The platinum catalysed diboration of alkynes using 1,2-$B_2Cl_2(NMe_2)_2$: formation of 1-azonia-2-borata-5-borole derivatives

Kirsty M. Anderson, M. J. Gerald Lesley,* Nicholas C. Norman,* A. Guy Orpen and Jonathan Starbuck

The University of Bristol, School of Chemistry, Cantock's Close, Bristol, UK BS8 1TS

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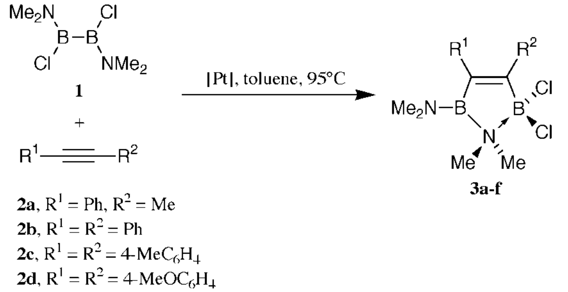
The platinum catalysed diboration of alkynes using the diborane(4) compound 1,2-$B_2Cl_2(NMe_2)_2$ affords high yields of cyclic 1-azonia-2-borata-5-borole compounds, which arise from redistribution of B–Cl and B–NMe_2 bonds.

Transition metal boryl compounds are known to be active catalysts for the diboration of unsaturated organic substrates[1] although in most cases the diborane(4) compounds employed have been either $B_2(cat)_2$ (cat = 1,2-$O_2C_6H_4$)[1,2] (and alkylated derivatives thereof) or $B_2(pin)_2$ (pin = 1,2-$O_2C_2Me_4$).[1,3] Herein we describe some preliminary results from a study of platinum catalysed alkyne diboration[4] using 1,2-$B_2Cl_2(NMe_2)_2$ (**1**)[5] as the diboration reagent, the chemistry of which is significantly different. Prior reactivity studies involving transition metal complexes and **1** have yielded products derived from both B–B and B–Cl activation, an example of the former being our own report of the reaction between **1** and [$Pt(PPh_3)_2(\eta$-$C_2H_4)$] affording *cis*-[$Pt(PPh_3)_2\{BCl(NMe_2)\}_2$][6] and the latter exemplified by the work of Braunschweig involving the formation of diboran(4)yl derivatives.[7]

The diboration of internal alkynes (**2a–d**) employing **1** in the presence of 5 mol% [$Pt(PPh_3)_2(\eta$-$C_2H_4)$] proceeded over 24 h in toluene at 95 °C to give compounds formulated as cyclic 1-azonia-2-borata-5-borole derivatives (**3a-d**) in excellent yield and purity (Scheme 1).† Analytical and spectroscopic data† were in accord with the proposed structures, which, for **3a**, **3c** and **3d**, were confirmed by X-ray crystallography.‡ A view of **3c** is shown in Fig. 1. Key features of the 1-azonia-2-borata-5-borole structure are the presence of three- and four-coordinate boron centres [B(2) and B(1), respectively] and three- and four-coordinate nitrogen centres [N(2) and N(1), respectively]. The two three-coordinate centres are associated with the shortest B–N bond [B(2)–N(2) 1.381(2) Å], consistent with a B–N double bond resulting from dative N → B π-bonding. The bonds B(1)–N(1) [1.622(2) Å] and B(2)–N(1) [1.563(2) Å] are both consistent with B–N single bonds, the difference being attributable to the coordination numbers of the two boron atoms [in the diagrams, the B(1)–N(1) bond is represented as a coordinate bond]. In all of **3a–d**, the solution NMR data are consistent with the retention of this structure in solution. In particular, the disparate ^{11}B chemical shifts are characteristic of three- and four-coordinate boron environments, and the observed inequivalence of the exocyclic amido methyl groups (at room temperature) is consistent with hindered rotation about the exocyclic B–N bond.

