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Developing nitrosocarborane chemistry†

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The new nitrosocarboranes [1-NO-2-R-1,2-*closo*-$C_2B_{10}H_{10}$] [R = CH_2Cl (**1**), CH_3OCH_2 (**2**) *p*-MeC_6H_4 (**3**), $SiMe_3$ (**4**) and $SiMe_2{}^tBu$ (**5**)] and [1-NO-7-Ph-1,7-*closo*-$C_2B_{10}H_{10}$] (**6**) were synthesised by reaction of the appropriate lithiocarborane in diethyl ether with NOCl in petroleum ether followed by quenching the reaction with aqueous $NaHCO_3$. These bright-blue compounds were characterised spectroscopically and, in several cases, crystallographically including structural determinations of **2** and **6** using crystals grown *in situ* on the diffractometer from liquid samples. In all cases the nitroso group bonds to the carborane as a 1e substituent (bent C–N–O sequence) and has little or no influence on $<\delta^{11}B>$, the weighted average ^{11}B chemical shift, relative to that in the parent (monosubstituted) carborane. Mono- and dinitroso derivatives of 1,1′-bis(*m*-carborane), compounds **7** and **8** respectively, were similarly synthesised but attempts to prepare the mononitroso 1,1′-bis(*o*-carborane) by the same protocol led only to the hydroxylamine species [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-N(H)OH-1,2-*closo*-$C_2B_{10}H_{10}$] (**9**); the desired compound [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$] (**10**) was only realised by switching to a non-aqueous work-up. The involvement of water in effecting the net reduction of the NO function in **10** to N(H)OH in **9** was confirmed by a series of experiments involving [1-N(H)OH-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (**11**), [1-(1′-2′-D-1′,2′-*closo*-$C_2B_{10}H_{10}$)-2-D-1,2-*closo*-$C_2B_{10}H_{10}$] (**12**) and [1-(1′-2′-D-1′,2′-*closo*-$C_2B_{10}H_{10}$)-2-N(H)OH-1,2-*closo*-$C_2B_{10}H_{10}$] (**13**). It is suggested that during aqueous work-up a water molecule, H-bonded to the acidic C2′H of **10**, is "delivered" to the adjacent C2NO unit. The ability of the NO group in nitrosocarboranes to undergo Diels–Alder cycloaddition reactions with cyclic 1,3-dienes was established *via* the syntheses of [1-($NOC_{10}H_{14}$)-1,2-*closo*-$C_2B_{10}H_{11}$] (**14**) and [1-(NOC_6H_8)-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (**15**). This strategy was then utilised to prepare derivatives of the elusive dinitroso compounds of [1,2-*closo*-$C_2B_{10}H_{12}$] and 1,1′-bis(*o*-carborane) leading to the sterically-crowded products [1,2-(NOC_6H_8)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$] (**16**, prepared as *meso* and racemic diastereoisomers), [1-{1′-2′-(NOC_6H_8)-1′,2′-*closo*-$C_2B_{10}H_{10}$}-2-(NOC_6H_8)-1,2-*closo*-$C_2B_{10}H_{10}$] (**17**) and [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-(NOC_6H_8)-1,2-*closo*-$C_2B_{10}H_{10}$] (**18**).

Introduction

Nitrosocarboranes (strictly *C*-nitrosocarboranes since the NO group in principle could be attached to either a cage C or a cage B atom, although only the former are currently known) were first reported in 1964 when Kauffman and co-workers prepared [1-NO-1,2-*closo*-$C_2B_{10}H_{11}$] (**I**) and [1-NO-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$] by reaction of the appropriate lithiocarborane with NOCl.[1] Subsequently, Zakharkin and colleagues described both [1-NO-1,12-*closo*-$C_2B_{10}H_{11}$][2] and [1-NO-1,7-*closo*-$C_2B_{10}H_{11}$] (**II**)[3] and then reported several reactions of [1-NO-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$] and [1-NO-1,7-*closo*-$C_2B_{10}H_{11}$] in a paper which also included a brief reference to the syntheses of [1-NO-7-Me-1,7-*closo*-$C_2B_{10}H_{10}$] and the dinitrosocarborane [1,7-$(NO)_2$-1,7-*closo*-$C_2B_{10}H_{10}$] (**III**).[4] The area then lay dormant for more than 30 years until Fox *et al.* reported detailed synthetic and spectroscopic studies of [1-NO-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$] and [1-NO-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (**IV**) as well as a crystallographic determination of the latter, the first such structural study of a nitrosocarborane.[5]

It is well established in transition-metal chemistry that the NO group can formally act as either a 1e ligand (bent M–N–O sequence) or a 3e ligand (linear M–N–O) to the metal centre[6] and that facile switching between these two modes is possible.[7] Since the structures (and consequent reactivity) of boranes, heteroboranes, carboranes and heterocarboranes are dependent on their numbers of skeletal electron pairs,[8]

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substituents to these clusters that have the capacity to alter by two the number of electrons they provide to the polyhedron are naturally of interest. Our ability to exploit this potential switching between 1e and 3e donation of the NO substituent is likely to rely on ready access to a range of nitrosocarboranes which is wider than that currently reported. Hence in this contribution we describe the synthesis and characterisation of a number of new nitrosocarboranes and related compounds including, in some cases, their Diels–Alder adducts with cyclic 1,3-dienes. Many of the species reported have been studied crystallographically including two examples where diffraction-quality crystals were grown by *in situ* cooling.

Results and discussion

The simple nitrosocarboranes [1-NO-1,2-*closo*-$C_2B_{10}H_{11}$] (**I**), [1-NO-2-CH_2Cl-1,2-*closo*-$C_2B_{10}H_{10}$] (**1**), [1-NO-2-CH_3OCH_2-1,2-*closo*-$C_2B_{10}H_{10}$] (**2**), [1-NO-2-(*p*-MeC_6H_4)-1,2-*closo*-$C_2B_{10}H_{10}$] (**3**), [1-NO-2-$SiMe_3$-1,2-*closo*-$C_2B_{10}H_{10}$] (**4**), [1-NO-2-$SiMe_2{}^t$Bu-1,2-*closo*-$C_2B_{10}H_{10}$] (**5**), [1-NO-1,7-*closo*-$C_2B_{10}H_{11}$] (**II**), [1-NO-7-Ph-1,7-*closo*-$C_2B_{10}H_{10}$] (**6**), and [1,7-$(NO)_2$-1,7-*closo*-$C_2B_{10}H_{10}$] (**III**) were either made (compounds **1–6**) or remade (compounds **I–III**) by the established method of deprotonation of the parent carborane with *n*-BuLi in Et_2O followed by reaction of the lithiocarborane with a large excess of NOCl in 40–60 °C petroleum ether (petrol). Work-up involved quenching the reaction mixture with aqueous $NaHCO_3$ and retention of the non-aqueous phase, with the product subsequently purified by column chromatography on silica. The bright-blue nitrosocarboranes, afforded in moderate yields except for **III**, are generally isolated as relatively volatile solids although **2** and **6** are both liquids at room temperature.

Although compound **I–III** are all literature compounds[1–3] relatively little data, and certainly no NMR spectroscopic data, were reported so we have re-synthesised them for comparison with the new nitrosocarboranes **1–6**. All compounds show a strong absorption for the NO group in the range 1560–1570 cm^{-1} which suggests the likelihood of a bent C–N–O sequence by comparison with that for the crystallographically-established compound [1-NO-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (ν_{max} = 1560 cm^{-1}),[5] although it has been pointed out that the NO stretching frequency is unreliable in distinguishing between bent and linear M–N–O fragments in transition-metal nitrosyls.[9]

Table 1 summarises the ^{11}B NMR patterns and $<\delta^{11}B>$, the weighted average ^{11}B chemical shifts, for **I–III** and **1–6**, together with those of their immediate precursors. Replacement of a CH by a CNO has little effect on the average chemical shift. Within each of the six pairs of compounds with 1,2-C_2B_{10} structures the maximum variation in $<\delta^{11}B>$ is only 0.4 ppm, for the (*p*-MeC_6H_4) species. For the 1,7-C_2B_{10} species there is perhaps more evidence of a systematic change in $<\delta^{11}B>$ in that each successive NO group seems to result in an increase in shielding with the average ^{11}B resonance falling by *ca.* 0.4–0.5 ppm. Further studies to determine the generality of this embryonic pattern appear warranted.

Table 1 ^{11}B NMR spectroscopic data for **1–6** and related compounds

Compound	^{11}B NMR pattern[a]	$<\delta^{11}B>$
[1,2-*closo*-$C_2B_{10}H_{12}$]	2 : 2 : 4 : 2	−10.7
[1-NO-1,2-*closo*-$C_2B_{10}H_{11}$] (**I**)	1 : 1 : 2 : 6	−10.5
[1-CH_2Cl-1,2-*closo*-$C_2B_{10}H_{11}$]	1 : 1 : 2 : 2 : 4	−9.7
[1-NO-2-CH_2Cl-1,2-*closo*-$C_2B_{10}H_{10}$] (**1**)	1 : 1 : 2 : 2 : 4	−9.8
[1-CH_2OCH_3-1,2-*closo*-$C_2B_{10}H_{11}$]	1 : 1 : 2 : 2 : 4	−10.3
[1-NO-2-CH_2OCH_3-1,2-*closo*-$C_2B_{10}H_{10}$] (**2**)	1 : 1 : 2 : 2 : 4	−10.2
[1-(*p*-MeC_6H_4)-1,2-*closo*-$C_2B_{10}H_{11}$]	1 : 1 : 2 : 4 : 2	−9.3
[1-NO-2-(*p*-MeC_6H_4)-1,2-*closo*-$C_2B_{10}H_{10}$] (**3**)	1 : 1 : 2 : 2 : 4	−9.7
[1-$SiMe_3$-1,2-*closo*-$C_2B_{10}H_{11}$]	1 : 1 : 2 : 2 : 2 : 2	−9.0
[1-NO-2-$SiMe_3$-1,2-*closo*-$C_2B_{10}H_{10}$] (**4**)	2 : 2 : 6	−9.0
[1-$SiMe_2{}^t$Bu-1,2-*closo*-$C_2B_{10}H_{11}$]	1 : 1 : 2 : 2 : 2 : 2	−8.8
[1-NO-2-$SiMe_2{}^t$Bu-1,2-*closo*-$C_2B_{10}H_{10}$] (**5**)	1 : 1 : 2 : 2 : 4	−8.7
[1,7-*closo*-$C_2B_{10}H_{12}$]	2 : 2 : 4 : 2	−12.1
[1-NO-1,7-*closo*-$C_2B_{10}H_{11}$] (**II**)	1 : 1 : 2 : 4 : 2	−12.4
[1,7-$(NO)_2$-1,7-*closo*-$C_2B_{10}H_{10}$] (**III**)	2 : 2 : 4 : 2	−12.9
[1-Ph-1,7-*closo*-$C_2B_{10}H_{11}$]	1 : 1 : 4 : 2 : 2	−11.0
[1-NO-7-Ph-1,7-*closo*-$C_2B_{10}H_{10}$] (**6**)	1 : 1 : 4 : 2 : 2	−11.5

[a] From high frequency to low frequency, in $CDCl_3$.

