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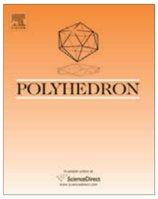

New synthetic and structural studies on nitroso-*ortho*-carboranes $RCB_{10}H_{10}CNO$ and bis(*ortho*-carboranyl)amines $(RCB_{10}H_{10}C)_2NH$ (R = Ph or Me)

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ABSTRACT

Improved procedures are reported for the preparation of nitroso-carboranes $RCb^\circ NO$ ($Cb^\circ = 1,2\text{-}C_2B_{10}H_{10}$; R = Ph, Me at cage carbon C2) in 44–77% yield, and of dicarboranylamines $(RCb^\circ)_2NH$ in 55–65% yield by reactions between the lithio-carboranes, $RCb^\circ Li$ and nitrosyl chloride, NOCl, in cold mixtures of diethyl ether and either pentane (for $RCb^\circ NO$) or dimethoxyethane (for $(RCb^\circ)_2NH$). Deprotonation of the amines by KO^tBu in toluene in the presence of 18-crown-6, $(CH_2CH_2O)_6$, affords the salts $[K(18\text{-crown-}6)]^+[(RCb^\circ)_2N]^-$. X-ray crystal structures of $PhCb^\circ NO$, $(PhCb^\circ)_2NH$, $(MeCb^\circ)_2NH$ and $[K(18\text{-crown-}6)]^+[(PhCb^\circ)_2N]^-$ are described, and the bonding implications of their cage C…C distances (1.68, 1.80, 1.75 and 1.99 Å, respectively) are discussed. These species provide further striking examples of the remarkable capacity of the *ortho*-carborane cage to act as a sensitive indicator of the π-donor characteristics of ligands attached to its cage carbon atoms.

1. Introduction

This paper reports a new study of reactions between lithio-carboranes, $RCb^\circ Li$ ($Cb^\circ = 1,2\text{-}C_2B_{10}H_{10}$, *ortho*-carboranyl; R = Ph, Me at cage carbon C2), and nitrosyl chloride, NOCl, carried out to optimise the syntheses and determine the structures of two important categories of *ortho*-carborane derivatives containing *exo*-C–N bonds, *viz* nitroso-carboranes $RCb^\circ NO$ and dicarboranylamines, $(RCb^\circ)_2NH$ (Scheme 1). Earlier studies [1–3] had already shown such products to be accessible by $RCb^\circ Li$/NOCl reactions, but had left unclear what preparative procedures (temperature, solvent, etc.) were best suited to each product, and had given no structural information on either type of product. Our interest in them, and in salts of amide anions $[(RCb^\circ)_2N]^-$ preparable by deprotonation of the amines $(RCb^\circ)_2NH$, concerned their use to explore further the remarkable sensitivity of the *ortho*-carborane cage, notably its C–C bond length, to the π-donor characteristics of C-attached ligands X in derivatives $RCb^\circ X$ or $XCb^\circ X$ [4–9].

Our experimental and computational studies [9] on compounds $PhCb^\circ X$ (X = H, F, OH or NH_2) had shown the cage C1–C2 bond lengths to increase (in that sequence) with the π-donor capacity of X, from 1.66 Å in $PhCb^\circ H$ to 1.77 Å in $PhCb^\circ NH_2$; significantly longer C1–C2 distances were found in anionic systems such as $PhCb^\circ O^-$ (2.00 Å) or $PhCb^\circ NH^-$ (2.30 Å) with recognisably stronger π-donors (Fig. 1). These findings have been supplemented by computational studies on $XCb^\circ X$ systems by Oliva et al. [10]. Related studies by Teixidor and Viñas on thiolato and phosphino derivatives of *ortho*-carboranes also showed similar C1–C2 distance lengthening attributed to *exo*-C–S or C–P π-bonding as well as steric effects [11]. The cage C–C bond lengthening caused by π-donors is readily intelligible if the *p*-AO involved in *exo*-C=X π-bonding is that which is also primarily responsible for cage C1–C2 σ-bonding (AO = atomic orbital, Fig. 1).

Because amides NR′R″ are expected to feature as π-donors, we considered that experimental evidence of the structures of species $RCb^\circ NO$, $(RCb^\circ)_2NH$ and $(RCb^\circ)_2N^-$, in particular their C1–C2 and C1–N distances and C1–N=O or C1–N–C1′ angles, would reveal whether the NO, $NHCb^\circ R$ and $NCb^\circ R^-$ ligands employed available ‘lone pair’ electrons for dative π-bonding, and shed further useful light on the sensitivity of the *ortho*-carborane cage to π-donor substituents.

Although first reported over 40 years ago, carboranes with C–nitrogen substituents have received only sporadic or highly selective attention. Isocyanates RCbNCO (Cb = 1,2-, 1,7- or 1,12-$C_2B_{10}H_{10}$), obtainable from acid chlorides RCbCOCl and lithium azide LiN_3 [12], have been quite widely exploited as intermediates from which to prepare various organo-nitrogen carboranes as suitable candidates for use in Boron Neutron Capture Therapy (BNCT)

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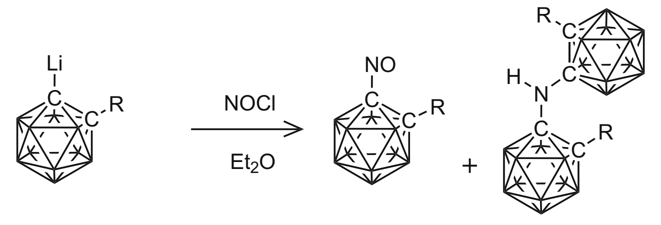

RCb°Li RCb°NO $(RCb^{\circ})_2NH$

R = Me	Pentane	-40°C	69%	11%
	Pentane	-117°C	77%	22%
	DME	-40°C	0%	63%
	DME	-78°C	10%	55%
R = Ph	Pentane	-40°C	61%	10%
	Pentane	-117°C	42%	0%
	DME	-40°C	0%	55%
	DME	-78°C	5%	56%

Scheme 1.

