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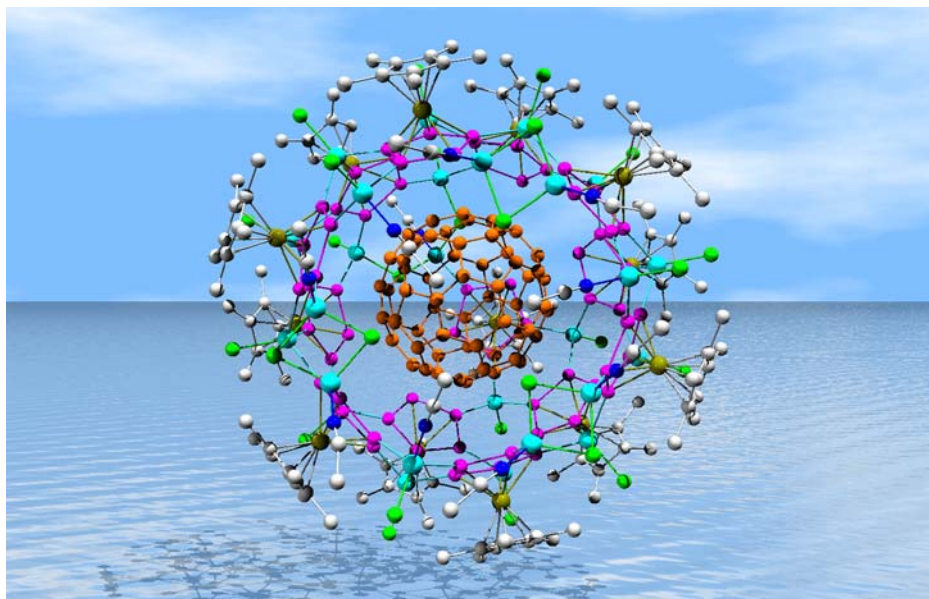
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Synthesis and structure of two new (guanidinate)boron dichlorides and their attempted conversion to boron(I) derivatives†‡

Michael Findlater,[a] Nicholas J. Hill[b] and Alan H. Cowley*[a]

To test the feasibility of the guanidinate architecture for the support of boron(I) carbene analogues the energy gap between the singlet and triplet states of the model compound, [Me$_2$NC{N(Ph)}$_2$B:] (**7**), has been probed by both DFT and second order Møller–Plesset (MP2) methods. The singlet state is calculated to be more stable than the triplet state by between 6.0 and 10.1 kcal mol^{-1}. The new (guanidinate)boron dichlorides [Ph$_2$NC{N(Mes)$_2$}]BCl$_2$ (**14**) and [Ph$_2$NC{N(Dipp)$_2$}]BCl$_2$ (**15**) have been prepared and characterized by single-crystal X-ray diffraction. Attempts to reduce **14** and **15** to the corresponding boron(I) species were not successful.
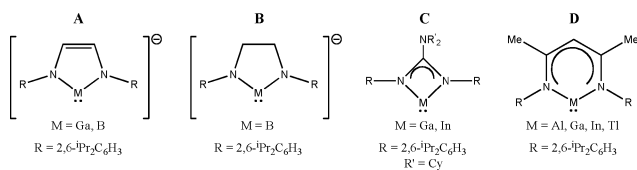
Introduction

One of the vibrant themes of current main group chemistry is focused on the preparation, structural characterization and ligative behaviour of group 13 carbene analogues. An early development in this respect was the isolation of the gallyl anions [Ga{N(R)CH}$_2$]$^-$ (**1**:[1] R = ^{t}Bu; **2**:[2] R = 2,6-^{i}Pr$_2$C$_6$H$_3$), which represent the first examples of anionic NHC analogues (**A**, Scheme 1). Gallyl anion **2** exhibits a rich coordination chemistry.[3] More recently the boryl anion [B{N(R)CH}$_2$]$^-$ (R = 2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**) has been isolated as its lithium salt[4] as has the saturated Wanzlick carbene analogue, [B{N(R)CH$_2$}$_2$]$^-$ (**4**)[5] (**B**, Scheme 1). The latter undergoes reactions with group 11 metal chlorides to afford the corresponding boryl complexes[5] and the former reacts with MgBr$_2$·OEt$_2$ to form boryl–magnesium derivatives.[6] In terms of neutral carbene-analogous systems, the guanidinate ligand [Cy$_2$NC{NR}$_2$]$^-$ has proved to be effective for the support of Ga (**5**)[7] and In (**6**)[7] in the +1 oxidation state (**C**, Scheme 1). Moreover, compounds **5** and **6** are interesting analogues of a recently reported four-membered NHC.[8] The use of the β-diketiminate supporting ligand [HC(CMe)$_2$(NR)$_2$]$^-$ (R = 2,6-^{i}Pr$_2$C$_6$H$_3$) has permitted the isolation of the widest range of group 13 metal (I) entities