The structural identity of [1-NO-2-$SiMe_2{}^t$Bu-1,2-*closo*-$C_2B_{10}H_{10}$] (**5**) was established by a crystallographic study using crystals grown by slow evaporation of a petrol solution, and a perspective view of a single molecule is shown in Fig. 1. The determination is highly precise with e.s.d.s on B–B connectivities of only 0.0013–0.0014 Å. The C1–N1–O1 sequence is bent,

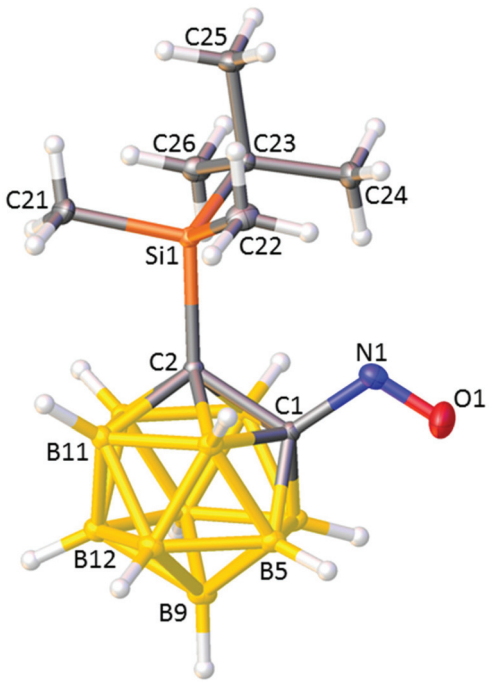

Fig. 1 Perspective view of compound **5**. In this and all subsequent figures the displacement ellipsoids are drawn at the 50% probability level, except for H atoms.

112.98(7)°, confirming that the NO group in **5** is a 1e substituent, and O1 lies effectively trans to the $SiMe_2{}^tBu$ group with the torsion angle O1–N1–C1–C2 being −176.44(7)°. A very similar orientation was observed by Fox and co-workers in [1-NO-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$].[5] Relative to this latter species, the only other nitrosocarborane to have been crystallographically-studied, the C1–N1 and N1–O1 distances in **5** are somewhat longer, 1.5143(11) *vs.* 1.421(7) Å, and somewhat shorter, 1.1736(10) *vs.* 1.241(7) Å, respectively.

As noted, the compounds [1-NO-2-CH_3OCH_2-1,2-*closo*-$C_2B_{10}H_{10}$] (**2**) and [1-NO-7-Ph-1,7-*closo*-$C_2B_{10}H_{10}$] (**6**) are liquids at room temperature, and we were attracted by the challenge of trying to grow single crystals of each of them *in situ* on the diffractometer. This was successful in both cases but particularly so for compound **2**, where a crystal was grown that diffracted well to θ_{max} = 25° (Mo-K_α radiation) and afforded a reasonably precise determination (e.s.d.s on B–B connectivities 0.006–0.008 Å). As shown in Fig. 2 the C1–N1–O1 unit is bent, 112.4(3) and 112.1(4)° for the two crystallographically-independent molecules, and the NO group adopts a similar orientation with respect to the substituent on C2 as was observed in [1-NO-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] and in **5** [O1–N1–C1–C2 = 179.7(3) and 178.1(4)°]. C1–N1 and N1–O1 are 1.494(5) and 1.185(4) Å for one independent molecule and 1.501(5) and 1.183(5) Å for the other.

The structural study of **6** was of lower precision (e.s.d.s on B–B connectivities 0.02–0.03 Å), in part because of the relatively poor quality of crystal that could be grown (not single and significant diffraction to only θ_{max} = 22°) and in part because there is 54 : 46 disorder between the {C1N1O1} and {B10H10} fragments (that shown in Fig. 3 is the major component). Nevertheless the structural identity of **6** as 1-NO-7-Ph-1,7-*closo*-$C_2B_{10}H_{10}$ with a bent C1–N1–O1 unit, 117(3)°, is fully confirmed by this study. As far as we are aware the crystallographic determinations of **2** and **6** represent the first such studies of carboranes in which single crystals were grown by cooling samples which are liquid at room temperature.

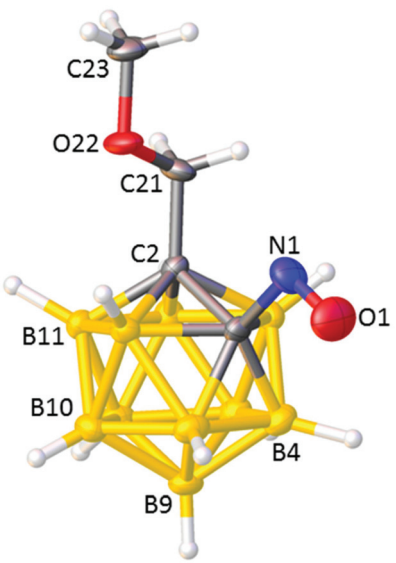

Fig. 2 Perspective view of compound **2**.

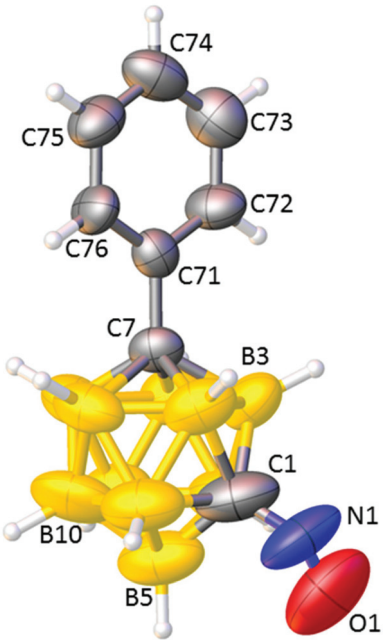

Fig. 3 Perspective view of compound **6**. The NO group is disordered between vertices 1 (54%) and 10 (46%) so that shown is the major component. The large thermal ellipsoids reflect the relatively imprecise determination but the structure of the molecule is nevertheless unambiguously established.

An area of considerable current activity in carborane chemistry is that of bis(carboranes),[10] molecules composed of two carborane units connected by a 2c–2e bond, and accordingly we have explored both mono-NO and di-NO derivatives of 1,1′-bis(*o*-carborane) and 1,1′-bis(*m*-carborane) (Fig. 4).

The deprotonation of 1,1′-bis(*m*-carborane) with three equivalents of *n*-BuLi followed by reaction with excess NOCl and the standard aqueous work-up results in the formation of two bright-blue products separated by column chromatography on silica, the mononitroso [1-(1′-1′,7′-*closo*-$C_2B_{10}H_{11}$)-7-NO-1,7-*closo*-$C_2B_{10}H_{10}$] (**7**) and the dinitroso [1-(1′-7′-NO-1′,7′-*closo*-$C_2B_{10}H_{10}$)-7-NO-1,7-*closo*-$C_2B_{10}H_{10}$] (**8**), in 10% and 42% yields, respectively. Both compounds were initially characterised by microanalysis, mass spectrometry and NMR spectroscopy, and ultimately compound **8** was subjected to crystallographic analysis. The molecule has crystallographically-imposed C_i symmetry about the centre of the C1–C1′ bond and the O atom is disordered over four sites with that shown in Fig. 5 the major (60%) component. The C7–N71 and N71–O73 distances are 1.502(2) and 1.089(3) Å and the C7–N71–O73 angle is 120.7(2)°.

An attempt to add one NO group to 1,1′-bis(*o*-carborane) was, however, not successful. Following deprotonation of 1,1′-bis(*o*-carborane) with one equivalent of *n*-BuLi in Et_2O and addition of the suspension thus formed to an excess of NOCl

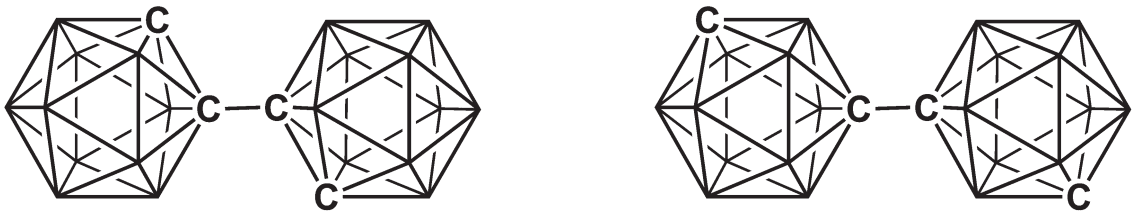

Fig. 4 (Left) 1,1′-Bis(*o*-carborane) and (right) 1,1′-bis(*m*-carborane).

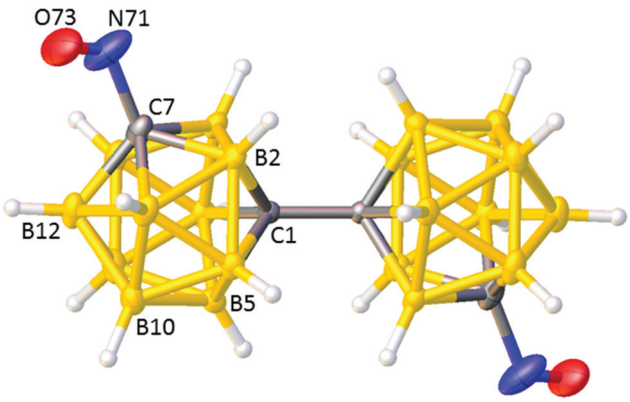

Fig. 5 Perspective view of compound **8**. The molecule sits on a crystallographic inversion centre located in the middle of the C1–C1′ bond. The O atom is disordered over four sites with that shown the major one.

