



Trends in *ortho*-carboranes 1-X-2-R-1,2-C₂B₁₀H₁₀ (R = Ph, Me) bearing an *exo*-CN-bonded substituent group (X = NO, N=NR' or NHR')

Mark A. Fox^{a,*}, Richard J. Peace^a, William Clegg^b, Mark R.J. Elsegood^{b,1}, Kenneth Wade^{a,*}

^aChemistry Department, Durham University Science Laboratories, South Road, Durham DH1 3LE, UK

^bSchool of Chemistry, Newcastle University, Newcastle Upon Tyne NE1 7RU, UK

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ABSTRACT

The preparation and crystal structures of four *ortho*-carboranyl-nitrogen compounds, PhCb^oN=N(C₆H₄Me-4) (**1**), PhCb^oNHNH(C₆H₄Me-4) (**2**), MeCb^oNHNHPh (**3**) and PhCb^oNHOH (**4**) (Cb^o = 1,2-C₂B₁₀H₁₀; nitrogen groups at cage carbon C1, Ph or Me at C2), the last as a 1,4-dioxane solvate, are reported. Comparisons of their structures with those of other *ortho*-carboranyl-nitrogen systems studied earlier reveal further correlations between their cage C–C and *exo*-C–N bond distances and bond orders. Substituent orientations and bond distances (cage C1–C2, *exo*-C1–N) in RCb^oNHR' systems (R = Ph or Me at C2) are consistent with dative π -bonding from a nitrogen lone pair into the cage carbon *p*-AO otherwise responsible for cage C1–C2 σ bonding. Their C1–C2 bond distances are remarkably sensitive to the planar (*sp*²) or pyramidal (*sp*³) nature of the NHR' group. The N=O and N=NR' residues in RCb^oX prefer to be orientated in plane with the cage C1–C2 in contrast to the RCb^oNHR' systems. Correlations between their cage C–C and *exo*-C–N bond distances and the ¹¹B NMR chemical shifts of their antipodal boron atoms reflect the π -bonding characteristics of the nitrogen substituent.

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1. Introduction

The remarkable capacity of π -donor substituents, attached to carbon atoms of an *ortho*-carborane C₂B₁₀ cage, to influence cage C1–C2 bond lengths was first detected some two decades ago [1] with the structural characterisation of the proton sponge salt of the anion PhCb^oO[−], (Cb^o = 1,2-C₂B₁₀H₁₀; O[−] at cage carbon C1, Ph at C2) followed by many related studies [2,3–7] on *ortho*-carboranes containing thiolato and phosphino groups. However, this area has only recently been documented systematically by experimental and computational studies on systems RCb^oX and XCb^oX in which X is a potential π -donor such as NH₂, OH, SH or anions derived therefrom by deprotonation [8,9]. *Exo*-C=X π -bonding in these systems between the cage carbon atom and substituent X involves a tangentially oriented *p*-AO on carbon that would otherwise be involved in cage bonding, and C1–C2 bond lengthening will occur if the *p*-AO used for *exo*-C=X π -bonding is the *p*-AO that in *ortho*-carborane itself is involved in C1–C2 σ -bonding (AO = atomic orbital; Fig. 1).

The extent to which the cage C1–C2 bond is affected by *exo* π -bonding will therefore depend on the orientation of the substituent in the *exo*-CN systems explored here. Though many *ortho*-carborane derivatives with *exo*-C–N bonds are known, only three structural studies have been carried out elsewhere to our knowledge: the first was on a rhenium complex ⁱPrCb^oN₂Re(CO)₄ [10], which contains a 6-membered –Re–N=N–C–B–H– ring in which the metal atom is attached to one nitrogen atom and to a boron-attached hydrogen; the second was on a hydrazocarborane, HCB^oNRNHR (R = CO₂^tBu) [11], which contains an intramolecular cage C–H...O hydrogen bond [12]; and the third was on a zirconium complex, PhN₃Cb^oZrCp₂ [13], which contains a 3-membered ZrN₂ ring. All three systems thus contain intramolecular interactions that influence the orientation about nitrogen at C1 with respect to the cage C1–C2 bond.

In 2004, we reported the crystal structures of PhCb^oNH₂ and the adduct PhCb^oNH₂·OP(NMe₂)₃ which revealed six independent molecules with C1–C2 bond distances ranging between 1.74 and 1.85 Å [8]. We also reported improved syntheses of *ortho*-carborane nitroso derivatives RCb^oNO and dicarboranylaminos (RCb^o)₂NH (R = Ph, Me) and discussed their structures, which in the case of the secondary amines (and amides [(RCb^o)₂N][−] derived therefrom) showed significant cage distortion (C1–C2 bond lengthening) attributable to *exo*-C=N π -bonding [14–16]. To supplement these studies, we have carried out a synthetic, spectroscopic, structural and computational investigation of the compounds

* Corresponding authors.

E-mail addresses: m.a.fox@durham.ac.uk (M.A. Fox), kenneth.wade@durham.ac.uk (K. Wade).

¹ Present address: Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK.

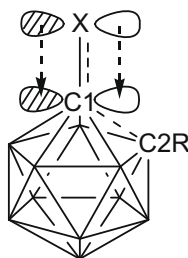


Fig. 1. Orbitals involved in the *exo* π -bonding for $\text{RCb}^{\circ}\text{X}$ where X is a π -donating group and R is not a donor group.