The mechanism by which **3a–d** are formed remains unclear although an initial diboration product **A**, which subsequently rearranges to **3**, is likely in view of the known structure of the platinum boryl catalyst precursor *cis*-[$Pt(PPh_3)_2\{BCl(NMe_2)\}_2$][6] in which each boron retains the one chlorine and one amido group present in the starting diborane(4) compound **1**. In relation to this study, particularly with regard to any mechanistic speculation, we note that Berndt *et al.* have described the *uncatalysed* reaction between **1** and the silyl alkynes $Me_3SiC{\equiv}CSiMe_3$ and $PhC{\equiv}CSiMe_3$ at 150 °C. Spectroscopic data on the products formed are consistent with species containing unrearranged boryl groups but in



2a, R^1 = Ph, R^2 = Me
2b, R^1 = R^2 = Ph
2c, R^1 = R^2 = 4-MeC_6H_4
2d, R^1 = R^2 = 4-$MeOC_6H_4$
2e, R^1 = *n*-octyl, R^2 = H
2f, R^1 = Ph, R^2 = H

Scheme 1

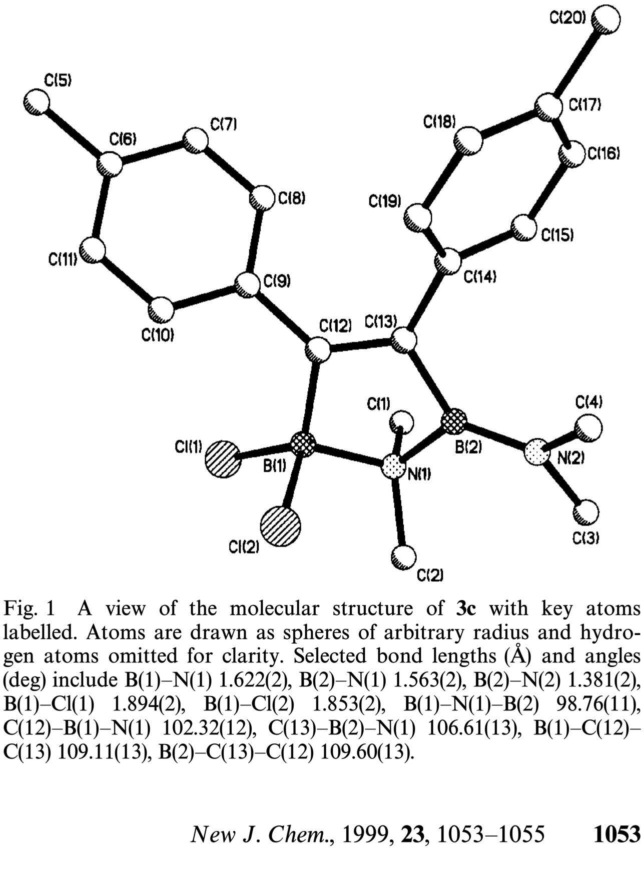
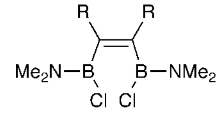


Fig. 1 A view of the molecular structure of **3c** with key atoms labelled. Atoms are drawn as spheres of arbitrary radius and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg) include B(1)–N(1) 1.622(2), B(2)–N(1) 1.563(2), B(2)–N(2) 1.381(2), B(1)–Cl(1) 1.894(2), B(1)–Cl(2) 1.853(2), B(1)–N(1)–B(2) 98.76(11), C(12)–B(1)–N(1) 102.32(12), C(13)–B(2)–N(1) 106.61(13), B(1)–C(12)–C(13) 109.11(13), B(2)–C(13)–C(12) 109.60(13).