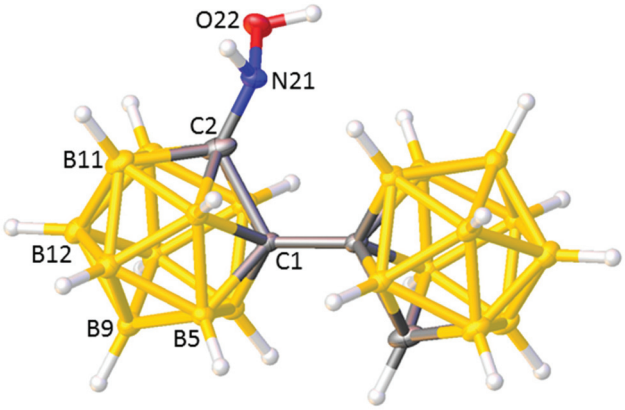

Fig. 6 Perspective view of compound **9**. The molecule has crystallographically-imposed C_i symmetry with the inversion centre located in the middle of the C1–C1′ bond. The N(H)OH group is disordered between C2 and C2′.

in petrol a dark-green solution was produced, but on adding this to aqueous $NaHCO_3$ the blue organic layer decolourised after a short time. Work-up subsequently afforded a low yield of the white hydroxylamine derivative [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-N(H)OH-1,2-*closo*-$C_2B_{10}H_{10}$] (**9**). An accurate mass determination confirmed the molecular formula and in the ^{1}H NMR spectrum are doublets at δ 6.11 (N*H*) and 5.51 (O*H*) ppm (identified as such by a ^{1}H,^{15}N HMQC experiment which also revealed a ^{15}N chemical shift of 133 ppm in **9**) each integrating for one H atom, together with a broad singlet at δ 3.98 ppm (cage C*H*). Finally, the molecular structure of **9** was established by a crystallographic study (Fig. 6). The molecule resides on a crystallographic inversion centre necessitating 1 : 1 disorder between the C2N(H)OH unit and the C2′H′ fragment. The N21–O22 distance is 1.427(3) Å and the C1–C2 distance 1.7677 (18) Å, the latter being significantly longer than that in **2** [1.661(5) and 1.646(5) Å, two independent molecules] and **5** [1.6597(11) Å] and in 1,1′-bis(*o*-carborane) itself [1.6950(8) and 1.6991(8) Å; C2 and B3 are equally disordered][11] as the result of intramolecular steric crowding between N(H)OH and $C_2B_{10}H_{11}$ substituents.

The formation of a hydroxylamine from a nitrosyl is formally reduction[12] and prompts consideration of the source of that reduction. Our first suspicions centred on the aqueous work-up that has been used in the synthesis of all nitrosocarboranes to date so initially we trialled a non-aqueous work-up of a well-characterised species, [1-NO-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (**IV**). By the standard aqueous procedure **IV** was isolated in 52% yield. Alternatively, following synthesis in Et_2O/petrol the solvent was evaporated and the product extracted into petrol and purified by column chromatography on florisil (using petrol as eluent) affording **IV** in 42% yield. In both cases the identity of the product was checked by comparison of its ^{11}B NMR spectrum against an authentic sample.[5]

Thereafter the reaction that led to the isolation of **9** was repeated substituting the aqueous work-up by this non-aqueous protocol, leading to the isolation of the desired compound [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$] (**10**) in effectively the same yield achieved for **9**. Compound **10** displays a clear NO stretch in the IR spectrum (1573 cm^{-1}) and no evidence of N*H* or O*H* resonances in the ^{1}H NMR spectrum, and an accurate mass determination is fully consistent with no reduction of the nitroso group having occurred. Final confirmation was provided by a crystallographic study (Fig. 7). Crystallographically compounds **9** and **10** are almost isomorphous and the NO group in **10** [C2–N21 1.441 (3), N21–O22 1.195(4) Å, C2–N21–O22 113.8(3)°] is equally disordered between C2 and C2′.

This strongly suggests that the source of the reduction of the NO function in **10** to the hydroxylamine unit in **9** is water, but it also suggests that the aqueous work-up of [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$] is somehow different

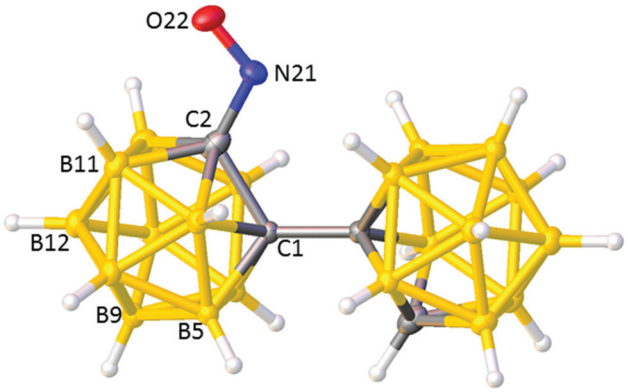

Fig. 7 Perspective view of compound **10**. The NO group is disordered between C2 and C2′ and there is a crystallographic inversion centre in the mid-point of the C1–C1′ bond.

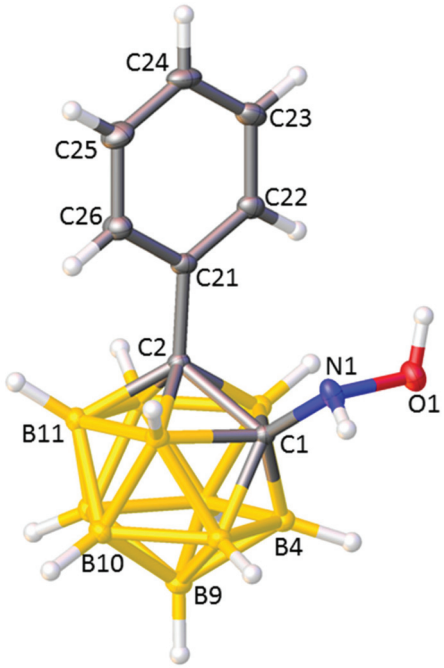

Fig. 8 Perspective view of compound **11**. Only one of the two crystallographically-independent molecules is shown.

to the aqueous work-up of the other nitrosocarboranes prepared to date since these latter species are not converted to hydroxylamines. It must be remembered, however, that although the work-up is aqueous it is also biphasic with the nitrosocarborane in the non-aqueous phase and therefore generally protected from the effects of water. Support for this arises from an experiment in which **IV** in THF was treated with water. The blue solution immediately begins to fade and the colourless hydroxylamine product [1-N(H)OH-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (**11**) was ultimately isolated. The identity of the compound was established by accurate mass measurement, by the presence of N*H* (δ 5.70 ppm) and O*H* (δ 5.18 ppm) resonances in the ^{1}H NMR spectrum (each integrating for 1H against the aromatic 5H) and ultimately by a crystallographic study (Fig. 8). There are two crystallographically-independent molecules in the asymmetric fraction of the unit cell which are practically identical. The N–O bond distances are 1.4305(13) and 1.4323(12) Å, close to the corresponding distance in **9**.

Although it seems likely that it is water which is converting the NO group in **10** to hydroxylamine we also considered the possibility of H transfer from the adjacent C2′ atom to the C2NO unit (were this to be the source of the reduction it is feasible that C2′ would subsequently pick up an H from the solvent). To test this possibility we first prepared **12**, the *C*,*C*′-dideutero analogue of 1,1′-bis(*o*-carborane) by double deprotonation of 1,1′-bis(*o*-carborane) and addition of D_2O. Compound **12** was afforded in >90% yield and its identity established by an accurate mass measurement (calculated 288.3850, found 288.3850). Compound **12** was then used in the targeted synthesis of its mononitroso derivative involving aqueous work-up, resulting in the isolation of the hydroxylamine product [1-(1′-2′-D-1′,2′-*closo*-$C_2B_{10}H_{10}$)-2-N(H)OH-1,2-*closo*-$C_2B_{10}H_{10}$] (**13**). This was identified by ^{1}H NMR spectroscopy (N*H* at δ 6.10 ppm, O*H* at δ 5.50 ppm, no cage C*H*) and by an accurate mass measurement (calculated 318.3846, found 318.3852). Although a small amount of the C2′H analogue **9** was also detected (presumably resulting from H/D exchange with solvent) compound **13** was clearly the major product.

These experiments conclusively establish that in the synthesis of compound **9** the nitroso group in [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$] is converted to hydroxylamine by water as part of the aqueous work-up. We propose that the unique structure of the 1,1′-bis(*o*-carborane) framework is responsible for this phenomenon. Even though the system is formally biphasic we believe that a water molecule becomes H-bonded to the acidic C2′H atom and is thus "delivered" to the adjacent C2NO unit effecting the reduction. This is a possibility unique to 1,1′-bis(*o*-carborane). Thus, for example, in the case of the synthesis of the mononitroso bis(*m*-carborane) compound **7** involving aqueous work-up, even if an H_2O molecule is similarly H-bonded to C7′H atom it never gets to be adjacent to the nitroso function.

Two glaring omissions from the list of nitrosocarboranes in this and previous papers are the dinitroso derivative of 1,2-*closo*-$C_2B_{10}H_{12}$ and the dinitroso derivative of 1,1′-bis(*o*-carborane). We have attempted to synthesise both of these on multiple occasions with both aqueous and non-aqueous work-up protocols but were never able to isolate blue products (although initial blue species are observed). This is presumably due to coupling of the two adjacent NO groups into either a furoxan or a *cis*-azodioxy unit as is well established in organodinitroso chemistry.[13] Indeed, the NO groups in the putative compound [1,2-$(NO)_2$-1,2-*closo*-$C_2B_{10}H_{10}$] are ideally oriented for furoxan coupling and those in the putative [1-(1′-2′-NO-1′,2′-*closo*-$C_2B_{10}H_{10}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$] are perfectly set up for *cis*-azodioxy coupling (Fig. 9).

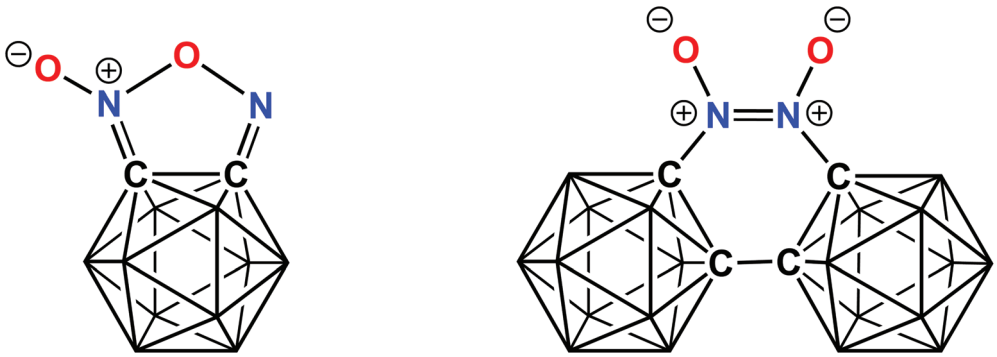

Fig. 9 (left) Possible formation of a furoxan from [1,2-$(NO)_2$-1,2-*closo*-$C_2B_{10}H_{10}$] and (right) possible formation of a *cis*-azodioxy compound from [1-(1′-2′-NO-1′,2′-*closo*-$C_2B_{10}H_{10}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$].

Since it is well-established that organonitroso compounds readily undergo Diels–Alder (DA) cycloaddition with cyclic 1,3-dienes[14] we have explored the possibility of using this to "trap out" the dinitroso derivatives of *o*-carborane and 1,1′-bis(*o*-carborane). Since DA cycloadducts of nitrosocarboranes have not previously been reported we initially targeted those of the simple compounds **I** and **IV**. Reaction of **I** with α-terpinene (1-isopropyl-4-methyl-1,3-cyclohexadiene) in CH_2Cl_2 (DCM) resulted in decolourisation and near-quantitative formation of the cycloadduct [1-($NOC_{10}H_{16}$)-1,2-*closo*-$C_2B_{10}H_{11}$] (**14**) characterised by mass spectrometry, ^{1}H and ^{11}B NMR spectroscopies and by a crystallographic study (Fig. 10). Somewhat unusually there are four crystallographically-independent molecules of **14** in the asymmetric fraction of the unit cell, but all are equivalent and a representative example is shown in the Figure. Clearly the cycloaddition has been successful. Also successful was the formation of a DA cycloadduct between **IV** and 1,3-cyclohexadiene, the resulting product [1-(NOC_6H_8)-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (**15**) being isolated in *ca.* 30% yield and fully characterised spectroscopically.