[13], and di-isocyanates $OCNCb^mNCO$ ($Cb^m = 1,7\text{-}C_2B_{10}H_{10}$) have been converted into diamines $H_2NCb^mNH_2$ for use in polymers [14]. The nitrosyl chloride–lithio-carborane reaction by contrast appears to have been studied by only two research groups, and not at all during the past thirty years, despite the range of C–N carborane derivatives in principle accessible *via* nitroso-carboranes [1,3]. Unfortunately the early reports by Kauffman et al. and Zakharkin et al. gave conflicting yields of nitroso derivatives (25–80%) and limited experimental details.

2. Results and discussion

2.1. Synthetic aspects

In our studies of low-temperature reactions between the lithio-carboranes, MeCb°Li or PhCb°Li, and nitrosyl chloride in equivalent amounts (Scheme 1), we used 1:1 mixtures of diethyl ether and pentane, or of diethyl ether and dimethoxyethane (DME), as solvent. The products obtained were broadly in line with those reported by Zakharkin et al. [2,3]. In diethyl ether and pentane, the nitroso-carboranes RCb°NO were the main product (42–77%), though some dicarboranylamine $(RCb^{\circ})_2NH$ could normally also be isolated (0–22%). However, when diethyl ether and DME were used as a solvent mix, the secondary amines $(RCb^{\circ})_2NH$ were the main products (55–63%), yields of nitroso-carboranes being 10% or less. Although overall yields varied with the temperature at which the reaction was carried out, the product balance did not. Our work-up procedure involved treatment with aqueous potassium hydrogen carbonate followed by sublimation to obtain the blue nitroso compounds RCb°NO. The strong NO stretching absorptions at *ca.* 1565 cm^{-1} in the IR spectra of these compounds show that their CNO units are bent at nitrogen [15], with the nitrosyl groups acting as one-electron ligands to the carborane cages. The colourless secondary amines $(RCb^{\circ})_2NH$ were recovered after treatment of the unsublimed material with methanol (for details, see Section 4).

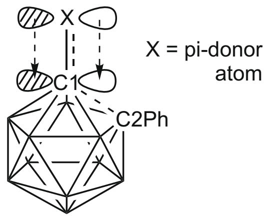

Fig. 1. Orbitals involved in the lengthening of the C1–C2 distance of PhCb°X.

We infer that the nitroso-carboranes are formed in the first stage of the reaction (Eq. (1)) and that the secondary amines result from the reaction of the nitroso-carborane with a second mole of lithio-carborane, despite competition from excess nitrosyl chloride (Eq. (2));

$$RCb^{\circ}Li + NOCl \rightarrow RCb^{\circ}NO + LiCl \tag{1}$$

$$RCb^{\circ}NO + RCb^{\circ}Li \rightarrow (RCb^{\circ})_2NOLi \tag{2}$$

It is not clear, however, how the lithio-hydroxylamine $(RCb^{\circ})_2NOLi$ is then reduced to the amine, $(RCb^{\circ})_2NH$. It may be significant that the bidentate coordinating solvent, 1,2-dimethoxyethane, $MeOCH_2CH_2OMe$, favours reaction (2). There are parallels here with aromatic ring chemistry, in that both aryl nitroso compounds ArNO and diarylamines Ar_2NH are accessible from ArLi or ArMgX and NOCl [16].

Our early preparations of anionic species $[RCb^{\circ}X]^-$ from neutral parent species used proton sponge, PS, $C_{10}H_6(NMe_2)_2$, to deprotonate the hydroxycarborane PhCb°OH and the thiol PhCb°SH [6,7]. We therefore attempted to deprotonate the amine $(PhCb^{\circ})_2NH$ in toluene by proton sponge. This failed; the amine crystallised unchanged from these solutions. However, addition of a solution of potassium *t*-butoxide and an equimolar proportion of 18-crown-6 deposited pale yellow crystals, with 77% yield of the salt $[K(18\text{-crown-}6)]^+[(PhCb^{\circ})_2N]^-$. This pale yellow salt is, surprisingly, stable to air and moisture, though the parent amine, $(PhCb^{\circ})_2NH$ is regenerated by ethanoic acid. In previous studies we were unable to obtain the amide $PhCb^{\circ}NH^-$ by deprotonation of the amine $PhCb^{\circ}NH_2$; cage degradation occurred instead [9]. Although the yellow salt appears to crystallise well from 1,2-dichlorobenzene, single crystals suitable for X-ray diffraction were grown from a solution in diethyleneglycol dimethyl ether, $(MeOC_2H_4)_2O$, into which cyclohexane diffused slowly from an upper layer. The colourless salt $[K(18\text{-crown-}6)]^+[(MeCb^{\circ})_2N]^-$ was similarly formed in 86% yield from a solution of potassium *t*-butoxide and an equimolar proportion of 18-crown-6 with amine $(MeCb^{\circ})_2NH$. The contrast in the formation and stability between the anions $PhCb^{\circ}NH^-$ and $(RCb^{\circ})_2N^-$ suggests that the $PhCb^{\circ}NH^-$ anion is capable of a nucleophilic attack on a second carborane molecule leading to cage degradation, whereas the two bulky cages in the anion $(RCb^{\circ})_2N^-$ inhibit the capacity of this amide to attack a second carborane molecule.