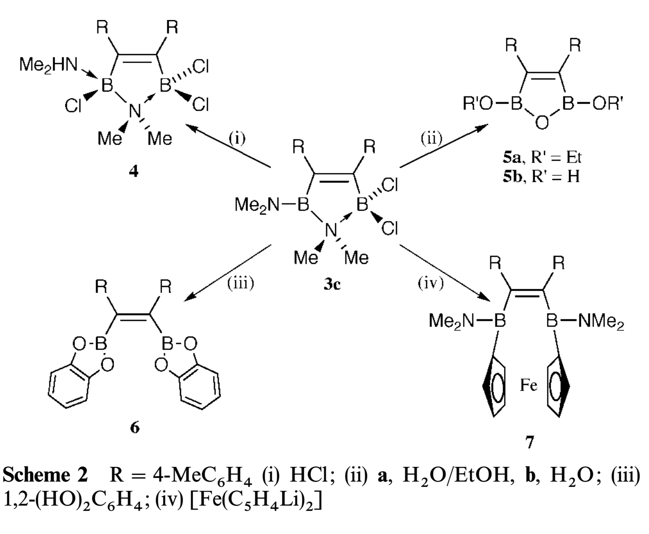
which silyl/boryl rearrangement has occurred, resulting in 1,1-isomers, such as $(Me_3Si)(R)C{=}C[BCl(NMe_2)]_2$ (R = Ph, Me_3Si).[8] More recently, Siebert *et al.* have presented spectroscopic data that reveal that alkenes derived from *cis*-1,2-addition of B_2Cl_4 to alkynes, for example *cis*-(R)-(BCl_2)C=C(BCl_2)(R′) (**B**), react with the silyl amide Me_3SiNMe_2 to afford compounds analogous to either **3** (R = R′ = Et, Me; R = Bu^t, R′ = H) or **A** (R = R′ = Bu^t).[9] Reactions between **B** and Pr^i_2NH also afforded species of type **A** (R = R′ = H, Me, Et; R = H, R′ = Bu^t). {This report[9] described the structure of the bromo derivative *cis*-(Bu^t)-[BBr(NMe_2)]C=C[BBr(NMe_2)](Bu^t), a structure analogous to **A**, although this compound was not prepared by a route relevant to this study.} The results of Siebert *et al.* indicate that structures **3** and **A** are probably close in energy (with a subtle dependence on the nature of the R group) and our preliminary *ab initio* calculations[10] carried out on **3b** and its isomer of type **A** confirm that the two isomers are very close in energy.§



A

In contrast to the reactions of internal alkynes, terminal alkynes reacted more slowly. Thus, the platinum catalysed reaction between **1** and 1-octyne (**2e**) gave **3e** but was complete only after three days. Reactions using phenylacetylene (**2f**) were incomplete even after several days although the reaction between phenylacetylene and **1** in the presence of a stoichiometric amount of $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ did afford the desired product (**3f**) after 3 h (Scheme 1).¶ Competing activation of the CH bonds in terminal alkynes has been noted in catalytic reactions involving alkoxy substituted diborane(4) compounds with phenylacetylene.[4e]

The availability of crystalline **3a-d** prepared in high yields under mild conditions has enabled an initial study of their reactivity to be carried out, preliminary details of which are reported here for **3c** with HCl, alcohols, diols and dilithioferrocene (Scheme 2). A previous study by Siebert *et al.*, wherein *cis*-(R)[BCl(NPr^i_2)]C=C[BCl(NPr^i_2)](R) (R = H, Et) was reacted with Me_3SnLi affording *cis*-(R)[B($SnMe_3$)(NPr^i_2)]-C=C[B($SnMe_3$)(NPr^i_2)](R), is noted.[11] Thus, **3c** reacts with two equiv. of HCl in Et_2O to give **4** in high yield,‖ resulting from the addition of HCl across the exocyclic B–N bond. ^{11}B NMR data were consistent with the presence of two distinct four-coordinate boron centres whilst the ^{1}H NMR spectrum revealed the presence of a coordinated $NHMe_2$ amine ligand; the asymmetric boron centre [B(2)] results in inequivalent (diastereotopic) ring NMe_2 and coordinated $NHMe_2$ methyl environments. The structure of **4** was confirmed by X-ray crystallography** (Fig. 2). In most respects, the structure of **4** is similar to that of **3c** with the exception of the environment around B(2), which now carries a chlorine and a datively bound $NHMe_2$ amine ligand; pertinent metric data are given in the caption to Fig. 2, which reveal that all B–N bond lengths are the same within experimental error, as expected for bonds between four-coordinate boron and nitrogen centres. Attempts to prepare an amine adduct of a bis(dichloroboryl)ethene derivative (*cf.*, **B** above) through addition of a second equivalent of HCl across the B(2)–N(1) bond were not successful. Thus, the reaction between **3c** and 4 equiv. HCl also afforded **4** whilst with the use of 10 equiv. of HCl, significant decomposition was evident by NMR.