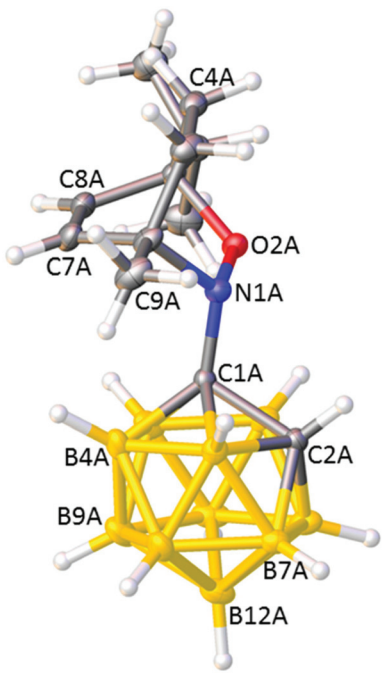

Fig. 10 Perspective view of one of four crystallographically-independent molecules of compound **14**.

With these sighting experiments completed we turned to [1,2-*closo*-$C_2B_{10}H_{12}$]. Double deprotonation followed by reaction with NOCl afforded a dark-green solution in Et_2O/petrol. Following removal of solvent and excess NOCl the green solid was extracted into DCM, filtered, and the filtrate treated with an excess of 1,3-cyclohexadiene at which point the colour began to fade affording the off-white product [1,2-(NOC_6H_8)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$] (**16**) as an almost equal mixture of meso (**16a**) and racemic (**16b**) diastereoisomers, separated by preparative thin-layer chromatography (TLC). Both diastereoisomers were characterised by mass spectrometry, ^{1}H and ^{11}B NMR spectroscopies and crystallographic studies (Fig. 11).

Both molecules have crystallographically-imposed symmetry, C_s for meso **16a** and C_2 for racemic **16b**. One interesting feature of both structures is the extended C1–C2 distance, 1.947(2) Å in **16a** and 1.9485(19) Å in **16b**. Undoubtedly this stretching arises from steric congestion between the two bulky substituents and is reminiscent of the deformations of the *o*-carborane cage that we have previously observed with two dimethylferrocenyl or pentamethyleneferrocenyl substituents.[15]

Similarly, treatment of 1,1′-bis(*o*-carborane) with two equivalents of *n*-BuLi and then NOCl afforded a blue-green product to which was quickly added an excess of 1,3-cyclohexadiene resulting in rapid decolourisation. Following work-up involving TLC compound **17**, the DA adduct of [1-(1′-2′-NO-1′,2′-*closo*-$C_2B_{10}H_{10}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$], was isolated together with a small amount of compound **18**, the DA adduct of the mononitroso species [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$]. As was the case with compound **16** it was be expected that compound **17** would be formed as both meso and racemic diastereoisomers however only a single band was observed by TLC. The crystallographically-determined structure has imposed C_i symmetry and shows disorder of the NOC_6H_8 substituent, with both enantiomers of the chiral N1

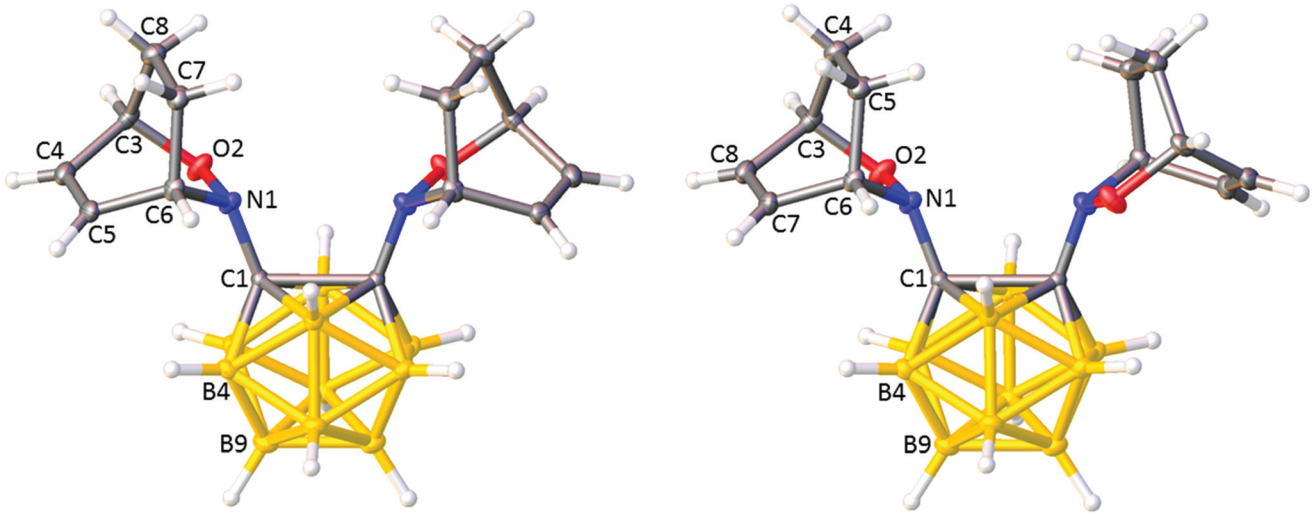

Fig. 11 Perspective views of (left) the *meso* and (right) the racemic isomers of compound **16**.

centre present in the ratio 75 : 25 (Fig. 12 shows only the major component of this disorder). This makes the precise interpretation of the crystallographic result ambiguous. The crystals could be composed of only the (disordered) meso form (implying that this disatereoisomer selectively crystallised) or alternatively the meso and racemic forms may have co-crystallised, up to the limit of 2 : 1 respectively. Irrespective of this ambiguity, however, the key conclusion of the isolation of the DA adducts **16** and **17** is confirmation that the initial reactions between NOCl and doubly-deprotonated [1,2-*closo*-$C_2B_{10}H_{12}$] and 1,1′-bis(*o*-carborane) do indeed produce the elusive dinitroso compounds [1,2-$(NO)_2$-1,2-*closo*-$C_2B_{10}H_{10}$] and [1-(1′-2′-NO-1′,2′-*closo*-$C_2B_{10}H_{10}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$].

A minor co-product in the synthesis of compound **17** was a small amount of the monosubstituted species [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-(NOC_6H_8)-1,2-*closo*-$C_2B_{10}H_{10}$] (**18**), clearly the result of DA addition of 1,3-cyclohexadiene to the nitrosocarborane [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$] formed by incomplete deprotonation of 1,1′-bis(*o*-carborane), and a perspective view of a single molecule of **18** is shown in Fig. 13.

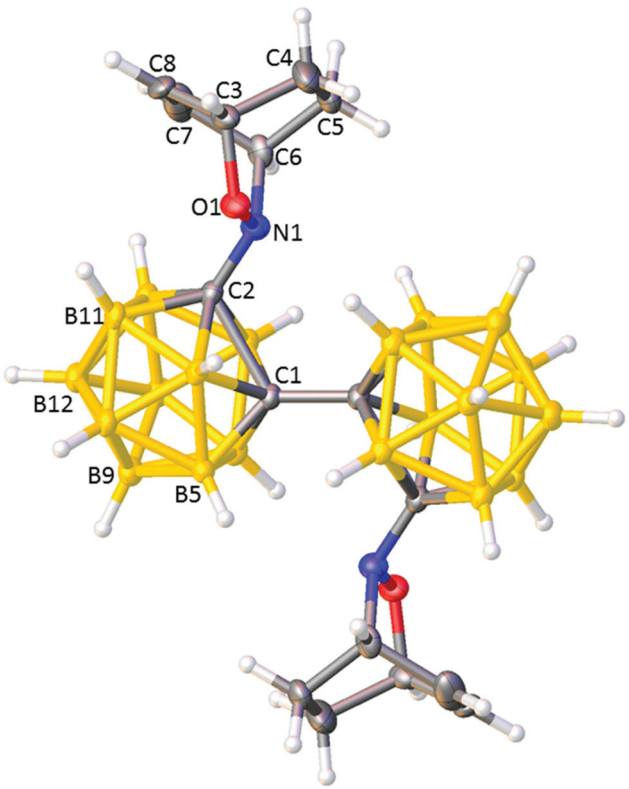

Fig. 12 Perspective view of compound **17**. The NOC_6H_8 substituent is disordered and that shown is the major component. There is a crystallographic inversion centre located at the mid-point of the C1–C1′ bond.

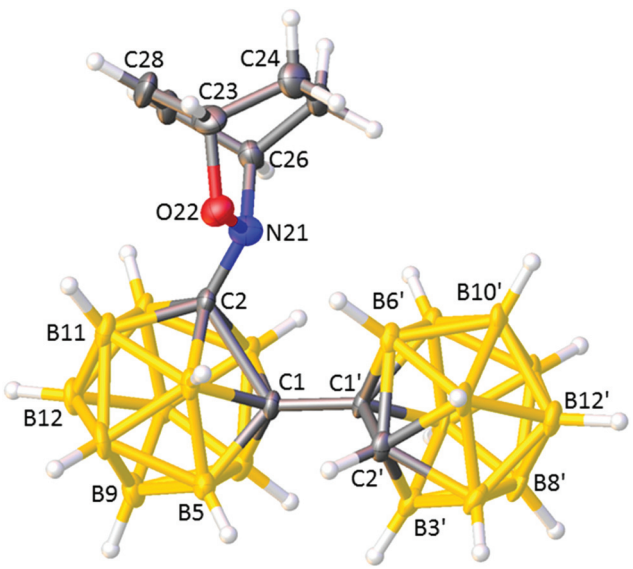

Fig. 13 Perspective view of compound **18**.

Both **17** and **18** feature long C1–C2 connectivities, 1.946(2) and 1.961(6) Å, respectively, as a result of steric crowding between the substituents on these atoms, as was noted for **16**.

Conclusions

The range of known nitrosocarboranes has been considerably expanded and spectroscopic properties of a number of such compounds previously synthesised have been reported. Single crystals of two nitrosocarboranes which are liquids at room temperature have been grown *in situ* on the diffractometer allowing their structures to be determined. The conversion of nitrosocarboranes to hydroxylaminocarboranes has been shown to be effected by water. Dinitroso derivatives of [1,2-*closo*-$C_2B_{10}H_{12}$] and 1,1′-bis(*o*-carborane) remain unknown since presumably such species are ideally suited to rearrange into a furoxan and a *cis*-azodioxy compound respectively, but nevertheless these nitroso compounds have been isolated in derivatised form by converting them to stable Diels–Alder cycloadducts.