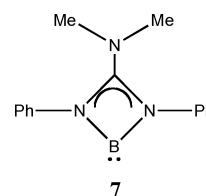**Scheme 1** Carbene analogous group 13 compounds.

reported thus far, namely M = Al,[9] Ga,[10] In,[11] and Tl.[12] However, a structurally authenticated example of a boron(I) carbenoid species of this type is conspicuous by its absence. On the basis of theoretical studies,[13,14] this absence has been attributed to the small energy gap between the singlet and triplet ground states of boron(I)-β-diketiminates. For example, B3LYP/LANL2DZ calculations by Chen *et al.*[13] on [{HC(CMe)$_2$(NPh)$_2$}B] revealed the triplet state to be more stable than the singlet state by 3.5 kcal mol^{-1}, while for the Al, Ga, In, and Tl analogues the singlet–triplet gap exceeds 45 kcal mol^{-1}. The triplet state of such β-diketiminate-supported boron(I) compounds can be visualized as featuring a single electron at the B atom and a second electron that is delocalized over the five remaining ring atoms.[14] In turn, this unpaired electron density on the ring periphery is capable of promoting facile reactions of boron(I)-β-diketiminates with *e.g.* solvents and residual reactants.

Results and discussion

The recent discovery that sterically encumbered guanidinate ligands are able to support N,N-chelated Ga(I) and In(I), compounds **5**[7] and **6**,[7] prompted our curiosity regarding the potential use of this ligand class for the stabilization and isolation of analogous B(I) derivatives. As the first step in this direction, we undertook a theoretical investigation of the singlet–triplet splitting in the model compound [Me$_2$NC{N(Ph)}$_2$]B (**7**).

It has been pointed out that hybrid DFT calculations inherently favor spin states of high multiplicities due to the explicit consideration of Fermi correlation through exchange admixture.[14,15] Accordingly, we considered it appropriate to carry out both DFT and MP2 calculations on our model compound **7**. The results are summarized in Table 1. The largest differences in the two sets of metrical parameters are found for the B–N bond length and the

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Table 1 Computed bond lengths (Å), bond angles (°) and singlet–triplet splitting (kcal mol^{-1}) for **7**

	B3LYP	MP2
B–N	1.553	1.589
C–N$_{ring}$	1.365	1.351
C–N$_{exo}$	1.348	1.343
N–B–N	83.59	82.41
C–N–B	86.42	87.97
N–C–N	98.62	101.66
Singlet–triplet gap	6.0	10.1

N–C–N angle. As expected on the basis of the overemphasis of triplet state stability in the DFT calculation, the singlet–triplet gap is computed to be smaller by this method than by the MP2 method. The salient point, however, is that according to either method the singlet ground state is preferred by between 6 and 10 kcal mol^{-1}. While the singlet–triplet splitting for **7** is less than that computed for e.g. [Cy$_2$NC(NDipp)$_2$]Al by the DFT method (61.8 kcal mol^{-1}),[7] our calculations suggest that an appropriately substituted (guanidinate)boron(I) derivative might be viable. The HOMO and LUMO of **7** are depicted in Fig. 1.
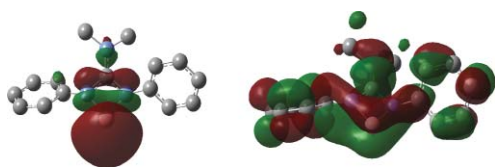
Fig. 1 HOMO and LUMO of **7**. Calculations performed at the MP2/6–31G* level of theory.