Scheme 2 R = 4-MeC_6H_4 (i) HCl; (ii) **a**, H_2O/EtOH, **b**, H_2O; (iii) 1,2-$(HO)_2C_6H_4$; (iv) $[Fe(C_5H_4Li)_2]$

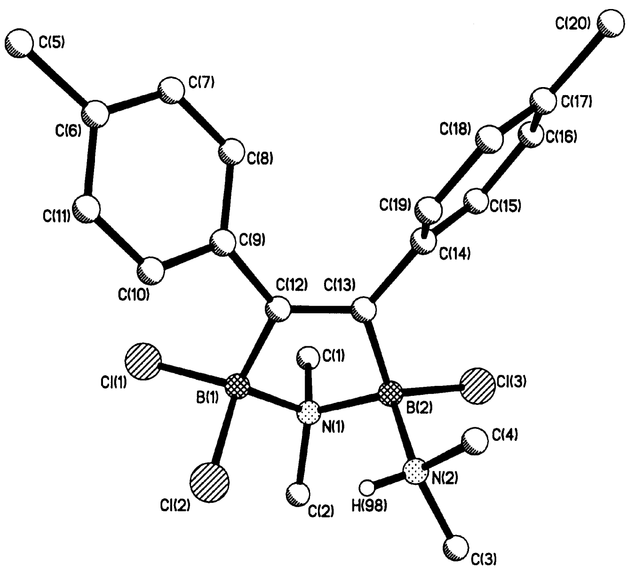


Fig. 2 A view of the molecular structure of **4** with key atoms labelled. Atoms are drawn as spheres of arbitrary radius and hydrogen atoms omitted for clarity with the exception of H(98). Selected bond lengths (Å) and angles (deg) include B(1)–N(1) 1.607(6), B(2)–N(1) 1.604(5), B(2)–N(2) 1.616(6), B(1)–Cl(1) 1.862(5), B(1)–Cl(2) 1.904(5), B(2)–Cl(3) 1.867(5), B(1)–N(1)–B(2) 101.3(3), C(12)–B(1)–N(1) 102.8(3), C(13)–B(2)–N(1) 101.6(3), B(1)–C(12)–C(13) 111.3(3), B(2)–C(13)–C(12) 109.7(3).

The addition of one equivalent of water in ethanol to a solution of **3c** in toluene afforded a compound formulated as the oxaborole species **5a** on the basis of the ^{11}B NMR chemical shift and the ^{1}H NMR spectrum integration (two equivalents of $[NH_2Me_2]Cl$ were also produced).†† In the absence of ethanol, reaction with 4 equiv. of water in toluene yielded **5b** plus two equivalents of $[NH_2Me_2]Cl$.†† The formulation of **5b** as an oxaborole species rather than a bis(boronic acid)[12] {*i.e.*, (R)[B$(OH)_2$]C=C[B$(OH)_2$](R)} was confirmed by obtaining a ^{1}H NMR spectrum in CD_3OD wherein an OH signal integrating to six protons was observed, corresponding to four from exchange with the $[NH_2Me_2]^+$ cations and two from B–OH groups.‡‡ Even in the presence of a large excess of water, no evidence was obtained for the formation of a bis(boronic acid) with only stilbene and boron containing compounds of unknown composition being formed. Reaction of **3c** with 2.2 equiv. catechol afforded the known[4e] bis(catecholatoboryl) derivative **6** quantitatively according to *in situ* ^{1}H and ^{11}B NMR spectroscopy.

Finally, the reaction between **3c** and 1,1′-dilithioferrocene afforded a species formulated as the [4]ferrocenophane compound **7**.§§ The boron chemical shift of **7** (δ 38.6) is consistent with that found for three-coordinate boron centres in related boron containing ferrocenophane derivatives, which have attracted some attention as precursors to polyferrocene polymers,[13–15] but the fact that the symmetrical species **7** is formed here indicates that **3c** is a synthetic equivalent of the type **A** structure.