Experimental

Synthesis

All experiments were performed under dry, oxygen-free, N_2 using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. Solvents were freshly distilled over Na wire (diethyl ether, petrol) or CaH_2 (DCM) or stored over 4 Å molecular sieves ($CDCl_3$) and were degassed (3 × freeze–pump–thaw cycles) before use. Preparative thin-layer chromatography (TLC) employed 20 × 20 cm Kieselgel F_{254} glass plates. NMR spectra at 300.1/400.1 MHz (^{1}H) or 96.3/128.4 MHz (^{11}B) were recorded on a Bruker AVIII 300/400 spectrometer respectively at ambient temperature from $CDCl_3$ solutions. EI mass spectra were recorded using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. Elemental analyses were carried out using an Exeter CE-440 elemental analyser. Infrared spectra were recorded as DCM solutions on a PerkinElmer Spectrum 100 FT-IR spectrometer. [1-R-1,2-*closo*-$C_2B_{10}H_{11}$] (R = CH_2Cl,[16] CH_2OCH_3,[17] *p*-MeC_6H_4,[18] $SiMe_3$ [19] or $SiMe_2{}^tBu$[20]), [1-Ph-1,7-*closo*-$C_2B_{10}H_{11}$],[21] 1,1′-bis(*o*-carborane)[10a] and 1,1′-bis(*m*-carborane)[22] were prepared by literature methods or variants thereof. All other reagents were supplied commercially.

Nitrosyl chloride. Following the general method of Morton and Wilcox,[23] $NaNO_2$ (10.5 g, 0.15 mol) was dissolved in water (25 mL) and added dropwise to 12M hydrochloric acid (60 mL, 0.72 mol). The resulting yellow-brown gas was carried by a flow of N_2 through drying tubes containing (in order) $NaNO_2$, KCl and $CaCl_2$. The gas was condensed using liquid N_2 into a bespoke vessel where it was stored at room temperature under its own pressure. When required, a small quantity of the gas was transferred under reduced pressure and condensed using liquid N_2 into the reaction vessel containing dry, degassed, petrol.

[1-NO-1,2-*closo*-$C_2B_{10}H_{11}$] (I). [1,2-*closo*-$C_2B_{10}H_{12}$] (500 mg, 3.47 mmol) was dissolved in degassed diethyl ether (30 mL). *n*-BuLi (3.50 mmol) was added and the solution was stirred under N_2 for 3 hours. The solution was added dropwise to a large excess of nitrosyl chloride in petrol (30 mL) at −78 °C and the resulting blue-green solution was stirred for 30 minutes, then added to a saturated solution of $NaHCO_3$ in water (100 mL). The resulting blue organic phase was separated, washed with water (60 mL), concentrated and applied to a silica column. Elution with petrol afforded a blue mobile band which yielded [1-NO-1,2-*closo*-$C_2B_{10}H_{11}$] (**I**) as a volatile blue solid on removal of solvent (146 mg, 24.3%). $C_2H_{11}B_{10}NO$ requires C 13.9, H 6.40, N 8.09. Found C 14.1, H 6.62, H 7.94%. $^{11}B\{^1H\}$ NMR, δ −2.6 (1B), −3.6 (1B), −9.3 (2B), −13.4 (6B). ^{1}H NMR, δ 4.45 (s, 1H, cage C*H*). IR, ν_{max} 2600 (BH), 1570 (NO) cm^{-1}. EIMS, envelope centred on *m*/*z* 173 (M^+).

[1-NO-2-CH_2Cl-1,2-*closo*-$C_2B_{10}H_{10}$] (1). Similarly, a diethyl ether solution of [1-CH_2Cl-1,2-*closo*-$C_2B_{10}H_{11}$] (500 mg, 2.26 mmol) was deprotonated with *n*-butyllithium and added to a petrol solution of an excess of nitrosyl chloride. Following work-up, **1** was isolated as a blue solid (258 mg, 44.9%). $C_3H_{12}B_{10}ClNO$ requires C 16.3, H 5.46, N 6.32. Found C 17.2, H 5.76, N 5.98%. $^{11}B\{^1H\}$ NMR, δ −2.6 (1B), −4.6 (1B), −9.8 (2B), −10.8 (2B), −12.5 (4B). ^{1}H NMR, δ 4.90 (s, 2H, CH_2Cl). IR, ν_{max} 2599 (BH), 1570 (NO) cm^{-1}. EIMS, envelope centred on *m*/*z* 221/222 (M^+).

[1-NO-2-CH_2OCH_3-1,2-*closo*-$C_2B_{10}H_{10}$] (2). Similarly, [1-CH_3OCH_2-1,2-*closo*-$C_2B_{10}H_{11}$] (450 mg, 2.39 mmol) in ether (20 mL) was treated with *n*-BuLi (3.75 mmol) and added dropwise to an excess of nitrosyl chloride in petrol (20 mL) at −78 °C. Work-up proceeded exactly as for **I** yielding [1-NO-2-CH_2OCH_3-1,2-*closo*-$C_2B_{10}H_{10}$] (**2**) as a blue liquid (200 mg, 38.5%). $C_4H_{15}B_{10}NO$ requires C 22.1, H 6.96, N 6.45. Found C 22.9, H 7.17, N 5.75%. $^{11}B\{^1H\}$ NMR, δ −2.6 (1B), −4.7 (1B), −10.6 (2B), −11.2 (2B), −12.8 (4B). ^{1}H NMR, δ 4.66 (s, 2H, CH_2O), 3.46 (s, 3H, OCH_3). IR, ν_{max} 2608 (BH), 1568 (NO) cm^{-1}. EIMS, envelope centred on *m*/*z* 217 (M^+). Diffraction-quality crystals grown by slow cooling a sample of **2** in a Lindemann tube.

[1-NO-2-(*p*-MeC_6H_4)-1,2-*closo*-$C_2B_{10}H_{10}$] (3). Similarly, [1-(*p*-MeC_6H_4)-1,2-*closo*-$C_2B_{10}H_{11}$] (503 mg, 2.15 mmol) in ether (20 mL) was deprotonated and added to an excess of nitrosyl chloride in petrol (20 mL) at −78 °C. Work-up afforded [1-NO-2-(*p*-MeC_6H_4)-1,2-*closo*-$C_2B_{10}H_{10}$] (**3**) as a blue solid (90 mg, 15.6%). $C_9H_{17}B_{10}NO$ requires C 41.1, H 6.51, N 5.32. Found C 40.3, H 6.64, N 5.76%. $^{11}B\{^1H\}$ NMR, δ −1.9 (1B), −4.6 (1B), −9.8 (2B), −10.4 (2B), −12.5 (4B). ^{1}H NMR, δ 7.70 (app d, 2H, C_6H_4), 7.20 (app d, 2H, C_6H_4), 2.38 (s, 3H, CH_3). IR, ν_{max} 2607 (BH), 2585 (BH), 1564 (NO) cm^{-1}. EIMS, envelope centred on *m*/*z* 263 (M^+).

[1-NO-2-$SiMe_3$-1,2-*closo*-$C_2B_{10}H_{10}$] (4). In an analogous fashion, a solution of [1-Me_3Si-1,2-*closo*-$C_2B_{10}H_{11}$] (400 mg, 1.85 mmol) was dissolved in ether (20 mL) and deprotonated. The resulting yellow solution was added dropwise to an excess of nitrosyl chloride in petrol (20 mL) which was cooled to −78 °C. Work-up gave 1-NO-2-$SiMe_3$-1,2-*closo*-$C_2B_{10}H_{10}$ (**4**) as a

blue solid (193 mg, 42.6%). $C_5H_{19}B_{10}NOSi$ requires 24.5, H 7.80, N 5.71. Found C 24.7, H 7.96, N 5.10%. $^{11}B\{^1H\}$ NMR, δ −1.7 (2B), −8.2 (2B), −11.7 (6B). ^1H NMR, δ 0.39 [s, 9H, Si(CH_3)]. IR, ν_{max} 2603 (BH), 2582 (BH), 1567 (NO) cm^{-1}. EIMS, envelope centred on m/z 245 (M^+).

[1-NO-2-SiMe$_2$^{t}Bu-1,2-*closo*-$C_2B_{10}H_{10}$] (5). Correspondingly, [1-SiMe$_2$^{t}Bu-1,2-*closo*-$C_2B_{10}H_{11}$] was dissolved in ether (20 mL), treated with *n*-BuLi (1.63 mmol) and added dropwise to nitrosyl chloride in petrol (20 mL) at −78 °C. After work-up, [1-NO-2-SiMe$_2$^{t}Bu-1,2-*closo*-$C_2B_{10}H_{10}$] (**5**) was isolated as a blue solid (236 mg, 53.1%). $C_8H_{25}B_{10}NOSi$ requires C 33.4, H 8.77, N 4.87. Found C 33.8, H 8.97, N 4.56%. $^{11}B\{^1H\}$ NMR, δ −0.8 (1B), −2.0 (1B), −7.9 (2B), −10.8 (2B), −11.8 (4B). ^1H NMR, δ 1.04 [s, 9H, C(CH_3)], 0.38 [s, 6H, Si(CH_3)$_2$]. IR, ν_{max} 2603 (BH), 2580 (BH), 1566 (NO) cm^{-1}. EIMS, envelope centred on m/z 288 (M^+). Diffraction-quality crystals grown by slow evaporation of a concentrated petrol solution of **5**.

[1-NO-1,7-*closo*-$C_2B_{10}H_{11}$] (II). *n*-Butyl lithium (2.78 mmol) was added to [1,7-*closo*-$C_2B_{10}H_{12}$] (400 mg, 2.78 mmol) in diethyl ether (10 mL) at 0 °C. The reaction was conducted as described previously to yield **II** as a blue solid (216 mg, 44.9%). $^{11}B\{^1H\}$ NMR, δ −6.6 (1B), −8.4 (1B), −11.1 (2B), −13.2 (4B), −17.0 (2B). ^1H NMR, δ 3.11 (br s, 1H, cage C*H*). IR, ν_{max} 2610 (BH), 1562 (NO) cm^{-1}. EIMS, envelope centred on m/z 173 (M^+).

[1-NO-7-Ph-1,7-*closo*-$C_2B_{10}H_{10}$] (6). Analogously, [1-Ph-1,7-*closo*-$C_2B_{10}H_{11}$] (850 mg, 3.86 mmol) in diethyl ether was treated with *n*-butyllithium solution (4.25 mmol) and added to a petrol solution of an excess of nitrosyl chloride to give, following workup, the product, **6**, as a blue liquid (594 mg, 61.7%). $C_8H_{15}B_{10}NO$ requires C 38.5, H 6.06, N 5.62. Found C 37.9, H 6.04, N 4.62%. $^{11}B\{^1H\}$ NMR, δ −5.5 (1B), −8.7 (1B), −11.0 (4B), −13.1 (2B), −15.3 (2B). ^1H NMR, δ 7.28 (m, 5H, Ph). IR, ν_{max} 2613 (BH), 1562 (NO) cm^{-1}. EIMS, envelope centred on m/z 249 (M^+). Diffraction-quality crystals were grown from cooling **6** in a Lindemann tube.