(Guanidinate)boron dihalides represented an obvious first choice as precursors to the desired boron(I) derivatives. However, as pointed out by Aldridge et al,[16] until recently there were no structurally authenticated examples of this type of compound and, at the time of writing, [Cy$_2$NC(NCy)$_2$BCl$_2$] (**8**) and [^{i}Pr$_2$NC(NCy)$_2$BCl$_2$] (**9**) represent the only such examples.[16] We now report the syntheses and X-ray crystal structures of two new examples of this rare class of compound, namely [Ph$_2$NC(NMes)$_2$BCl$_2$] (Mes = 2,4,6-trimethylphenyl) and [Ph$_2$NC(NDipp)$_2$BCl$_2$] (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$). Previously, we have shown[17] that [(Me$_3$Si)$_2$NC{NCy}$_2$BCl$_2$] can be prepared either by the metathetical reaction of (Me$_3$Si)$_2$NLi with the carbodiimide CyN=C=NCy or by the insertion of this carbodiimide into (Me$_3$Si)$_2$NBCl$_2$. Unfortunately, neither method resulted in crystals suitable for X-ray diffraction experiments. For the syntheses of the new (guanidinate)boron dichlorides we chose the metathetical route summarized in Scheme 2.

R = Mes (**10**) and Dipp (**11**)

HgO/MgSO$_4$
Toluene, reflux, 12h

R = Mes (**12**) and Dipp (**13**)

(i) Ph$_2$N-Li, Et$_2$O, -78 - RT, 2h
(ii) BCl$_3$, Et$_2$O, -78 - RT, 12h

R = Mes (**14**) and Dipp (**15**)
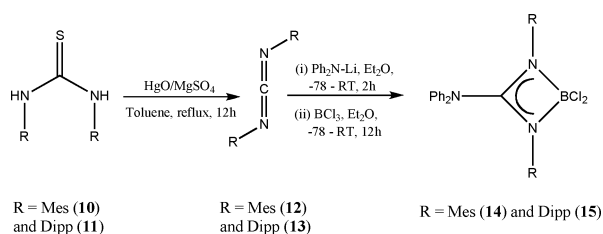
Scheme 2

The thioureas **10** and **11** were isolated as colorless microcrystalline solids from the reaction of CS$_2$ with a solution of the appropriate aniline, trimethylamine and water. Although both compounds were claimed in a Japanese patent,[18] we considered it useful to provide full details of the synthetic method as well as the X-ray crystal structure of **12** (vide infra). Treatment of thioureas **10** and **11** with mercuric oxide and magnesium sulfate in refluxing toluene solution afforded the corresponding carbodiimides **12** and **13** in yields of 85 and 87%, respectively.[19] The initial step in the synthesis of the guanidinate(boron) dichlorides **14** and **15** involved the insertion of one equivalent of the appropriate carbodiimide into the lithium–nitrogen bond of LiNPh$_2$. Subsequent treatment of these reaction mixtures with boron trichloride in diethyl ether solution at low temperature readily afforded these compounds in yields of 90 and 88%, respectively. Attempts were made to reduce **14** and **15** to the corresponding boron(I) derivatives. Typically, toluene solutions of **14** or **15** were stirred with an excess of Na, K, or Na/K alloy at ambient temperature. Following this, each of the stirred reaction mixtures was heated to reflux for ~12 h. Monitoring of the reaction mixtures by ^{11}B NMR revealed no new resonances.

Crystals of **11** suitable for study by X-ray diffraction were grown from toluene solution at −40 °C. Thiourea **11** crystallizes in the monoclinic space group C2/c and the solid state consists of arrays of individual molecules with no unusually short intermolecular contacts. The molecular structure is depicted in Fig. 2 and data collection/refinement details are presented in Table 2. Interestingly, despite the presence of the bulky Dipp substituents, the N–C–N bond angle [116.61(19)°] is less than the ideal trigonal planar value. Note, however, that the Dipp substituents are arranged in a transoid fashion to minimize steric interactions. Compound **12** crystallizes from toluene solution in the triclinic space group P-1. The solid state comprises monomers of **12** (Fig. 3) and there are no short intermolecular contacts. The N–C–N bond angle of 167.82(15)° deviates substantially from the ideal value of 180° and the bulky Mes substituents are arranged in a mutually orthogonal fashion. The average N–C bond distance of 1.213(2) Å is consistent with those reported previously for carbodiimides with less bulky substituents.[20]
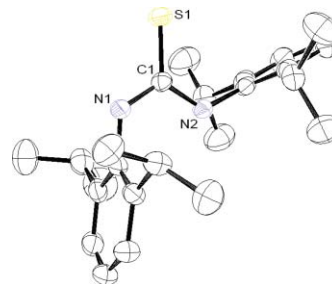
Fig. 2 ORTEP diagram of **11**, with thermal ellipsoids at 40% probability. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.346(3), N(2)–C(1) 1.353(3), C(1)–S(1) 1.682(2), N(1)–C(1)–N(2) 116.61(19), N(1)–C(1)–S(1) 121.38(17), N(2)–C(1)–S(1) 122.00(17).