2.2. Structural aspects

In crystalline PhCb°NO (Fig. 2), the N=O bond (length 1.182(2) Å) lies roughly in the C(2)–C(1)–N(1) plane. The phenyl ring is perpendicular to this plane. The C(1)–N(1) bond length of 1.490(2) Å is consistent with negligible *exo*-C–N π-bonding, as is the C(1)–C(2) cluster bond length of 1.677(2) Å, virtually identical to that in the computed geometry of PhCb°F (1.674 Å), and slightly different from that in the computed geometry of PhCb°H (1.659 Å) with a similarly orientated phenyl group [9]. Reported X-ray-derived geometries of PhCb°H with the orientation of the phenyl group roughly coplanar with the H(1)–C(1)–C(2) plane reveal shorter C(1)–C(2) bond distances of 1.643(2) and 1.649(2) Å [5,17–19]. The C(1)–N=O bond angle of 113.0(2)° is midway between typical trigonal planar and tetrahedral bond angles. As a comparison nitrosobenzene, PhNO, has N=O and C–N bond lengths of 1.241(7) and 1.421(7) Å, respectively, and its C–N=O bond angle is 114.8(5)° [20]. All of these features imply that the NO substitu-

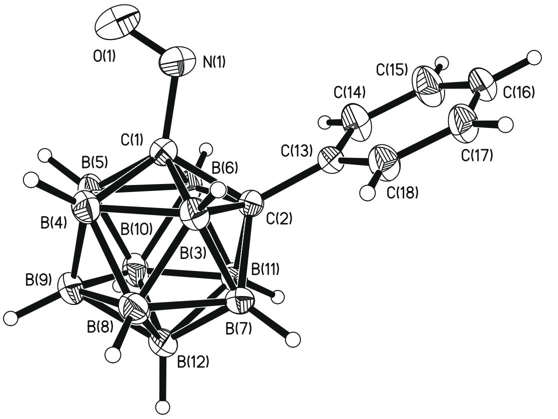

Fig. 2. Molecular structure of PhCb°NO (**1**). Selected bond lengths (Å) and angles (°), N(1)–O(1) 1.182(2), C(2)–C(13) 1.510(2), C(2)–C(1)–N(1) 112.1(2), C(13)–C(2)–C(1) 120.3(2). Displacement ellipsoids are drawn at the 50% probability level.

ent is acting as a one-electron ligand to the cage even though its orientation aligns the nitrogen lone pair sp^2 AO in the same plane as (though divergent from) the C1 p–AO involved in C1–C2 σ-bonding.

Table 1
Selected bond lengths (Å) and angles (°) for $(MeCb^{\circ})_2NH$, $(PhCb^{\circ})_2NH$ and $[(PhCb^{\circ})_2N]^-$ (averages for equivalent bonds).

	$(MeCb^{\circ})_2NH$ (**2**)	$(PhCb^{\circ})_2NH$ (**3**)	$(PhCb^{\circ})_2N^-$ (**4**)
C(1)–N(1)	1.410(4)	1.405(2)	1.350(4)
C(1)–C(2)	1.750(4)	1.798(3)	1.987(3)
C(2)–C(13)	1.512(4)	1.504(3)	1.491(4)
C(1)–N(1)–C(1′)	131.1(2)	132.0(2)	127.0(2)
N(14)–C(1)–C(2)	117.2(2)	117.09(14)	118.8(2)
C(13)–C(2)–C(1)	117.0(2)	117.94(14)	116.7(2)

The molecular structures of the secondary amines, $(MeCb^{\circ})_2NH$ and $(PhCb^{\circ})_2NH$, and of the anion $(PhCb^{\circ})_2N^-$ of the salt $[K(18\text{-crown-}6)]^+[(PhCb^{\circ})_2N]^- \cdot 0.5(MeOC_2H_4)_2O$, are shown in Fig. 3. Selected bond distances and angles are given in Table 1. There are small differences between the lengths of corresponding bonds in the two cages in each compound that are not regarded as significant; average values for equivalent bonds are used in the discussion where appropriate. The conformations of the two amines and amide anion in their respective crystal structures are very similar, and the trigonal nitrogen atoms of the two amines have a planar configuration. Fig. 4 shows the environment surrounding the amide anion in the salt, including the cation and diglyme molecule.