[1,7-(NO)$_2$-1,7-*closo*-$C_2B_{10}H_{10}$] (III). A solution of [1,7-*closo*-$C_2B_{10}H_{12}$] (200 mg, 1.39 mmol) in dry, degassed, diethyl ether (20 mL) was treated with *n*-BuLi (3.00 mmol) at −78 °C. The solution was warmed to room temperature and then heated at reflux for 60 minutes to give a cloudy white suspension. This was added dropwise to a solution of an excess of nitrosyl chloride in 10 mL of dry, degassed, petrol at −78 °C. The resulting green solution was stirred for 10 minutes and then quenched by addition to a saturated solution of $NaHCO_3$ (50 mL). The green-blue organic layer was separated, washed with 30 mL water, dried and reduced to dryness *in vacuo*. The residue was extracted into petrol and filtered. The blue filtrate was reduced in volume and purified by preparative thin layer chromatography (petrol eluent) to give **III** as a volatile blue solid (4.1 mg, 1.5%) at R_f 0.90. $^{11}B\{^1H\}$ NMR, δ −8.3 (2B), −11.8 (2B), −13.6 (4B), −17.4 (2B). IR, ν_{max} 2618 (BH), 1565 (NO) cm^{-1}. EIMS, envelopes centred on m/z 231 (M^+ + NO) and 201 (M^+).

[1-(1′-1′,7′-*closo*-$C_2B_{10}H_{11}$)-7-NO-1,7-*closo*-$C_2B_{10}H_{10}$] (7) and [1-(1′-7′-NO-1′,7′-*closo*-$C_2B_{10}H_{10}$)-7-NO-1,7-*closo*-$C_2B_{10}H_{10}$] (8). 1,1′-Bis(*m*-carborane) (200 mg, 0.70 mmol) was dissolved in dry, degassed, diethyl ether (20 mL) and treated with *n*-butyllithium solution (2.10 mmol). The solution was stirred for 30 minutes at room temperature and heated at reflux for a further 30 minutes. The carborane solution was added dropwise to an excess of nitrosyl chloride in dry, degassed, petrol (20 mL) at −78 °C. The reaction mixture was quenched with $NaHCO_3$ in water, and the resulting blue organic layer was separated, washed with water and dried. Purification by column chromatography with petrol eluent on silica gave two blue bands, **7** (23 mg, 10.0%) at R_f 0.67 and **8** (101 mg, 42.5%) at R_f 0.79.

7: $^{11}B\{^1H\}$ NMR, δ −3.2 (1B), −4.8 (1B), −7.6 (2B), −10.5 (6B), −11.5 (2B), −13.6 (4B), −14.5 (4B). ^1H NMR, δ 3.00 (br s, 1H, cage C*H*). IR, ν_{max} 2614 (BH), 1564 (NO) cm^{-1}. EIMS, envelope centred on m/z 315 (M^+).

8: $C_4H_{20}B_{20}N_2O_2$ requires C 14.0, H 5.85, N 8.13. Found C 14.1, H 5.98, N 8.12%. $^{11}B\{^1H\}$ NMR, δ −4.9 (2B), −7.6 (2B), −10.2 (4B), −11.3 (4B), −13.5 (4B), −14.9 (4B). IR, ν_{max} 2618 (BH), 1565 (NO) cm^{-1}. EIMS, envelope centred on m/z 344 (M^+). Diffraction-quality crystals of **8** were grown from cooling a concentrated ethanol-hexane solution.

[1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-N(H)OH-1,2-*closo*-$C_2B_{10}H_{10}$] (9). A solution of 1,1′-bis(*o*-carborane) (100 mg, 0.35 mmol) in diethyl ether (15 mL) was treated with *n*-BuLi (0.38 mmol) and added dropwise to nitrosyl chloride in petrol (15 mL) at −78 °C. The dark green solution was added to a saturated aqueous $NaHCO_3$ solution, giving a blue organic layer which decolourised after 2 minutes. The organic phase was separated and washed with water (30 mL) resulting in a pale yellow solution. This was dried with $MgSO_4$, filtered and reduced to give a yellow solid. Purification by elution through a short silica plug with DCM eluent followed by preparative TLC (DCM/petrol 3 : 1) gave **9** as a white solid (6 mg, 5.4%) at R_f 0.44. $C_4H_{23}B_{20}NO$ requires C 15.1, H 7.30, N 4.41. Found C 16.1, H 7.04, N 3.66%. $^{11}B\{^1H\}$ NMR, δ −1.9 (3B), −6.2 (1B), −9 to −13 (overlapping resonances with maxima at −9.5, −10.5, −12.8, 16B). ^1H NMR, δ 6.11 (br d, 1H, N*H*), 5.51 (d, 1H, O*H*), 3.98 (br s, 1H, cage C*H*). EIMS, centred on m/z 317. Accurate mass: calculated 317.3783, found: 317.3780. Cooling a petrol solution of **9** yielded diffraction-quality crystals.

[1-NO-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (IV). [1-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (250 mg, 1.13 mmol) in dry, degassed, diethyl ether (15 mL) was treated with *n*-BuLi (1.25 mmol) and the resulting yellow solution was added dropwise to an excess of nitrosyl chloride in dry, degassed, petrol (15 mL) at −78 °C to give a dark green solution.

Aqueous work-up. Quenching the reaction mixture with $NaHCO_3$ in water and work-up as described previously, including purification by silica column chromatography (petrol eluent) gave **IV** in 52.2% yield.

Non-aqueous work-up. Warming to room temperature and evaporation of the excess nitrosyl chloride and solvents gave a light blue residue. This was extracted into petrol and filtered. Removal of solvent from the filtrate and purification by column chromatography on florisil (petrol eluent) gave **IV** in 42.2% yield.

[1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-NO-1,2-*closo*-$C_2B_{10}H_{10}$] (10). A solution of 1,1′-bis(*o*-carborane) (180 mg, 0.63 mmol) was dissolved in dry, degassed, diethyl ether (15 mL) and treated with *n*-BuLi (0.7 mmol) at 0 °C. The cloudy white suspension was stirred at room temperature for 45 minutes then added dropwise to an excess of nitrosyl chloride in petrol (15 mL) at −78 °C. The resulting dark green solution was stirred for 60 minutes at low temperature. After warming to room temperature, the nitrosyl chloride and solvents were removed under reduced pressure to leave a light blue solid. This was extracted into petrol (20 mL) and filtered. The blue filtrate was reduced and purified by chromatography on florisil with petrol as the eluent. A single blue mobile band was collected which, following removal of solvent, gave **10** as a blue solid (10 mg, 5.0%). $C_4H_{21}B_{20}NO$ requires C 15.2, H 6.71, N 4.44. Found C 14.6, H 6.72, N 4.04%. $^{11}B\{^1H\}$ NMR, δ −1.6 (2B), −2.8 (2B), −8.9 (8B), −9.6 (4B), −12.7 (4B). ^1H NMR, δ 4.25 (br s, 1H, cage C*H*). IR, ν_{max} 2590 (BH), 1573 (NO) cm^{-1}. EIMS, envelope centred on *m*/*z* 315 (M^+). Accurate mass: calculated 315.3627, found: 315.3620. Diffraction-quality crystals of **10** were obtained from cooling a concentrated petrol solution.

[1-N(H)OH-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (11). [1-NO-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (40 mg, 0.16 mmol) was dissolved in THF (5 mL) and water (1 mL) was added. The blue solution began decolourising immediately and, after stirring overnight, had become very pale yellow. The solvent was removed and the residue was extracted into diethyl ether and filtered. Reduction of the volume of the filtrate and purification by TLC (DCM/petrol 1 : 1) gave **11** as a colourless band at R_f 0.30 (5 mg, 12.4%). $C_8H_{17}B_{10}NO$ requires C 38.2, H 6.82, N 5.57. Found C 38.3, H 6.43, N 5.31%. $^{11}B\{^1H\}$ NMR, δ −3.8 (1B), −5.7 (1B), −10.6 (4B), −12.1 + shoulder (4B). ^1H NMR, δ 7.70 (m, 2H, Ph), 7.44 (m, 3H, Ph), 5.70 (br d, 1H, N*H*), 5.18 (d, 1H, O*H*). EIMS, envelope centred on *m*/*z* 252 (M^+). Accurate mass: calculated 251.2312, found: 251.2314. Diffraction-quality crystals of **11** were grown by cooling a concentrated petrol solution.

[1-(1′-2′-D-1′,2′-*closo*-$C_2B_{10}H_{10}$)-2-D-1,2-*closo*-$C_2B_{10}H_{10}$] (12). 1,1′-Bis(*o*-carborane) (200 mg, 0.70 mmol) was dissolved in 15 mL of dry, degassed, diethyl ether and treated with *n*-BuLi (1.5 mmol) at 0 °C. The white suspension was stirred at room temperature for 1 hour before D_2O (1 mL, 55 mmol) was added and the mixture agitated before being allowed to settle. H_2O (15 mL) was added and the layers separated. The aqueous phase was extracted with diethyl ether (15 mL) and the combined organic phases were dried over $MgSO_4$, filtered and reduced *in vacuo* to give **12** as a white solid (186 mg, 92.1%). EIMS, envelope centred on *m*/*z* 288 (M^+). Accurate mass calculated: 288.3850. Found: 288.3850.

[1-(1′-2′-D-1′,2′-*closo*-$C_2B_{10}H_{10}$)-2-N(H)OH-1,2-*closo*-$C_2B_{10}H_{10}$] (13). Compound **12** (170 mg, 0.59 mmol) was treated with *n*-BuLi, nitrosylated and worked up exactly as for **9**. Purification of the crude mixture by thin layer chromatography (DCM/petrol 3 : 1) afforded **13** as a colourless band at R_f 0.51 (20 mg, 10.7%), together with minor contamination of **9**. $C_4H_{22}B_{20}DNO$ requires C 15.1, H 7.60, N 4.40. Found C 15.0, H 7.40, N 4.05%. $^{11}B\{^1H\}$ NMR, δ −1.9 (3B), −6.2 (1B), −9 to −13 (overlapping resonances with maxima at −9.5, −10.5, −12.8, 16B). ^1H NMR, δ 6.10 (br d, 1H, N*H*), 5.50 (d, 1H, O*H*). EIMS, envelope centred on *m*/*z* 318 (M^+). Accurate mass: calculated 318.3846, found 318.3852.