The Dipp-substituted analogue **13** crystallizes in the monoclinic space group P2$_1$/c as an ensemble of monomers. While the N–C–N bond angle of **13** [169.3(2)°] is marginally less distorted than that of **12**, the more striking structural feature is the fact

Table 2 Selected crystal data, data collection and refinement parameters for **11**, **12**, **13**, **14** and **15**

	11	**12**	**13**	**14**	**15**
Formula	$C_{25}H_{34}N_2S$	$C_{19}H_{22}N_2$	$C_{25}H_{34}N_2$	$C_{31}H_{32}N_3BCl_2$	$C_{37}H_{44}N_3BCl_2$
Formula weight	394.6	278.39	362.54	528.31	612.46
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P\text{-}1$	$P2(1)/c$	$P2(1)/c$	Pc
$a/\text{Å}$	25.444(5)	8.400(5)	9.0454(18)	16.925(5)	12.258(5)
$b/\text{Å}$	14.858(5)	8.612(5)	13.424(3)	12.612(5)	10.481(5)
$c/\text{Å}$	18.332(5)	11.692(5)	18.684(4)	16.354(5)	16.149(5)
$a/°$	90	76.709(5)	90	90	90
$\beta/°$	122.823(5)	75.502(5)	102.93(3)	104.074(5)	124.90(2)
$\gamma/°$	90	82.349(5)	90	90	90
$V/\text{Å}^3$	5824(5)	794.4(7)	2211.1(9)	3386(2)	1701.5(12)
Z	8	2	4	4	2
$\rho_{calcd}/\text{g cm}^{-3}$	0.900	1.164	1.089	1.036	1.195
$F(000)$	1712	300	792	1112	652
Crystal size/mm	$0.30 \times 0.30 \times 0.25$	$0.40 \times 0.40 \times 0.30$	$0.30 \times 0.25 \times 0.20$	$0.35 \times 0.35 \times 0.25$	$0.10 \times 0.06 \times 0.06$
θ range/°	2.39 to 26.99	2.75 to 27.52	2.70 to 27.43	2.56 to 27.50	1.94 to 27.49
No. of reflns. collected	11537	5357	4989	13089	6945
No. of indep reflns.	6670	3594	2375	7728	6936
$R_1[I > 2\sigma(I)]$	0.0716	0.0488	0.0566	0.0562	0.0581
wR_2 (all data)	0.2144	0.1294	0.1250	0.1426	0.1242
Peak and hole/e Å^{-2}	0.426 and −0.296	0.210 and −0.241	0.181 and −0.182	0.378 and −0.295	0.433 and −0.743

Fig. 3 ORTEP diagrams of **12** (left) and **13** (right), with thermal ellipsoids at 40% probability. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): (for **12**) N(1)–C(1) 1.2107(18), N(2)–C(1) 1.2179(18), N(1)–C(2) 1.4072(19), N(2)–C(11) 1.4077(18), N(1)–C(1)–N(2) 167.82(15), C(1)–N(1)–C(2) 137.62(13), C(1)–N(2)–C(11) 135.75(13); (for **13**) N(1)–C(1) 1.213(2), N(2)–C(1) 1.221(2), N(1)–C(2) 1.415(2), N(2)–C(14) 1.425(2), N(1)–C(1)–N(2) 169.3(2), C(1)–N(1)–C(2) 138.73(17), C(1)–N(2)–C(14) 131.51(17).

that the dihedral angle between the aryl rings of **12** (68.56 °) is appreciably greater than that for **13** (47.95 °). Examination of the packing diagram for **13** shows that this confirmation is influenced by the existence of weak intermolecular interactions between the carbon atoms of one monomer with the methyl-hydrogens of another.