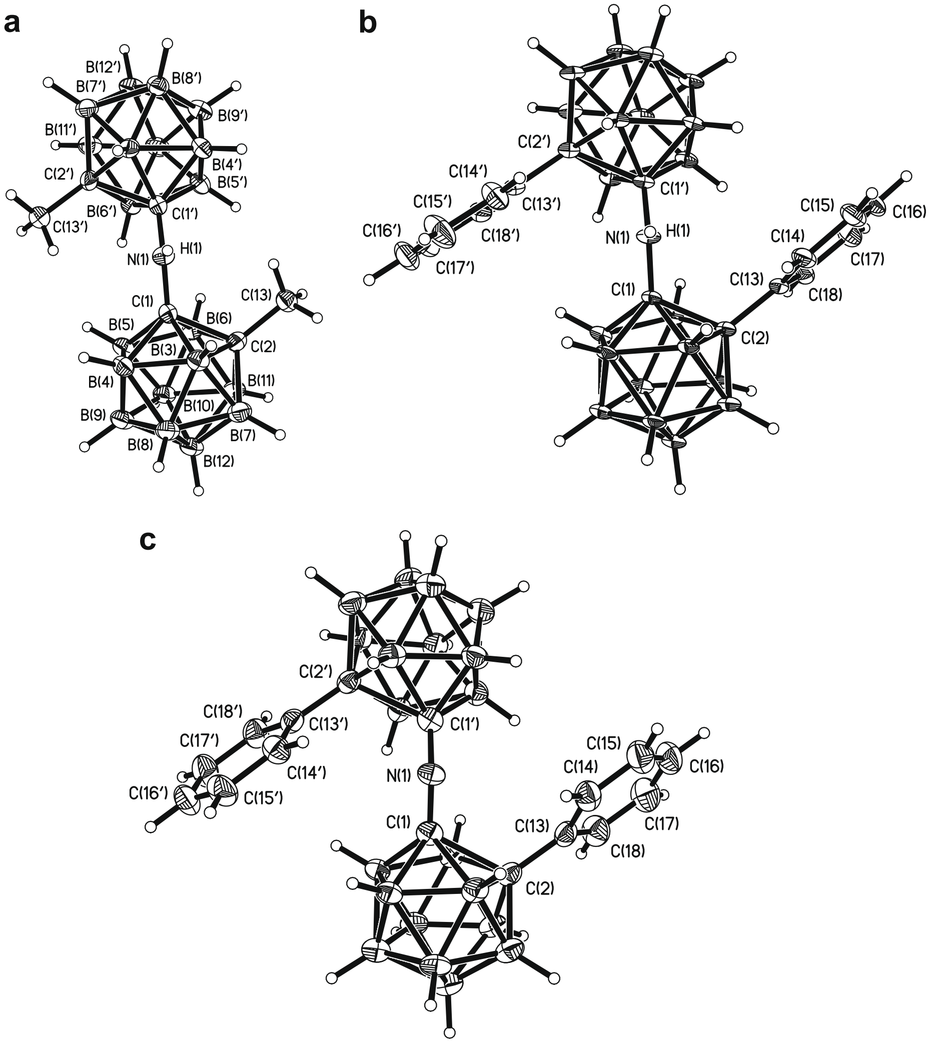

Fig. 3. Molecular structures of the dicarboranyl amines, (a) $(MeCb^{\circ})_2NH$ (**2**) and (b) $(PhCb^{\circ})_2NH$ (**3**), and (c) the $(PhCb^{\circ})_2N^-$ anion of the salt $[K(18\text{-crown-}6)][(PhCb^{\circ})_2N] \cdot 0.5(MeOC_2H_4)_2O$ (**4**).

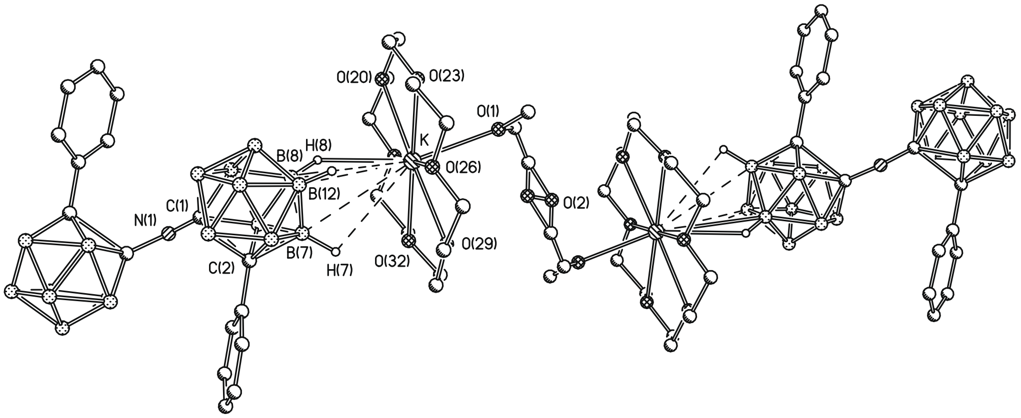

Fig. 4. Crystal structure of the salt $[K(18\text{-crown-}6)][(PhCb^{\circ})_2N]\cdot 0.5(MeOC_2H_4)_2O$ (**4**) showing interactions between the cation and anion and between cation and solvent. Selected distances in Å, B(8)…K 3.53, B(7)…K 3.85, B(12)…K 3.74, O(1)…K 2.756(4). Both disorder components are shown for the solvent molecule. H atoms have been omitted except for those involved in the cation-anion interactions.

The potassium cation effectively caps a triangular face of one of the two cages (a face remote from the two cage carbon atoms) in a manner common in potassium-18-crown-6 salts of carborane anions [21]. The diglyme molecule, with its central oxygen atom O(2) disordered over two sites in the crystal structure, is coordinated through its outer oxygen atoms to two cations.

The structures of the amines and amide anion differ from that of the nitroso derivative $PhCb^{\circ}NO$ in showing clear evidence, in their conformations, bond distances and angles, of significant *exo*-N=C dative π-bonding from one nitrogen *p*-AO to both cages, which show concomitant distortion (C(1)–C(2) bond lengthening). The features that lead us to this conclusion are as follows (see Table 1).

The CNC angle in the phenyl amine $(PhCb^{\circ})_2NH$ is 132° and falls to 127° in the amide anion $[(PhCb^{\circ})_2N]^-$, showing that the nitrogen atom remains sp^2 hybridised on deprotonation, the 'lone pair' having greater repulsive effect than the NH bond which it replaces. The CNC angles are perhaps slightly affected by the repulsion between the two cages since the closest H⋯H separation between the cages is *ca.* 2.47 Å, longer than corresponding distances of 2.27 and 2.25 found in the related biscarboranyl sulfide, $(PhCb^{\circ})_2S$, and sulfoxide, $(PhCb^{\circ})_2SO$, respectively [8]. The CNC angle in diphenylamine Ph_2NH is 129° and falls to 121° in the Ph_2N^- anion [22,23].

In all three compounds the radial planes of the C–C bonds of both cages, *i.e.* their CCN planes, are roughly perpendicular to the trigonal nitrogen CNC plane so that the nitrogen *p*-orbital containing an electron pair is aligned with the cage C–C bonds. The closely similar conformation of the three compounds effectively precludes the possibility that this conformation is the fortuitous result of crystal packing forces, since these are unlikely to have the same effect in the crystal structures of the amines, still less in that of the ionic amide with large counter-ions.