$\text{RCb}^{\circ}\text{X}$ (R = Ph, Me; X = NNR' , NHNHR' , NHOH ; R' = Ph or $\text{C}_6\text{H}_4\text{Me-4}$), and further spectroscopic and computational studies on systems with X = NH_2 , NO, $\text{NHCb}^{\circ}\text{R}$ and $[\text{NCb}^{\circ}\text{R}]^-$, which have revealed hitherto unremarked characteristics and trends in *ortho*-carborane systems $\text{RCb}^{\circ}\text{X}$ containing *exo*-CN units, which we report here.

2. Results and discussion

In this section, we outline the synthetic procedures used to prepare the new compounds, and describe their structures. We then explore the structural, bonding and spectroscopic characteristics of *ortho*-carboranyl-nitrogen systems $\text{RCb}^{\circ}\text{N}=\text{O}$, $\text{RCb}^{\circ}\text{N}=\text{NR}'$ and $\text{RCb}^{\circ}\text{NHR}''$ in general, including both the new systems and those previously characterised [8,14]. We also compare the structural and bonding relationships of these 3D pseudoaromatic cages with 2D aromatic ring analogues.

2.1. Synthetic aspects

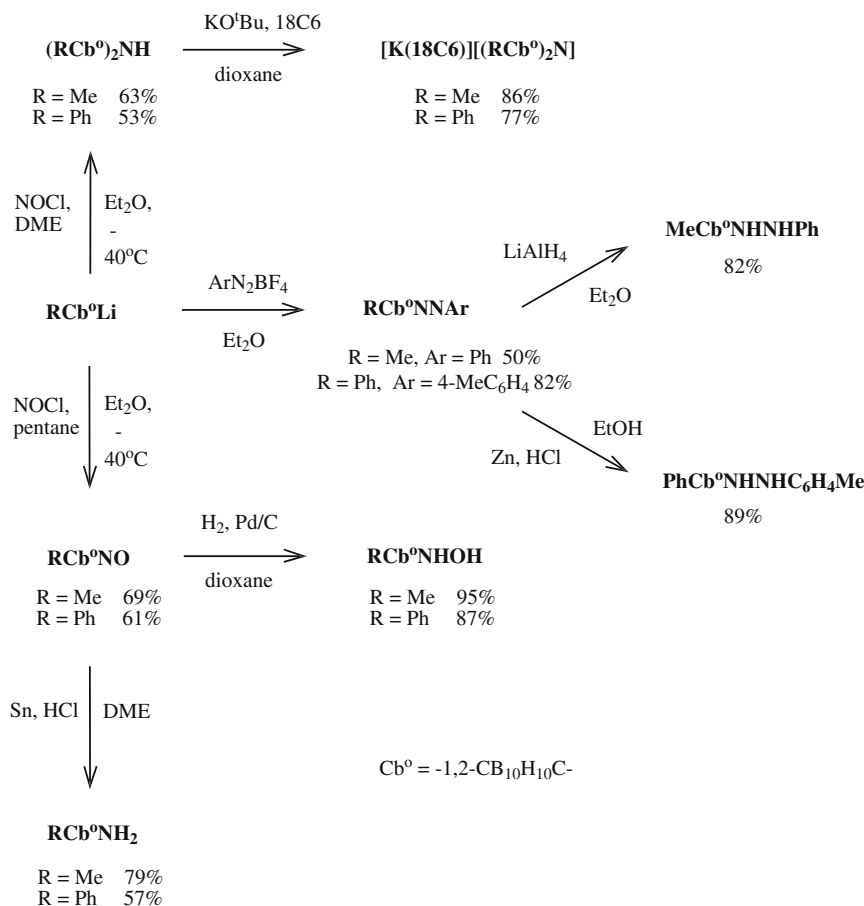
Scheme 1 summarises the experimental procedures used for the syntheses of the carboranes investigated in this definitive study. Synthetic methods that have not been reported in our earlier papers [8,14] are described in detail in Section 4. The azocarboranes were synthesised using a reported literature procedure [17]. The reductions of the nitroso-carboranes $\text{RCb}^{\circ}\text{NO}$ with hydrogen using a palladium/carbon catalyst gave the known [18,19] hydroxylamines $\text{RCb}^{\circ}\text{NHOH}$ in high yields. High-yield reductions of the azocarboranes $\text{RCb}^{\circ}\text{NNAr}$ to the hydrazines $\text{RCb}^{\circ}\text{NHNHAr}$ were carried out here using the reducing agents LiAlH_4 and Zn/HCl .

2.2. Structural aspects: new experimentally determined structures

2.2.1. The azo-carborane $\text{PhCb}^{\circ}\text{N}_2(\text{C}_6\text{H}_4\text{Me-4})$ (**1**) and hydrazo-carboranes $\text{PhCb}^{\circ}\text{NHNH}(\text{C}_6\text{H}_4\text{Me-4})$ (**2**) and $\text{MeCb}^{\circ}\text{NHNHPh}$ (**3**)

The crystal structures of these three compounds were determined by X-ray diffraction (for details, see Section 4). Their molecular structures are illustrated in Figs. 2 and 3.

The structures of the azo-carborane (**1**) and its hydrazo analogue (**2**) (Fig. 2) are similar, differing significantly, and as expected, only in the bond lengths and angles in the region of their $-\text{N}=\text{N}-$ and $-\text{N}(\text{H})\text{N}(\text{H})-$ units. Their NN links, at 1.250(2) in (**1**) and 1.409(2) Å in (**2**), are of normal length for double and single bonds, respectively, between nitrogen atoms. The CNN bond angles, at both ends of the N(1)–N(2) links, appear not to differ between the two ends (implying that the link to the carboranyl residue resembles that to the aryl group in both **1** and **2**) nor between **1** and **2**, suggesting both **1** and **2** contain sp^2 -hybridised



Scheme 1. Routes to carboranyl-nitrogen derivatives.

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