Crystals of **14** and **15** suitable for X-ray diffraction studies were grown from toluene solution at −40 °C. Compounds **14** and **15** crystallize in the monoclinic space groups $P2_1/c$ and Pc, respectively. Neither solid state structure exhibits any unusually short intermolecular contacts. The molecular structures of **14** and **15** are illustrated in Fig. 4 and 5, respectively. Both compounds feature a four-membered B–N–C–N chelate ring, the average C–N bond distances for which are 1.350(3) (**14**) and 1.351(6) Å (**15**). These values are approximately intermediate between those of typical C=N double and C–N single bonds. Moreover, the B–N–C–N torsion angles for both compounds are zero (within experimental error), which is indicative of π-electron delocalization about the N–C–N junction. The average B–N distances of 1.564(3) (**14**) and 1.574(2) Å (**15**) fall within the typical range of 1.55–1.61 Å that has been observed for a four-coordinate boron atom bound to

a three-coordinate nitrogen atom.[21] The N–B–N bite angles for the guanidinate rings are 83.69(14) and 83.4(3)° for **14** and **15**, respectively, and are more acute than those reported by Aldridge *et al.*[16] By contrast, the bite angles in closely related amidinate rings fall within the range of approximately 85–86°.[17,22] The average N–B–Cl bond angles are 114.90(16)° and 117.6(3)° for **14** and **15**, respectively, hence the geometry about the boron atom is appreciably distorted from that of a regular tetrahedron. Finally, it is worth noting that the C(1)–N(3) distances of 1.342(3) (**14**) and 1.353(6) Å (**15**) are remarkably short and therefore consistent with the idea of a substantial contribution from the iminium/diamide resonance form to the bonding descriptions of both compounds.

The ^{1}H, ^{13}C{^{1}H} and ^{11}B NMR spectra of both **14** and **15** indicate that the solid state structure is retained in solution. The ^{11}B NMR spectra exhibit intense singlet resonances at δ 6.8 (**14**) and 9.2 (**15**), values which are typical of those reported for four-coordinate boron atoms[23] and are in good agreement with values reported for closely related (guanidinate)boron dihalides.[17] Moreover, due to the inherent difficulty in detecting low intensity quaternary carbon centers, the carbon atom of the N–C–N fragment could not be detected.
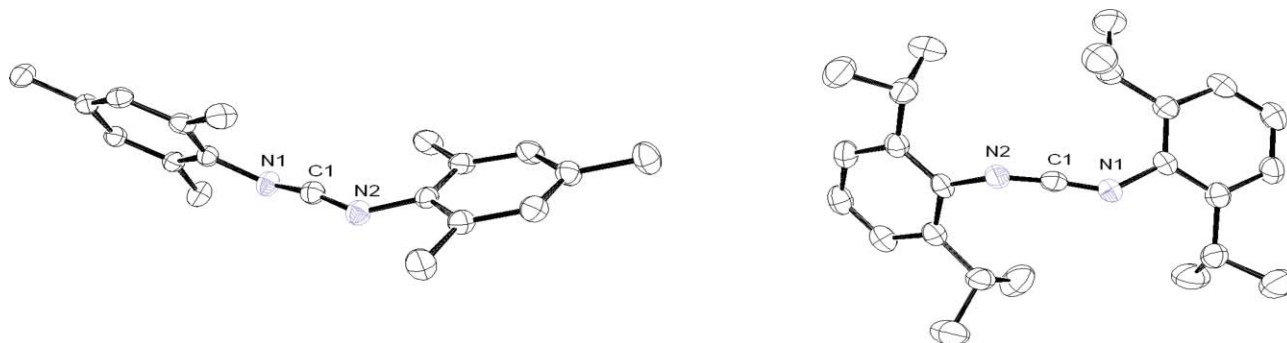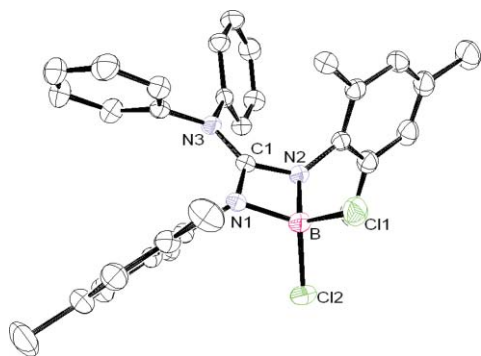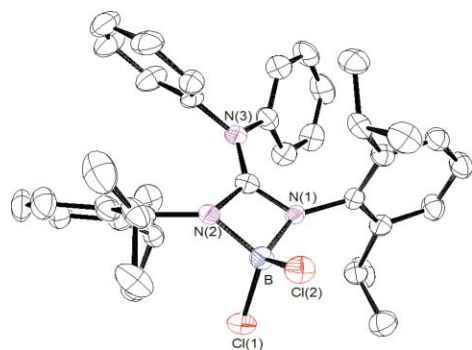
Fig. 4 ORTEP diagram of **14**, with thermal ellipsoids at 40% probability. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.346(3), N(2)–C(1) 1.353(2), N(3)–C(1) 1.342(2), N(1)–B(1) 1.559(3), N(2)–B(1) 1.566(3), B(1)–Cl(1) 1.833(3), B(1)–Cl(2) 1.837(3), N(1)–C(1)–N(2) 101.15(16), N(1)–C(1)–N(3) 129.00(17), N(2)–C(1)–N(3) 129.84(18), N(1)–B(1)–N(2) 83.69(14), N(1)–B(1)–Cl(1) 117.56(16), N(1)–B(1)–Cl(2) 112.95(15), N(2)–B(1)–Cl(1) 113.36(16), N(2)–B(1)–Cl(2) 116.84(17), N(1)–C(1)–N(2)–B(1) 0.15(0.17).