We conclude that both carborane cages in each amine $(RCb^{\circ})_2NH$, and in the anion $(PhCb^{\circ})_2N^-$, are oriented to allow dative π-bonding from the *p*-orbital perpendicular to the C–N–C plane into the *p*-orbital on C1 that is aligned for cage C1–C2 σ-bonding (Fig. 1). Evidence for that *exo*-C=N π-bonding is provided by the C–N distances in these systems (Table 1), which at 1.404(2)–1.410(4) Å in the amines $(RCb^{\circ})_2NH$ and 1.354(4)–1.355(4) Å in the amide $(PhCb^{\circ})_2N^-$ are far shorter than would be appropriate for single C–N bonds between three- or even two-coordinate nitrogen and six-coordinate carbon atoms. The shorter C=N bond in the amide $(PhCb^{\circ})_2N^-$ is intelligible in that deprotonation of the amine $(PhCb^{\circ})_2NH$ increases the π-donor capacity of the nitrogen atom. The average C–N distances in diphenylamine Ph_2NH and in the diphenylamide Ph_2N^- anion are 1.400(4) and 1.370(5) Å, respectively [22,23].

Involvement of the tangentially orientated *p*-AO at C1 in the X–C1–C2 plane as the acceptor orbital for dative *exo*-π-bonding from nitrogen reduces the C1–C2 σ-bonding contribution to the cage bonding orbital, and so lengthens the cage C–C bond (Fig. 1). The effect is most marked in the amide anion $(PhCb^{\circ})_2N^-$, which has C–C bonds of length 1.980(3) and 1.995(3) Å, effectively the same length as in the anion $[PhCb^{\circ}O]^-$ (2.001(3) and 2.065(7) Å) [6,9], even though one nitrogen lone pair is shared between two cages. In the amines $(RCb^{\circ})_2NH$, the cage C–C bonds, 1.748(4) and 1.752(4) Å when R = Me and 1.794(3) and 1.799(3) Å when R = Ph, are understandably shorter than those in the amide. The difference of 0.05 Å between the two amines can be attributed to a π-bonding contribution from the phenyl group [5].

3. Conclusions

This paper reports improved low-temperature procedures by which reactions between lithio-carboranes and nitrosyl chloride can be used as preparative routes to two important categories of carborane derivatives, *viz.* nitroso derivatives $RCb^{\circ}NO$, and dicarboranylamines $(RCb^{\circ})_2NH$, the former using mixtures of diethyl ether and pentane as solvent and the latter using 1,2-dimethoxyethane instead of pentane in the solvent mix. Deprotonation of the amines $(RCb^{\circ})_2NH$ in toluene by potassium *t*-butoxide in the presence of the macrocyclic ether 18-crown-6 afforded the air- and moisture-stable salts $[K(18\text{-crown-}6)]^+\ [(RCb^{\circ})_2N]^-$.

The crystal structures of $PhCb^{\circ}NO$, $(PhCb^{\circ})_2NH$, $(MeCb^{\circ})_2NH$ and $[K(18\text{-crown-}6)]^+[(PhCb^{\circ})_2N]^-\cdot 0.5(MeOC_2H_4)_2O$ have been determined, and shown to shed further useful light on the capacity of the *ortho*-carborane cage to function as a sensitive probe of the π-donor characteristics of cage C-attached ligands. The cage C1–C2 and the *exo*-C–N bond lengths and the ligand orientations in these compounds reinforce the generalisation that π-donor ligands attached to an *ortho*-carborane carbon atom adopt an orientation that involves in *exo*-π-bonding the *p*-orbital on carbon that otherwise participates in cage C1–C2 σ-bonding.

4. Experimental

All air-sensitive manipulations were carried out under dry, oxygen-free N_2. Stirring refers to use of a magnetic stirrer. Pentane was distilled over sodium. 1,2-Dimethoxyethane was dried by reflux and distillation over potassium; ether refers to diethyl ether dried, where appropriate, over sodium. Ether solutions were dried over magnesium sulfate and evaporated near room temperature. 1-

Methyl-*ortho*-carborane [24] and 1-phenyl-*ortho*-carborane [25] were prepared by literature methods and dried by sublimation at 0.01 mm Hg. Commercial nitrosyl chloride (BDH Chemicals Ltd.) was used as received.

Melting points were measured in capillary tubes with an Electrothermal 9200 heating block. Infrared spectra were recorded from KBr discs on Perkin–Elmer 1600 series FTIR or Perkin–Elmer 1720× FTIR spectrometers and ultraviolet spectra with a Shimadzu UV 1201. Elemental carbon, hydrogen and nitrogen analyses were performed using Exeter Analytical CE-440 or Carlo Erba Strumentazione EA Model 1106 instruments. Mass spectra (MS) were recorded on a VG Micromass 7070E instrument under E.I conditions (EI) at 70 eV. Values of *M* show the isotope range $^{10}\text{B}_n$ to $^{11}\text{B}_n$ including a ^{13}C contribution if observed. NMR spectra were measured using Varian Unity-300 (^{1}H, ^{11}B, ^{13}C), Bruker AM250 (^{1}H, ^{13}C), Bruker Avance 400 (^{1}H, ^{11}B, ^{13}C) and/or Varian Inova 500 (^{1}H, ^{11}B) instruments. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^{1}H NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm; CD_3CN, 1.85 ppm). ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$, 77.0 ppm; CD_3CN, 118.3 ppm). ^{11}B NMR spectra were referenced externally to $Et_2O \cdot BF_3$, $\delta = 0.0$ ppm. Peak assignments of cage boron and hydrogen atoms were determined where possible with the aid of 2D $^{11}\text{B}\{^{1}\text{H}\}$–$^{11}\text{B}\{^{1}\text{H}\}$ COSY, selective $^{1}\text{H}\{^{11}\text{B}\}$ and $^{1}\text{H}\{^{11}\text{B}\}$–$^{11}\text{B}\{^{1}\text{H}\}$ correlation spectra.