[1-($NOC_{10}H_{16}$)-1,2-*closo*-$C_2B_{10}H_{11}$] (14). [1-NO-1,2-*closo*-$C_2B_{10}H_{11}$] (40 mg, 0.23 mmol) was dissolved in DCM (5 mL) and α-terpinene (0.04 mL, 0.25 mmol) was added. The solution was stirred until it decolourised. Removal of solvent *in vacuo* and purification by preparative TLC (1 : 2 CH_2Cl_2/petrol) gave **14** as a white solid at R_f 0.74 (69 mg, 96.9%). $C_{12}H_{27}B_{10}NO$ requires C 46.6, H 8.79, N 4.53. Found C 46.6, H 8.99, N 4.43%. $^{11}B\{^1H\}$ NMR δ −4.0 (1B), −6.0 (1B), −10.7 (2B), −11.7 (4B), −14.1 (1B), −14.8 (1B). ^1H NMR δ 6.48 (d, 1H, C═C*H*), 6.24 (d, 1H, C═C*H*), 3.91 (br s, 1H, cage C*H*), 1.91 (m, 2H, CH_2), 1.76 (m, 1H, C*H*), 1.69 (s, 3H, CH_3), 1.30 (m, 2H, CH_2), 1.03 (d, 3H, CH_3), 1.00 (d, 3H, CH_3). EIMS, envelope centred on *m*/*z* 309 (M^+). Diffraction-quality crystals were grown by cooling a DCM/petrol solution.

[1-(NOC_6H_8)-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (15). [1-NO-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$] (224 mg, 0.90 mmol) was dissolved in 5 DCM (5 mL) and 1,3-cyclohexadiene (0.1 mL, 1.05 mmol) was added. The blue solution decolourised to pale yellow over 10 minutes stirring. The solvent was removed *in vacuo* to leave a pale yellow oil which crystallised overnight under a nitrogen atmosphere. The crude residue was adsorbed onto silica and washed with petrol to remove any unreacted starting material and then 1 : 1 DCM/petrol to extract the product. Removal of solvent from the eluent gave the **15** as a white solid (113 mg, 30.6%). $C_{14}H_{23}B_{10}NO$ requires C 51.0, H 7.04, N 4.25. Found C 50.8, H 7.11, N 4.08%. $^{11}B\{^1H\}$ NMR, δ −4.5 (1B), −5.2 (1B), −9.3 (1B), −11.2 (4B), −12.8 (3B). $^1H\{^{11}B\}$ NMR δ 7.64 (m, 2H, Ph), 7.41 (m, 1H, Ph), 7.35 (m, 2H, Ph), 6.58 (m, 1H, C═C*H*), 6.43 (m, 1H, C═C*H*), 4.41 (m, 1H, bridgehead C*H*), 4.07 (m, 1H, bridgehead C*H*), 1.75 (m, 1H, CH_2), 1.55 (m, 1H, CH_2), 1.27 (m, 1H, CH_2), 1.17 (m, 1H, CH_2). EIMS, envelope centred on *m*/*z* 329 (M^+).

[1,2-(NOC_6H_8)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$] (16). [1,2-*closo*-$C_2B_{10}H_{12}$] (100 mg, 0.69 mmol) was dissolved in dry, degassed, diethyl ether (15 mL) and treated with *n*-BuLi (1.5 mmol) at 0 °C. The white suspension was stirred for 20 minutes at room temperature then added dropwise to an excess of nitrosyl chloride in dry, degassed, petrol (15 mL) at −78 °C. The resulting dark-green solution was stirred for 15 minutes at −78 °C and warmed to room temperature before both the excess nitrosyl chloride and solvents were removed *in vacuo*. The residue was extracted into DCM and filtered. The blue filtrate was treated with 1,3-cyclohexadiene (0.25 mL, 3.7 mmol) and stirred for 1 hour. The yellow-brown solution was reduced in volume and purified by preparative TLC (silica, 1 : 1 DCM/petrol eluent) to give the desired product as two diastereoisomers **16a** (*meso*) at R_f 0.44 (16 mg, 6.4%) and **16b** (racemic) at R_f 0.59 (15 mg, 6.0%), both off-white solids.

16a: $C_{14}H_{26}B_{10}N_2O_2$ requires C 46.4, H 7.23, N 7.73. Found C 46.3, H 7.49, N 8.02%. $^{11}B\{^1H\}$ NMR δ −7.0 (2B), −10.8 (2B), −13.6 (4B), −16.8 (2B). ^1H NMR δ 6.63 (m, 2H, C═C*H*), 6.51 (m, 2H, C═C*H*), 4.57 (m, 2H, bridgehead C*H*), 4.19 (m, 2H,

bridgehead C*H*), 2.24 (m, 2H, CH_2), 2.14 (m, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.34 (m, 2H, CH_2). EIMS, envelope centred on *m*/*z* 362 (M^+).

16b: $C_{14}H_{26}B_{10}N_2O_2$ requires C 46.4, H 7.23, N 7.73. Found C 46.9, H 7.48, N 7.41%. $^{11}B\{^1H\}$ NMR δ −7.1 (2B), −12.3 + shoulder (4B), −14.2 (1B), −15.2 (3B). ^1H NMR δ 6.62 (m, 2H, C═C*H*), 6.50 (m, 2H, C═C*H*), 4.52 (m, 2H, bridgehead C*H*), 4.25 (m, 2H, bridgehead C*H*), 2.20 (m, 2H, CH_2), 2.13 (m, 2H, CH_2), 1.50 (m, 2H, CH_2), 1.37 (m, 2H, CH_2). EIMS, envelope centred on *m*/*z* 362 (M^+).

Diffraction-quality crystals of **16a** and **16b** were grown by slow diffusion of petrol and DCM solutions at −30 °C.

[1-{1′-2′-(NOC$_6$H$_8$)-1′,2′-*closo*-C$_2$B$_{10}$H$_{10}$}-2-(NOC$_6$H$_8$)-1,2-*closo*-C$_2$B$_{10}$H$_{10}$] (17) and [1-(1′-1′,2′-*closo*-C$_2$B$_{10}$H$_{11}$)-2-(NOC$_6$H$_8$)-1,2-*closo*-C$_2$B$_{10}$H$_{10}$] (18). 1,1′-Bis(*o*-carborane) (100 mg, 0.35 mmol) was dissolved in dry, degassed, ether (15 mL) and treated with *n*-BuLi (0.76 mmol) at 0 °C. Reaction with nitrosyl chloride and 1,3-cyclohexadiene analogously to **16a**/**b**, and work-up involving preparative TLC (silica, 1 : 2 DCM/petrol eluent) gave **17** (R_f 0.66) as a yellow solid (20 mg, 11.3%) together with a small quantity of **18** (R_f 0.84) as a pale yellow solid.

17: $^{11}B\{^1H\}$ NMR δ −1 to −12 (overlapping resonances with maxima at −1.09, −6.56, −9.95, −11.77, 20B). ^1H NMR δ 6.63

Table 2 Crystallographic data

	2	5	6	8	9	10
Formula	$C_4H_{15}B_{10}NO_2$	$C_8H_{25}B_{10}NOSi$	$C_8H_{15}B_{10}NO$	$C_4H_{20}B_{20}N_2O_2$	$C_4H_{23}B_{20}NO$	$C_4H_{21}B_{20}NO$
M	217.27	287.48	249.31	344.42	317.43	315.42
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Tetragonal	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	*Pbca*	$P4_2/n$	$P2_1/n$	$P2_1/n$
a/Å	23.339(2)	7.0341(7)	8.009(2)	16.3052(5)	7.2022(8)	7.2275(19)
b/Å	7.5382(8)	19.1795(18)	15.970(4)	16.3052(5)	9.5053(10)	9.678(3)
c/Å	14.5428(17)	12.5279(11)	22.139(6)	6.9144(3)	12.9926(15)	12.993(4)
α (°)	90	90	90	90	90	90
β (°)	106.471(6)	98.544(4)	90	90	97.350(7)	93.226(9)
γ (°)	90	90	90	90	90	90
U/Å^3	2453.6(5)	1671.4(3)	2831.7(13)	1838.26(14)	882.15(17)	907.4(4)
Z, *Z*′	8, 2	4, 1	8, 1	4, 0.5	2, 0.5	2, 0.5
F(000)/e	896	608	1024	696	324	320
D_{calc}/Mg m^{-3}	1.176	1.142	1.170	1.244	1.195	1.154
μ(Mo-K$_\alpha$)/mm^{-1}	0.067	0.128	0.062	0.064	0.055	0.054
θ_{max} (°)	25.78	33.21	22.07	29.61	29.66	31.29
Data measured	61 791	44 494	21 512	37 192	17 862	21 179
Unique data, *n*	4605	6302	3783	2593	2481	2950
R_{int}	0.0832	0.0411	0.1327	0.0433	0.0512	0.0432
Obs. data ($I > 2\sigma(I)$)	2855	5279	1858	2457	2063	2353
R, wR_2 (obs. data)	0.0927, 0.1910	0.0341, 0.0878	0.1302, 0.3038	0.0438, 0.1137	0.0532, 0.1271	0.0536, 0.1483
S (all data)	1.091	1.042	1.105	1.145	1.107	1.147
Variables	370	225	202	177	167	160
E_{max}, E_{min}/e Å^{-3}	0.25, −0.31	0.52, −0.28	0.28, −0.21	0.33, −0.21	0.24, −0.19	0.28, −0.39

	13	14	16a	16b	17	18
Formula	$C_8H_{17}B_{10}NO$	$C_{12}H_{27}B_{10}NO$	$C_{14}H_{26}B_{10}N_2O_2$	$C_{14}H_{26}B_{10}N_2O_2$	$C_{16}H_{36}B_{20}N_2O_2$	$C_{10}H_{29}B_{20}NO$
M	251.32	309.44	362.47	362.47	504.67	395.54
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pnma*	*C*2/*c*	$P2_1/n$	$P2_1/n$
a/Å	10.4155(10)	11.9847(18)	11.409(4)	17.316(5)	10.1193(7)	9.5006(11)
b/Å	11.0414(10)	16.213(3)	16.464(5)	10.390(3)	10.6700(7)	12.0225(15)
c/Å	13.1547(12)	20.179(3)	10.356(3)	11.385(4)	12.4753(8)	19.411(2)
α (°)	67.377(3)	87.624(6)	90	90	90	90
β (°)	79.186(3)	88.802(5)	90	110.266(19)	99.648(3)	93.031(6)
γ (°)	89.541(3)	71.721(5)	90	90	90	90
U/Å^3	1368.2(2)	3719.8(10)	1945.1(10)	1921.6(10)	1327.94(15)	2214.1(4)
Z, *Z*′	4, 2	8, 4	4, 0.5	4, 0.5	2, 0.5	4, 1
F(000)/e	520	1312	760	760	524	816
D_{calc}/Mg m^{-3}	1.220	1.105	1.238	1.253	1.262	1.187
μ(Mo-K$_\alpha$)/mm^{-1}	0.065	0.059	0.071	0.072	0.067	0.057
θ_{max} (°)	27.96	26.46	28.44	30.93	27.16	24.80
Data measured	24 224	30 882	29 025	22 471	19 862	26 104
Unique data, *n*	6469	14 855	2531	3025	2902	3762
R_{int}	0.0241	0.0377	0.0713	0.0551	0.0503	0.1410
Obs. data ($I > 2\sigma(I)$)	5427	10 171	1848	2275	2254	2065
R, wR_2 (obs. data)	0.0382, 0.1012	0.0483, 0.1033	0.0436, 0.0984	0.0426, 0.1171	0.0570, 0.1325	0.0900, 0.2205
S (all data)	0.931	1.024	1.039	1.068	1.026	1.054
Variables	433	1009	150	142	257	353
E_{max}, E_{min}/e Å^{-3}	0.35, −0.39	0.21, −0.25	0.31, −0.25	0.38, −0.28	0.48, −0.48	0.43, −0.40

(m, 2H, C=C*H*), 6.50 (m, 2H, C=C*H*), 4.63 (m, 2H, bridgehead C*H*), 4.38 (m, 2H, bridgehead C*H*), 2.30 (m, 2H, CH_2), 2.14 (m, 2H, CH_2), 1.41 (m, 4H, CH_2). EIMS, envelope centred on *m*/*z* 504/505 (M^+).