Fig. 5 ORTEP diagram of **15**, with thermal ellipsoids at 40% probability. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.341(6), N(2)–C(1) 1.360(5), N(3)–C(1) 1.353(6), N(1)–B(1) 1.578(6), N(2)–B(1) 1.570(7), B(1)–Cl(1) 1.833(6), B(1)–Cl(2) 1.833(5), N(1)–C(1)–N(2) 101.6(4), N(1)–C(1)–N(3) 131.6(4), N(2)–C(1)–N(3) 126.8(4), N(1)–B(1)–N(2) 83.4(3), N(1)–B(1)–Cl(1) 118.1(3), N(1)–B(1)–Cl(2) 112.4(3), N(2)–B(1)–Cl(1) 112.4(3), N(2)–B(1)–Cl(2) 117.1(3), N(1)–C(1)–N(2)–B(1) 0.9(0.3)

Experimental

(a) General procedures

All manipulations and reactions were performed under a dry, oxygen-free, catalyst scrubbed argon atmosphere using a combination of standard Schlenk techniques or in an M-Braun or Vacuum Atmospheres drybox. All glassware was oven dried and vacuum- and argon-flow degassed before use. All solvents were distilled over sodium benzophenone ketyl, except dichloromethane, which was distilled over CaH_2, and degassed prior to use. All reagents were purchased from commercial sources and used without further purification.

(b) Physical measurements

Low-resolution mass spectra were obtained on a Finnigan MAT TSQ-700 mass spectrometer and high-resolution CI mass spectra recorded on a VG analytical ZAB-VE sector instrument. All MS

analyses were performed on samples that had been sealed in glass capillaries under an argon atmosphere. ^1H, $^{13}C\{^1H\}$ and ^{11}B NMR spectra were recorded at 295 K on a GE QE 300 instrument (^1H, 300 MHz ^{13}C, 75 MHz, ^{11}B, 96 MHz) immediately following removal of the sample from the drybox. ^1H and $^{13}C\{^1H\}$ chemical shift values are reported in parts per million (ppm) relative to $SiMe_4$ (δ 0.00), using residual solvent resonances as internal standards. ^{11}B NMR data are referenced to $BF_3 \cdot OEt_2$ (δ 0.00).

(c) X-Ray crystallography

For compounds **11**, **12**, **13**, **14** and **15**, a crystal of suitable quality was removed from a Schlenk flask under positive argon pressure, covered immediately with degassed hydrocarbon oil and mounted on a glass fiber. The X-ray diffraction data were collected at 153 K on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream low-temperature device and a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Corrections were applied for Lorentz and polarization effects. All structures were solved by direct methods[24] and refined by full-matrix least-squares cycles on F^2. All non-hydrogen atoms were allowed anisotropic thermal motion, and all hydrogen atoms were placed in fixed, calculated positions using the riding model (C–H 0.96 Å). Selected crystal data, and data collection and refinement parameters are listed in Table 2.