5. Reaction of 1-methyl- and 1-phenyl-*ortho*-carboranes with nitrosyl chloride

Nitrosyl chloride (5 ml) was condensed into a calibrated tube cooled to *ca.* −25 °C, transferred under reduced pressure into the co-solvent, ether or pentane (20 ml), at *ca.* −40 °C and the flask was brought to atmospheric pressure with dinitrogen. A solution of the lithio-carborane, prepared by slowly adding butyllithium (6.6 ml, 1.6 M in hexane; 10.5 mmol) to the substituted *ortho*-carborane (10.0 mmol) in 1,2-dimethoxyethane or pentane, (20 ml), was added dropwise with stirring at −40 °C (acetone/CO_2), −78 °C (acetone/CO_2) or −117 °C (ethanol/N_2) during *ca.* 35 min and the mixture was allowed to warm to room temperature during *ca.* 3 h. The solution was added in small portions to potassium hydrogen carbonate (40 g) in water (110 ml), the organic layer was diluted with ether, washed with water, dried and evaporated. The blue nitroso-compounds were separated from the resulting semi-solid by sublimation at *ca.* 70 °C/0.01 mm Hg and the residue was triturated with methanol (12 ml; the nitroso-carboranes are unstable to this solvent) to give the amines as white crystalline powders. The yields of nitroso-compounds and amines obtained using various bath temperatures and co-solvents are summarised in Scheme 1.

1-Methyl-2-nitroso-*ortho*-carborane formed volatile blue crystals identical with a sample prepared under the literature conditions; attempts to measure the melting point of this compound in open capillary tubes caused evaporation of the sample, leaving a colourless residue which melted sharply at the temperature, 208–210 °C, given in the literature [3] for the nitroso-derivative. A DSC scan showed a broad exotherm at 230 °C and the residue was shown by IR to consist of boric acid and *closo*-carborane products. 1-Phenyl-2-nitroso-*ortho*-carborane gave blue crystals m.p. 43–44 °C (literature [2] 54–55 °C).

1-Methyl-2-nitroso-*ortho*-carborane: Found: C, 19.2, H, 8.0, N, 7.0 $C_3H_{15}B_{10}NO$ requires C, 19.2, H, 8.0, N, 7.4; MS (EI$^+$, *m/z*)[*M*]$^+$ 186–190; 188 (100); IR (KBr disc, cm^{-1}) 3106w, 3063w, 2948w (methyl CH); 2599s, br (BH); 1567s (NO); 1445; 1389; 1111; 1046; 1022; 948; 921; 892; 721m (carborane skeleton); 697w, 640w, 540w; $^{1}\text{H}\{^{11}\text{B}\}$ NMR ($CDCl_3$) δ: 2.74 (s, 3H, CH_3), δ: 2.53 (s, 2H, H7, 11), 2.50 (s, 1H, H12), 2.41 (s, 2H, H3,6), 2.19 (s, 3H, H8,9,10), 1.88 (s, 2H, H4,5); $^{11}\text{B}\{^{1}\text{H}\}$ NMR ($CDCl_3$) δ: −2.4 (s, 1B, B12), −6.6 (s, 1B, B9), −10.2 (s, 4B, B7,8,10,11), −11.0 (s, 2B, B3,6), −12.6 (s, 2B, B4,5); $^{13}\text{C}\{^{1}\text{H}\}$ NMR ($CDCl_3$) δ: 111.4 (s, carborane C1), 73.3 (s, carborane C2), 23.0 (s, CH_3).

1-Phenyl-2-nitroso-*ortho*-carborane (**1**) (crystals for X-ray diffraction were obtained by slow vacuum sublimation 40°C/0.01 mm Hg): Found: C, 38.9; H, 6.0; N, 5.2; $C_8H_{15}B_{10}NO$ requires: C, 38.5; H, 6.1; N, 5.6%; MS (EI$^+$, *m/z*) [*M*]$^+$ 245–253; 249 (100); IR (KBr disc, cm^{-1}) 3098, 3072 (Ar CH); 2577br (BH); 1560s (NO), 1493m, 1446m; 1340w; 1270w, 1059s; 897; 867m; 753s; 724w (carborane skeleton), 688.8s; $^{1}\text{H}\{^{11}\text{B}\}$ NMR ($CDCl_3$) δ: 7.83 (d, $^{3}J_{HH}$ 8 Hz, 2H, *ortho*-phenyl), 7.49 (t, $^{3}J_{HH}$ 7.4 Hz, 1H, *para*-phenyl), 7.42 (t, $^{3}J_{HH}$ 7.8 Hz, 2H, *meta*-phenyl), 2.99 (s, 2H, H4,5), 2.67 (s, 3H, H7,11,12), 2.33 (s, 3H, H8,9,10), 2.09 (s, 2H, H3,6). $^{11}\text{B}\{^{1}\text{H}\}$ NMR ($CDCl_3$) δ: −2.0 (s, 1B, B12), −4.4 (s, 1B, B9), −9.8 (s, 2B, B7, 11), −10.4 (s, 2B, B8, 10), −12.6 (s, 2B, B3, 4, 5, 6); ^{13}C NMR ($CDCl_3$) δ: 131.1 (d of t, $^{1}J_{CH}$ 159 Hz, $^{2}J_{CH}$ 7 Hz, *m*-C phenyl), 130.1 (d of t, $^{1}J_{CH}$ 161 Hz, $^{2}J_{CH}$ 7 Hz, *m*-C phenyl), 128.9 (d of d, $^{1}J_{CH}$ 162 Hz, $^{2}J_{CH}$ 8 Hz, *o*-C phenyl), 114.1 (carborane C1), 81.3 (carborane C2).

