 4H, $CH(CH_3)_2$, $^3J_{H,H} = 6.8$ Hz), 7.24 (d, 4H, *m*-C_6H_3, $^3J_{H,H} = 7.6$ Hz), 7.36 (t, 2H, *p*-C_6H_3, $^3J_{H,H} = 7.6$ Hz), 7.57 ppm (s, 1H, N_2CH); ^{13}C NMR (100 MHz, CD_2Cl_2, −40 °C): $\delta = 0.1$ (br, BCH_3), 16.9 (B_2CCH_3), 23.6, 24.8 ($CH(CH_3)_2$), 27.9 ($CH(CH_3)_2$), 119.2 (br, B_2CCH_3), 123.8 (*m*-C_6H_3), 128.2 (*p*-C_6H_3), 139.1 (*i*-C_6H_3), 144.1 (*o*-C_6H_3), 146.8 ppm (N_2CH); ^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C): $\delta = 38.4$ ppm; MS (EI, 70 eV): *m*/*z* 442(24) [M^+], 427(80) [$M^+ - CH_3$]; HRMS (EI, 70 eV): found *m*/*z* 442.3656, calcd for $H_{44}C_{29}N_2{}^{11}B_2$ *m* = 442.3691.

3: Solid *n*BuLi (5 mg, 0.9 μmol) was added at room temperature to a solution of **2** (20 mg, 0.45 μmol) in THF (1 mL). The solvent was removed in vacuo, and the colorless product (19 mg, 0.32 μmol, 71 %) was recrystallized from toluene to yield colorless crystals. ^{1}H NMR (400 MHz, [D_8]THF, 25 °C): $\delta = 0.02$ (s, 6H, BCH_3), 1.09, 1.12 (d, 12H, $CH(CH_3)_2$, $^3J_{H,H} = 6.9$ Hz), 1.89 (s, 3H, B_2CHCH_3), 3.23 (sept., 4H, $CH(CH_3)_2$, $^3J_{H,H} = 6.9$ Hz), 7.15 ppm (s, 6H, C_6H_3); ^{13}C NMR (100 MHz, [D_8]THF, 25 °C): $\delta = 2.3$ (s, br, BCH_3), 17.8 (B_2CCH_3), 25.2, 25.4 ($CH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 124.1 (*m*-C_6H_3), 126.4 (*p*-C_6H_3), 146.2 (*o*-C_6H_3), 149.7 ppm (*i*-C_6H_3); ^{11}B NMR (128 MHz, [D_8]THF, 25 °C): $\delta = 36.3$ ppm; ^{7}Li NMR (155 MHz, [D_8]THF, 25 °C): $\delta = 0.15$ ppm.

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[7] Crystallographic data: **1**: $C_{30}H_{45}B_2F_3N_2O_3S$, 193 K, $0.31\times0.26\times0.21$ mm^3, monoclinic, space group $P2_1/c$, $a=19.2460(17)$, $b=10.6805(10)$, $c=15.7888(14)$ Å, $\alpha=\gamma=90°$, $\beta=90.9307(15)°$, $V=3245.01(5)$ Å^3, $Z=4$, $\rho_{calcd}=1.212$ g cm^{-3}, $2.30=\theta=25.86°$, $R_1=0.0507$ ($I>2\sigma(I)$), $wR_2=0.1330$ (all data); residual electron density: 0.280/−0.276 e Å^{-3}. **2**: $C_{29}H_{44}B_2N_2$, 193 K, $0.65\times0.57\times0.23$ mm^3, orthorhombic, space group $Pbca$, $a=15.6004(13)$, $b=21.0211(18)$, $c=17.1099(15)$ Å, $\alpha=\gamma=\beta=90°$, $V=5611.0(8)$ Å^3, $Z=8$, $\rho_{calcd}=1.047$ g cm^{-3}, $2.27=\theta=26.36°$, $R_1=0.0472$ ($I>2\sigma(I)$), $wR_2=0.1415$ (all data); residual electron density: 0.287/−0.224 e Å^{-3}. **3**: $C_{37}H_{59}B_2LiN_2O_2$, 173 K, $0.16\times0.12\times0.08$ mm^3, monoclinic, space group $C2/c$, $a=12.227(4)$, $b=18.309(6)$, $c=16.603(3)$ Å, $\alpha=\gamma=90°$, $\beta=97.74(2)°$, $V=3683.0(18)$ Å^3, $Z=4$, $\rho_{calcd}=1.068$ g cm^{-3}, $3.30=\theta=27.50°$, $R_1=0.070$ ($I>2\sigma(I)$), $wR_2=0.209$ (all data); residual electron density: 0.53/−0.37 e Å^{-3}. $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined by using the riding model. CCDC-602682–602684 (**1**–**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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