(d) Syntheses

Synthesis of MesN(H)C(S)N(H)Mes (10). Carbon disulfide (9.53 g, 125 mmol) was added dropwise to a stirred mixture of $MesNH_2$ (33.8 g, 250 mmol) and NEt_3 (25.5 g, 250 mmol) in 100 mL of water at room temperature. The reaction mixture was stirred for 1 h at room temperature and then heated to 90 °C for 14 h. After re-cooling the reaction mixture to room temperature, it was poured into 100 mL of CH_2Cl_2, following which the organic layer was separated and dried over $MgSO_4$. After filtration, the filtrate was concentrated and stored at −40 °C to afford a 90% yield of white powder **10**. ^1H NMR ($CDCl_3$): δ 7.66 (s, 1H, NH), 7.01 (s, 2H, Ar–H), 6.87 (s, 2H, Ar–H), 6.51 (s, 1H, NH), 2.41 (s, 6H, Ar–CH_3), 2.35 (s, 3H, Ar–CH_3), 2.25 (s, 3H, Ar–CH_3), 2.18 (s, 6H, Ar–CH_3); ^{13}C NMR ($CDCl_3$): δ 181.7 (C=S), 138.0 (Ar), 137.6 (Ar), 136.3 (Ar), 130.1 (Ar), 129.3 (Ar), 21.3 (Ar–CH_3), 18.8 (Ar–CH_3), 18.4 (Ar–CH_3). MS (CI$^+$, CH_4): m/z 313 (M + H). HRMS (CI, CH_4) calcd. For $C_{19}H_{25}N_2S$ 313.1738; found 313.1735.

Synthesis of DippN(H)C(S)N(H)Dipp (11). Colorless crystals of **11** were prepared in 93% yield from $DippNH_2$ (94 g, 530 mmol), CS_2 (20.20 g, 260 mmol) and NEt_3 (54.0 g, 530 mmol) using the procedure described above for **10**. ^1H NMR ($CDCl_3$): δ 8.93 (s, 1H, NH), 7.29 (dd, 2H, Ar–H), 7.20 (d, 4H, Ar–H), 6.41 (s, 1H, NH), 3.42 (sept, 2H, Ar–C(H)Me$_2$), 3.05 (sept, 2H, Ar–C(H)Me$_2$), 1.38 (m, 18H, Ar–CH(Me)$_2$), 1.08 (d, 6H, Ar–CH(Me)$_2$); ^{13}C NMR ($CDCl_3$): δ 182.6 (C=S), 148.4 (Ar), 146.9 (Ar), 133.4 (Ar), 131.1 (Ar), 130.4 (Ar), 128.9 (Ar), 124.6 (Ar), 123.9 (Ar), 29.3 (Ar–C(H)Me$_2$), 28.9 (Ar–C(H)Me$_2$), 26.2 (Ar–CH(Me)$_2$), 24.5 (Ar–C(H)Me$_2$), 24.0 (Ar–C(H)Me$_2$), 22.1 (Ar–CH(Me)$_2$ MS (CI$^+$, CH_4): m/z 397 (M + H). HRMS (CI, CH_4) calcd. for $C_{25}H_{37}N_2S$ 397.2677; found 397.2671.

Synthesis of MesN=C=NMes (12). A mixture of **10** (624 mg, 2 mmol), HgO (870 mg, 4 mmol) and anhydrous MgSO$_4$ (580 mg, 4.8 mmol) in 50 mL of toluene was refluxed overnight. After cooling to room temperature, the reaction mixture was filtered over Celite® and the filtrate concentrated to dryness to afford an 85% yield of the title compound as a colorless microcrystalline solid. ^{1}H NMR (CD$_2$Cl$_2$): δ 6.89 (s, 4H, Ar–H), 2.40 (s, 12H, Ar–CH$_3$), 2.30 (s, 6H, Ar–CH$_3$); ^{13}C NMR (CD$_2$Cl$_2$): δ 134.5 (Ar), 132.9 (Ar), 129.5 (Ar), 129.4 (Ar), 21.1 (Ar–CH$_3$), 19.2 (Ar–CH$_3$). MS (CI$^+$, CH$_4$): m/z 278 (M + H). HRMS (CI, CH$_4$) calcd. for C$_{19}$H$_{23}$N$_2$, 279.1861; found 279.1860.