Acknowledgements

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Notes and references

† In a typical reaction, a solution of **1** (0.502 g, 2.78 mmol) in toluene (5 cm^3) containing [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)]^{4e} (0.035 g, 5 mol%) was transferred to a Young's tap tube containing **2c** (0.478 g, 2.32 mmol), which was then sealed and heated to 95 °C overnight. The toluene was removed *in vacuo* and addition of Et$_2$O (5 cm^3) resulted in the formation of a precipitate **3c** (0.680 g, 76%) that was isolated by filtration and washed with hexane (3 × 5 cm^3). Slow diffusion of hexane into the initial filtrate resulted in the formation of a crop of red crystals of **3c**, one of which was used for X-ray crystallography. NMR data for **3c** (C$_7$D$_8$): ^{11}B-{^{1}H} δ 34.4 (B–NMe$_2$), 9.1 (BCl$_2$); ^{1}H δ 7.51 (d, 2H, C$_6$H$_4$, J_{HH} = 8.0 Hz), 6.89 (m, 4H, C$_6$H$_4$), 6.87 (d, 2H, C$_6$H$_4$, J_{HH} = 8.0 Hz), 2.51 (s, 6H, B$_2$NMe$_2$), 2.11 (s, 3H, BNMe$_2$), 2.08 (s, 3H, BNMe$_2$), 2.03 (s, 3H, C$_6$H$_4$*Me*), 2.02 (s, 3H, C$_6$H$_4$*Me*); ^{13}C-{^{1}H} δ 138.9, 137.3 (*ipso*-C), 136.2, 135.5 (*p*-C), 129.6, 129.4 (*o*-C), 129.2, 128.5 (*m*-C), 44.4 (B$_2$NMe$_2$), 42.2, 38.9 (BNMe$_2$), 21.2, 21.1 (C$_6$H$_4$*Me*). ^{11}B, ^{1}H and ^{13}C spectra were referenced to BF$_3$ · Et$_2$O, Me$_4$Si and Me$_4$Si, respectively. HRMS (EI) for C$_{20}$H$_{26}$B$_2$Cl$_2$N$_2$: Calcd 384.173 181, found 384.171 333. Compounds **3a**, **3b** and **3d** were prepared similarly. Selected data for **3a**: ^{11}B-{^{1}H} NMR (C$_7$D$_8$) δ 33.8 (B–NMe$_2$), 9.5 (BCl$_2$); **3b**: ^{11}B-{^{1}H} NMR (C$_7$D$_8$) δ 34.2 (B–NMe$_2$), 9.0 (BCl$_2$), HRMS (EI) for C$_{18}$H$_{22}$B$_2$Cl$_2$N$_2$: Calcd 356.141 880, found 356.140 419; **3d**: ^{11}B-{^{1}H} NMR (C$_7$D$_8$) δ 34.7 (B–NMe$_2$), 8.7 (BCl$_2$), HRMS (EI) for C$_{20}$H$_{26}$B$_2$Cl$_2$N$_2$O$_2$: Calcd 416.163 010, found 416.162 476. The ^{11}B resonances for the B–NMe$_2$ borons for all **3** are significantly broader than those for the BCl$_2$ borons consistent with their respective coordination geometries. Satisfactory ^{1}H and ^{13}C NMR data were also obtained for **3a**, **3b** and **3d**. All alkynes were either procured commercially or prepared by literature methods.

‡ Crystal data for **3a**: C$_{13}$H$_{20}$B$_2$Cl$_2$N$_2$, $M = 296.83$, monoclinic, space group $P2_1/c$ (no. 14), $a = 16.121(3)$, $b = 7.1894(6)$, $c = 13.5772(17)$ Å, $\beta = 95.567(15)°$, $U = 1566.2(4)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $\mu = 0.40$ mm^{-1}, $T = 173(2)$ K. Crystal data for **3c**: C$_{20}$H$_{26}$B$_2$Cl$_2$N$_2$, $M = 386.95$, monoclinic, space group $P2/c$ (no. 13), $a = 12.410(2)$, $b = 12.8779(14)$, $c = 13.0655(16)$ Å, $\beta = 90.428(14)°$, $U = 2088.0(5)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $\mu = 0.317$ mm^{-1}, $D_{calc} =$ 1.231 Mg m^{-3}, $F(000) = 816$, $T = 173(2)$ K, 4779 unique data, $R1 = 0.0372$. Crystal data for **3d**: C$_{20}$H$_{26}$B$_2$Cl$_2$N$_2$O$_2$, $M = 418.95$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.870(3)$, $b = 12.404(2)$, $c = 16.086(3)$ Å, $\beta = 92.185(9)°$, $U = 2167.3(7)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $\mu = 0.32$ mm^{-1}, $T = 173(2)$ K.

§ Gas phase energies of **3b** and its type **A** isomer were evaluated by full geometry optimisation at the SCF 6-31G level, followed by single point energy calculations with 6-31G** basis sets. At this level the acyclic **A** isomer is 6.9 kcal mol^{-1} more stable. We note however, that these calculations do not model any intermolecular interactions that might influence the preferred geometry in condensed phases.

¶ ^{11}B NMR data (C$_7$D$_8$) for **3e**: ^{11}B-{^{1}H} δ 37.9 (B–NMe$_2$), 11.1 (BCl$_2$); **3f**: 36.2 (B–NMe$_2$), 9.1 (BCl$_2$). Satisfactory ^{1}H NMR data were also obtained.