Bis(2-methyl-1-*ortho*-carboranyl)amine (**2**) gave colourless crystals from hexane, m.p. 205.5–207 °C. Found: C, 21.4; H, 8.3; N, 4.0. $C_6H_{27}B_{20}N$ requires: C, 21.9; H, 8.2; N, 4.3. MS (EI$^+$, *m/z*) [*M*]$^+$ 245–253; 249(100); IR ν_{max} (KBr) [cm^{-1}]: 3389 (NH); 2963, 2943 (methyl CH); 2680w, 2670w, 2606, 2573, 2541 (BH); 1496; 1443, 1383 (methyl CH); 1297 (CN); 1261; 1084; 1029; 800; 727 (carborane skeleton); 475; 416; $^{1}\text{H}\{^{11}\text{B}\}$ NMR ($CDCl_3$), δ: 4.84 (br.s, 1H, NH), 2.51 (s, 4H, H4,5), 2.41 (s, 4H, H3,6), 2.30 (s, 4H, H7,11), 2.28 (s, 2H, H9), 2.22 (s, 2H, H12), 2.10 (s, 6H, CH_3), 2.09 (s, 4H, H8,10); $^{11}\text{B}\{^{1}\text{H}\}$ NMR ($CDCl_3$), δ: −5.2 (2B, B9), −6.4 (2B, B12), −10.3 (12B), −11.7 (4B, B8,10); $^{13}\text{C}\{^{1}\text{H}\}$ NMR ($CDCl_3$), δ: 90.9 (C1), 81.8 (C2), 22.1 (CH_3). $^{1}\text{H}\{^{11}\text{B}\}$ NMR (CD_3CN), δ: 6.76 (br.s, 1H, NH), 2.58 (s, 4H, BH), 2.38 (s, 4H, BH), 2.35 (s, 6H, CH_3), 2.29 (s, 4H, BH), 2.16 (s, 4H), 2.02 (s, 4H); $^{11}\text{B}\{^{1}\text{H}\}$ NMR (CD_3CN), δ: −6.1, −7.0 (4B, B9,12), −10.8 (12B), −12.3 (4B); $^{13}\text{C}\{^{1}\text{H}\}$ NMR (CD_3CN), δ: 93.3 (C1), 83.7 (C2), 22.2 (CH_3).

Bis(2-phenyl-1-*ortho*-carboranyl) amine (**3**) formed colourless rhombic crystals from xylene m.p. 242–244.5 °C, literature [2] 239–241 °C. Found: C, 41.8; H, 7.0; N, 2.9; $C_{16}H_{31}B_{20}N$ requires: C, 42.4; H, 6.9; N, 3.1%. MS (EI$^+$, *m/z*) 440–458; 454(100), IR (KBr disc, cm^{-1}) : 3391 (NH); 3062w, 2989w (Aryl CH); 2654, 2633, 2602s, 2584 (BH); 1508 (NH); 1495, 1447 (Ar. skeleton); 1306s (CN); 1069; 1039; 1004; 798; 755, 689 (C_6H_5); 729 (carborane skeleton). $^{1}\text{H}\{^{11}\text{B}\}$ NMR ($CDCl_3$), δ: 7.57 (d, 4H, *ortho* phenyl CH), 7.52 (t, 2H, *para* phenyl CH), 7.52 (t, 4H, *meta* phenyl CH); 4.46 (m, 1H, NH); 2.71 (s, 4H, H3,6), 2.30 (s, 4H, H4,5), 2.28 (s, 2H, H12), 2.21 (s, 2H, H9), 2.03 (s, 8H, H7,8,10,11); $^{11}\text{B}\{^{1}\text{H}\}$ NMR ($CDCl_3$), δ: −3.6 (s, 2B, B9), −5.8 (s, 2B, B12), −10.4 (8B, B3,4,5,6), −12.2 (8B, B7,8,10,11); ^{13}C NMR ($CDCl_3$), δ: 131.3 (C_6H_5 *para*), 129.6 (C_6H_5 *ipso*); 131.7, 128.9 (C_6H_5 *ortho* and *meta*), 94.4 (C2 or C1), 90.3 (C1 or C2). $^{1}\text{H}\{^{11}\text{B}\}$ NMR (CD_3CN), δ: 7.73 (d, 4H, *ortho* phenyl CH), 7.59 (t, 2H, *para* phenyl CH), 7.47 (t, 4H, *meta* phenyl CH); 6.55 (m, 1H, NH); 3.00 (s, 4H, H3,6), 2.20 (s, 8H, BH), 1.90 (s, 4H, BH), 1.77 (s, 4H, BH); $^{11}\text{B}\{^{1}\text{H}\}$ NMR (CD_3CN), δ: −4.2 (s, 2B, B9), −6.7 (s, 2B, B12), −10.7 (8B), −12.1 (4B), −13.1 (4B).

6. Potassium-18-crown-6 salt of bis(2-phenyl-1-*ortho*-carboranyl)amide

Bis(2-phenyl-1-*ortho*-carboranyl)amine (255 mg, 5.6 mmol) in warm (*ca.* 55 °C) toluene (10 ml) was added under nitrogen to a solution of potassium *t*-butoxide (160 mg, 13.4 mmol) and 18-crown-6 (390 mg, 14.5 mmol) in toluene (5 ml). The mixture was heated briefly (*ca.* 90 °C, 1 min) and the blue–green oil which separated initially formed a pale yellow granular solid within a few seconds. After standing overnight at room temperature the solid was washed with toluene to give the amide salt as a pale yellow powder (325 mg, 77%). Found: C, 44.2; H, 7.3; N, 1.7. $C_{28}H_{54}B_{20}KO_6N$ requires: C, 44.5; H, 7.2; N, 1.9%. Recrystallisation from 1,2-dichlorobenzene furnished yellow rectangular prisms, m.p. 254–257 °C, whose colour deepens reversibly on warming and which gave the same analysis as before. The crystalline amide is unchanged by exposure to air or contact with water but rapidly forms the parent amine in contact with ethanoic acid. Single crystals of the hemisolvate (**4**) suitable for X-ray diffraction were grown from a solution in diethyleneglycol dimethyl ether into which cyclohexane was diffused slowly from an upper layer.