Synthesis of DippN=C=NDipp (13). Colorless crystals of **13** were prepared in 87% yield from **11** using the procedure described above for **12**. ^{1}H NMR (CDCl$_3$): δ 7.39 (dd, 2H, Ar–H), 7.31 (d, 4H, Ar–H), 3.62 (sept, 4H, Ar–C(H)Me$_2$), 1.41 (d, 24H, Ar–CH(Me)$_2$); ^{13}C NMR (CDCl$_3$): δ 143.2 (Ar), 129.1 (Ar), 125.3 (Ar), 123.7 (Ar), 29.6 (Ar–C(H)Me$_2$), 23.6 (Ar–CH(Me)$_2$). MS (CI$^+$, CH$_4$): m/z 363 (M + H). HRMS (CI, CH$_4$) calcd. for C$_{25}$H$_{35}$N$_2$ 363.2800; found 363.2789.

Synthesis of [Ph$_2$NC{NMes}$_2$]BCl$_2$ (14). A stirred solution of diphenylamine (339 mg, 2 mmol) in diethyl ether (20 mL) was cooled to −78 °C and ^{n}BuLi (1 eq.) added *via* syringe. The reaction mixture was allowed to warm to room temperature and stirred for a further hour, at which point it was re-cooled to −78 °C and an ethereal solution (10 mL) of **12** (558 mg, 2 mmol) was added. The reaction mixture was once more allowed to warm to room temperature following which it was stirred for 1 h. For a third time the solution was cooled to −78 °C and BCl$_3$ (2 mL, 1.0 M solution in hexane, 1 eq.) was added *via* syringe. The reaction mixture was then allowed to warm slowly to room temperature and was stirred overnight. After filtration and solvent stripping, **14** was isolated as a white solid in 90% yield. ^{1}H NMR (CD$_2$Cl$_2$): δ 6.93 (dd, 2H, Ar–H), 6.66 (m, 4H, Ar–H), 6.57 (m, 4H, Ar–H), 6.46 (s, 4H, Ar–H), 2.43 (s, 12H, Ar–CH$_3$), 2.21 (s, 6H, Ar–CH$_3$); ^{13}C NMR (CD$_2$Cl$_2$): δ 140.3 (Ar), 136.0 (Ar), 135.73 (Ar), 129.65 (Ar), 129.52 (Ar), 127.50 (Ar), 125.43 (Ar), 21.06 (Ar–Me), 20.26 (Ar–Me); ^{11}B NMR (CD$_2$Cl$_2$): δ 6.79. MS (CI$^+$, CH$_4$): m/z minor 528 (M + H), major 491 (M-Cl).

Synthesis of [Ph$_2$NC{NDipp}$_2$]BCl$_2$ (15). Colorless needle-like, crystals of **15** were prepared in 88% yield from **13** using the same procedure that was described for **14**. ^{1}H NMR (CDCl$_3$): δ 7.24 (m, 8H, Ar-H), 7.10 (m, 8H, Ar-H), 3.78 (sept, 2H, Ar–C(H)Me$_2$), 3.61 (sept, 2H, Ar–C(H)Me$_2$), 1.41 (m, 24H, Ar–CH(Me)$_2$); ^{13}C NMR (CDCl$_3$): δ 147.32 (Ar), 146.80 (Ar), 142.96 (Ar), 128.79 (Ar), 127.60 (Ar), 125.1 (Ar), 124.89 (Ar), 124.63 (Ar), 123.48 (Ar), 29.35 (Ar–(C)HMe$_2$), 23.45 (Ar–CH(Me)$_2$); ^{11}B NMR (CDCl$_3$): δ 9.17. MS (CI$^+$, CH$_4$): m/z 612 (M + H). HRMS (CI, CH$_4$) calcd. for C$_{37}$H$_{44}$BCl$_2$N$_3$ 611.3131; found 611.3123.

Conclusions

In summary, we have explored the possibility of synthesizing guanidinate-supported boron(I) derivatives by reduction of two new (guanidinate)boron dichlorides. Although the desired compounds were not obtained, DFT and MP2 calculations on a model system revealed the ground state is a singlet and that the HOMO-LUMO gap may be sufficiently large to permit the future isolation of the desired boron(I) species.

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Notes and references

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