‖ NMR data for **4** (CD$_2$Cl$_2$): ^{11}B-{^{1}H} δ 8.7 (sh), 7.3 (sh); ^{1}H δ 7.03 (d, 2H, C$_6$H$_4$, J_{HH} = 8.1 Hz), 6.96 (d, 2H, C$_6$H$_4$, J_{HH} = 8.1 Hz), 6.92 (s, 4H, C$_6$H$_4$), 6.59 (br s, 1H, N*H*Me$_2$), 2.84 (s, 3H, NMe$_2$), 2.74 (d, 3H, NH*Me*$_2$, $^3J_{HH}$ = 5.5 Hz), 2.72 (s, 3H, NMe$_2$), 2.37 (d, 3H, NH*Me*$_2$, $^3J_{HH}$ = 5.5 Hz), 2.25 (s, 3H, C$_6$H$_4$*Me*), 2.24 (s, 3H, C$_6$H$_4$*Me*); ^{13}C-{^{1}H} δ 157.8, 147.5 (BC=CB), 139.3, 138.4 (*ipso*-C), 135.5 (*p*-C), 130.3, 128.9 (*o*-C), 128.6, 128.5 (*m*-C), 49.4, 42.8, 40.1, 40.3 (NMe$_2$ and NHMe$_2$), 21.4, 21.3 (C$_6$H$_4$*Me*).

** Crystal data for **4**: C$_{20}$H$_{27}$B$_2$Cl$_3$N$_2$, $M = 423.41$, monoclinic, space group $P2_1$/c (no. 14), $a = 20.496(9)$, $b = 9.775(4)$, $c = 23.894(13)$ Å, $\beta = 114.37(6)°$, $U = 4360(3)$ Å^3, $Z = 8$, $\lambda = 0.71073$ Å, $\mu = 0.428$ mm^{-1}, $D_{calc} = 1.290$ Mg m^{-3}, $F(000) = 1776$, $T = 173(2)$ K, 7670 unique data, $R1 = 0.0563$.

CCDC reference number 440/150. See http://www.rsc.org/suppdata/nj/1999/1053/ for crystallographic files in .cif format.

†† NMR data for **5a** (CD$_2$Cl$_2$): ^{11}B-{^{1}H} δ 30.2; ^{1}H δ 7.13 (d, 4H, C$_6$H$_4$, J_{HH} = 7.8 Hz), 7.02 (d, 4H, C$_6$H$_4$, J_{HH} = 7.8 Hz), 4.19 (q, 4H, C*H*$_2$CH$_3$), 2.29 (s, 6H, C$_6$H$_4$*Me*), 1.31 (t, 6H, CH$_2$C*H*$_3$). **5b** (CD$_3$OD): ^{11}B-{^{1}H} δ 24.5; ^{1}H (including data for the [NH$_2$Me$_2$]$^+$ cation, see text) δ 6.91 (s, 8H, C$_6$H$_4$), 4.88 (s, 6H, OH), 2.69 (s, 12H, NH$_2$*Me*$_2$), 2.24 (s, 6H, C$_6$H$_4$*Me*); ^{13}C-{^{1}H} δ 139.2 (*ipso*-C), 136.9 (*p*-C), 130.2 (*o*-C), 129.7 (*m*-C), 21.3 (C$_6$H$_4$*Me*).

‡‡ Evidence for oxaborole species was also seen in the mass spectra of **3b-d**. Thus, in the case of **3d**, HRMS data were obtained for the species $\overline{\text{C(4-MeOC}_6\text{H}_4\text{)=C(4-MeOC}_6\text{H}_4\text{)B(NMe}_2\text{)OB}}$ (NMe)$_2$). Calcd C$_{20}$H$_{26}$B$_2$N$_2$O$_3$ 364.213959, found 364.212954.

§§ NMR data for **7** (CDCl$_3$): ^{11}B-{^{1}H} δ 38.6; ^{1}H *δ* 7.02 (d, 4H, C$_6$H$_4$, J_{HH} = 8.6 Hz), 6.68 (d, 4H, C$_6$H$_4$, J_{HH} = 8.6 Hz), 4.28 (br s, 4H, C$_5$H$_5$), 4.19 (br s, 4H, C$_5$H$_5$), 3.74 (s, 6H, NMe$_2$), 2.98 (s, 6H, NMe$_2$), 2.86 (s, 6H, C$_6$H$_4$*Me*).

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