M.p. 254–257 °C; MS (EI^+, *m*/*z*) 440–457; 453(100, M^+), MS (CI^+, NH_3, m/z) 282 (18-C-6+NH_4^+); IR (KBr disc, cm^{-1}): 3062w (Ar. CH); 2899, 1472, 1351, 1108s, 966, 838 (18-crown-6); 2575s, 2555s (BH); 1495, 1447 (Ar. skeleton); 1395s, br (CN); 1284; 1248; 1072; 1039, 1004w; 775, 883w, 806w, 775w; 745, 691 (C_6H_5 o.o.p.); 732w (carborane skeleton); 643w; 570w; 525. $^1H\{^{11}B\}$ NMR (CD_3CN), δ: 7.36 (d, 4H, *ortho* phenyl CH), 7.23 (t, 2H, *para* phenyl CH), 7.17 (t, 4H, *meta* phenyl CH); 3.47 (s, 24H, 18-C-6); 2.68 (s, 4H, H4,5), 2.13 (s, 10H, H3,6,7,9,11), 1.72 (s, 2H, H12), 1.58 (s, 4H, H8,10). $^{11}B\{^1H\}$ NMR (CD_3CN), δ: −4.4 (1B, B9), −8.3 (2B, B3,6); −10.5 (2B, B7,11); −12.6 (3B, B4,5,12); −16.3 (2B, B8,10). $^{13}C\{^1H\}$ NMR (CD_3CN), δ: 137.7 (C_6H_5 *ipso*); 129.3 (C_6H_5 *para*); 131.1, 128.8 (C_6H_5 *ortho* and *meta*); 129.5 (C1), 89.8 (C2); 70.9 (18-C-6). λ_{max} (THF, 20 °C): 317 nm (log ε, 3.92).

7. Potassium-18-crown-6 salt of bis(2-methyl-1-*ortho*-carboranyl)amide

By a similar procedure as above with bis(2-methyl-1-*ortho*-carboranyl)amine as the starting carborane, colourless crystals of the desired salt (86% yield) were obtained from toluene solution. M.p. 209–210 °C; Found: C, 34.3; H, 8.1; N, 1.8. $C_{18}H_{50}B_{20}KO_6$ N requires: C, 34.2; H, 8.0; N, 2.2%. MS (ES^-, *m*/*z*) 323–332; 328 (100, M^-), MS (ES^+, m/z) 303 (K18-C-6^+); IR (KBr disc, cm^{-1}): 2914, 1471, 1350, 1110s, 967, 839 (18-crown-6); 2560s (BH); 1413s, br (CN); 1369; 1283; 1246; 1072; 1034, 730w (carborane skeleton); 695w; 419. $^1H\{^{11}B\}$ NMR (CD_3CN), δ: 3.47 (s, 24H, 18-C-6); 2.30 (s, 4H, H4,5), 2.15 (s, 4H, H3,6), 1.98 (s, 4H, H7,11), 1.85 (s, 6H, CH_3), 1.82 (s, 2H, H9), 1.59 (s, 4H, H8,10), 1.53 (s, 1H, H12). $^{11}B\{^1H\}$ NMR (CD_3CN), δ: −7.5 (1B, B9), −8.8 (2B, B3,6); −11.3 (2B, B7,11); −12.3 (2B, B4,5); −13.7 (1B, B12), −15.4 (2B, B8,10). $^{13}C\{^1H\}$ NMR (CD_3CN), δ: 120.0 (C1), 87.0 (C2), 70.9 (18-C-6), 22.2 (CH_3).

Table 2
Crystal data and refinement information for compounds **1**–**4**.

Compound	**1**	**2**	**3**	**4**
Formula	$C_8H_{15}B_{10}NO$	$C_6H_{27}B_{20}N$	$C_{16}H_{31}B_{20}N$	$C_{31}H_{61}B_{20}KNO_{7.5}$
M	249.3	329.5	453.6	823.1
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	10.942(2)	11.302(6)	10.560(3)	10.370(3)
b (Å)	8.4999(12)	12.705(7)	13.135(4)	14.629(4)
c (Å)	15.068(2)	14.167(7)	18.695(6)	15.790(4)
α (°)				101.80(3)
β (°)	102.986(4)	107.03(2)	97.48(3)	92.53(2)
γ (°)				102.81(2)
V (Å^3)	1365.6(3)	1945(2)	2571.0(14)	2276.3(11)
Z	4	4	4	2
Data collected	6842	7511	4420	5825
Unique data	2392	2784	4356	5825
R_{int}	0.038	0.055	0.030	
Refined parameters	182	251	339	551
R (on *F*, $F^2 > 2\sigma$)	0.049	0.076	0.059	0.063
R_w (on F^2, all data)	0.143	0.168	0.165	0.196
Min., max. electron density (e Å^{-3})	0.25, −0.23	0.22, −0.20	0.30, −0.28	0.76, −0.35

8. Crystal structure determinations

Crystals of the compounds **1**–**4** were examined on Bruker SMART (**1**, **2**) and Stoe STADI4 (**3**, **4**) diffractometers with Mo Kα radiation (λ = 0.71069 Å; Cu Kα with λ = 1.54184 Å for **3**) at 160 K (180 K for **4**). Crystal data and other information are given in Table 2. Standard methods and software were employed, including refinement on all F^2 values [26]; no absorption corrections were applied, and no structural disorder was found.

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Appendix A. Supplementary data

CCDC 690385, 690386, 690387 and 690388 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.12.014.

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