18: $^{11}B\{^1H\}$ NMR δ −2.02 (2B), −5.97 (1B), −7 to −13 (overlapping resonances with maxima at −9.99, −12.94, 17B). ^1H NMR δ 6.65 (m, 1H, C=C*H*), 6.50 (m, 1H, C=C*H*), 4.66 (m, 1H, bridgehead C*H*), 4.34 (m, 1H, bridgehead C*H*), 4.24 (br s, 1H, cage C*H*), 2.29 (m, 1H, CH_2), 2.07 (m, 1H, CH_2), 1.54 (m, 1H, CH_2), 1.43 (m, 1H, CH_2). EIMS, envelope centred on *m*/*z* 395 (M^+).

Diffraction-quality crystals of **17** were grown by slow evaporation of a DCM solution and crystals of **18** were grown from petrol.

Crystallographic studies

Conditions under which single crystals were grown are given above. Compounds **2** and **6** are liquids at room temperature, so single crystals of these species were grown *in situ* in a 0.3 mm glass capillary tube on the diffractometer.[24] Variable and carefully controlled cooling was supplied by an Oxford Cryosystems series 700 Cryostream. The liquid sample (*ca.* 1.5 cm) was carefully introduced into the capillary to minimise air gaps and the capillary mounted in a brass pin and sealed as close to the meniscus as possible so that the capillary tube would not collide with the Cryostream during data collection. The capillary has to be sufficiently long so that the meniscus could be moved in and out of the cold stream using the height adjustment on the goniometer head. In particular it is necessary that the liquid level can be moved far enough beyond the cold stream so that the uppermost layer melts providing a liquid–solid interface where crystal growth could take place. With the goniometer at χ = 90° (capillary horizontal) the sample was cooled at 250 K h^{-1} to determine the approximate freezing point, warmed to *ca.* 20 °C above the freezing point then cooled slowly at 30 K h^{-1}. Evidence of crystallinity was checked by taking *X*-ray images as well as observing the sample with the video microscope. Successive warming and cooling cycles took place close to the melting point until a diffraction pattern suitable for data collection was obtained. Finally the samples were cooled slowly to 150 K for data collection.

All other samples (crystalline at room temperature) were mounted in inert oil on a cryoloop and cooled to 100 K by the Cryostream. Unit cell and intensity data were collected on the diffractometer (Bruker X8 APEXII) using Mo-K_α *X*-radiation. Indexing, data collection and absorption correction were performed using the APEXII suite of programs.[25] Using OLEX2[26] structures were solved with the OLEX2.solve programme[27] and refined by full-matrix least-squares (SHELXL).[28] Compound **2** was refined as a racemic twin using HKLF 4. The crystal of **6** was not single and refined as three components with contributions 0.62 : 0.28 : 0.09 (HKLF 5). Cage C atoms not identified by the fact that they were bound to a substituent (compounds **10**, **14** and **18**) were distinguished from B atoms by application of the Vertex-Centroid Distance Method[29] and the Boron-H Distance Method,[30] with both methods affording excellent agreement.

In compound **8** the crystallographically-unique O atom is disordered over four sites and in **6** the C1N1O1 and B10H10 units are mutually disordered. In compounds **9** and **10** the imposed C_i symmetry requires the NO group (**10**) and the N(H)OH group (**9**) to be disordered between vertices C2 and C2′ and the NOC_6H_8 substituent in compound **17** suffers from internal disorder between the two possible enantiomers. All other structures are fully ordered.

For all structures except for that of compound **6** (for which B–H was fixed at 1.12 Å) H atoms bound to cage B or C atoms were allowed to refine positionally, although in the disordered **9** and **10** B2–H2 was restrained to 1.10(1) Å. In compounds with hydroxylamine groups (**9** and **11**) the NH and OH H atoms were also allowed positional refinement. Other H atoms were constrained to idealised geometries; C_{phenyl}–H = C_{ene}–H = 0.95 Å, C_{methyl}–H = 0.98 Å, $C_{methylene}$–H = 0.99 Å, $C_{tertiary}$–H = 1.00 Å. All H displacement parameters, U_{iso}, were constrained to be 1.2 × U_{eq} (bound B, C, N or O) except Me H atoms [U_{iso}(H) = 1.5 × U_{eq} C(Me)]. Table 2 contains further experimental details.

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References

1 J. M. Kauffman, J. Green, M. S. Cohen, M. M. Fein and E. L. Cottrill, *J. Am. Chem. Soc.*, 1964, **86**, 4210.
2 L. I. Zakharkin, V. N. Kalinin and G. G. Zhigareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 912.
3 L. I. Zakharkin and G. G. Zhigareva, *Zh. Obshch. Khim.*, 1971, **41**, 712.
4 L. I. Zakharkin and G. G. Zhigareva, *Zh. Obshch. Khim.*, 1975, **45**, 1293.
5 M. A. Fox, J. A. H. MacBride, R. J. Peace, W. Clegg, M. R. J. Elsegood and K. Wade, *Polyhedron*, 2009, **28**, 789.
6 C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry*, Pearson Education Ltd, Harlow, Essex, UK, 3rd edn, 2008, p. 653.
7 J. Mason, D. M. P. Mingos, G. Sherman and R. W. M. Wardle, *J. Chem. Soc., Chem. Commun.*, 1984, 1223.
8 (*a*) K. Wade, *J. Chem. Soc. D*, 1971, 792; (*b*) D. M. P. Mingos, *Nature (London) Phys. Sci.*, 1972, 99.
9 (*a*) L. K. Bell, D. M. P. Mingos, D. G. Tew, L. F. Larkworthy, B. Sandell, D. C. Povey and J. Mason, *J. Chem. Soc., Chem.*

Commun., 1983, 125; (*b*) L. K. Bell, J. Mason, D. M. P. Mingos and D. G. Tew, *Inorg. Chem.*, 1983, **22**, 3497.

10 (*a*) S. Ren and Z. Xie, *Organometallics*, 2008, **27**, 5167; (*b*) D. Ellis, D. McKay, S. A. Macgregor, G. M. Rosair and A. J. Welch, *Angew. Chem., Int. Ed.*, 2010, **49**, 4943; (*c*) D. Ellis, G. M. Rosair and A. J. Welch, *Chem. Commun.*, 2010, **46**, 7394; (*d*) W. Y. Man, S. Zlatogorsky, H. Tricas, D. Ellis, G. M. Rosair and A. J. Welch, *Angew. Chem., Int. Ed.*, 2014, **53**, 12222; (*e*) G. Thiripuranathar, W. Y. Man, C. Palmero, A. P. Y. Chan, B. T. Leube, D. Ellis, D. McKay, S. A. Macgregor, L. Jourdan, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2015, **44**, 5628; (*f*) Z.-J. Yao, Y.-Y. Zhang and G.-X. Jin, *J. Organomet. Chem.*, 2015, **798**, 274; (*g*) M. J. Martin, W. Y. Man, G. M. Rosair and A. J. Welch, *J. Organomet. Chem.*, 2015, **798**, 36; (*h*) L. E. Riley, A. P. Y. Chan, J. Taylor, W. Y. Man, D. Ellis, G. M. Rosair, A. J. Welch and I. B. Sivaev, *Dalton Trans.*, 2016, **45**, 1127; (*i*) G. S. Kazakov, I. B. Sivaev, K. Yu. Suponitsky, A. D. Kirilin, V. I. Bregadze and A. J. Welch, *J. Organomet. Chem.*, 2016, **805**, 1.

11 W. Y. Man, G. M. Rosair and A. J. Welch, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2014, **70**, 462.

12 *E.g.* H. Awano, T. Hirabayashi and W. Tagaki, *Tetrahedron. Lett.*, 1984, **25**, 2005.

13 B. G. Gowenlock and G. B. Richter-Addo, *Chem. Soc. Rev.*, 2005, **34**, 797; and references therein.

14 *E.g.* B. Yang and M. J. Miller, *Org. Lett.*, 2010, **12**, 392.

15 B. W. Hutton, F. MacIntosh, D. Ellis, F. Herisse, S. A. Macgregor, D. McKay, V. Petrie-Armstrong, G. M. Rosair, D. S. Perekalin, H. Tricas and A. J. Welch, *Chem. Commun.*, 2008, 5345.

16 M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz and M. S. Cohen, *Inorg. Chem.*, 1963, **2**, 1115.

17 K. F. Shaw and A. J. Welch, *Polyhedron*, 1992, **11**, 157.

18 I. M. Wyzlic, W. Tjarks, A. H. Soloway, D. J. Perkins, M. Burgos and K. P. O'Reilley, *Inorg. Chem.*, 1996, **35**, 4541.

19 J. Cai, H. Nemoto, H. Nakamura, B. Singaram and Y. Yamamoto, *Chem. Lett.*, 1996, 791.

20 W. Jiang, I. T. Chizhevsky, M. D. Mortimer, W. Chen, C. B. Knobler, S. E. Johnson, F. A. Gomez and M. F. Hawthorne, *Inorg. Chem.*, 1996, **35**, 5417.

21 R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride and K. Wade, *J. Organomet. Chem.*, 1993, **462**, 19.

22 X. Yang, W. Jiang, C. B. Knobler, M. D. Mortimer and M. F. Hawthorne, *Inorg. Chim. Acta*, 1995, **240**, 371.

23 J. R. Morton and H. W. Wilcox, *Inorg. Synth.*, 1953, **4**, 48.

24 *E.g.* J. E. Davies and A. D. Bond, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2001, **57**, o947.

25 *Bruker AXS APEX2, version 2009-5*, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.

26 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

27 L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2015, **71**, 59.

28 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **C71**, 3.

29 A. McAnaw, G. Scott, L. Elrick, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2013, **42**, 645.

30 A. McAnaw, M. E. Lopez, D. Ellis, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2014, **43**, 5095.