A Pentuply-bridging Carbonyl Group: Crystal and Molecular Structure of a Salt of the 1-Oxo-2-phenyl-1,2-dicarbadodecaborate(12) Anion, $[LH]^+[O(Ph)C_2B_{10}H_{10}]^-$ (L = 1,8-*N,N,N′,N′*-tetramethylnaphthalenediamine)

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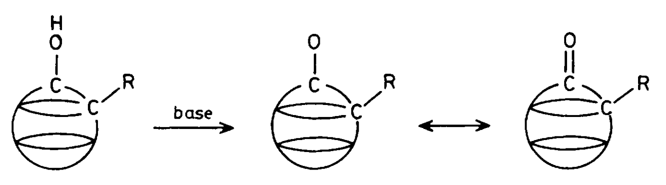
Deprotonation of the C-hydroxy *ortho*-carborane 1,2-$HO(Ph)C_2B_{10}H_{10}$ by 1,8-*N,N,N′,N′*-tetramethylnaphthalenediamine gives a salt whose anion, $[O(Ph)C_2B_{10}H_{10}]^-$, effectively consists of a *nido*-shaped $[PhCB_{10}H_{10}]^-$ residue capped by a pentuply-bridging carbonyl group whose C–O distance of 1.245(3) Å and position over the open carborane face, 2.001(3) Å from the cage carbon atom, are readily rationalized by frontier orbital considerations.

Although the derivative chemistry of icosahedral carboranes $C_2B_{10}H_{12}$ is now extensive,[1—3] C-hydroxy species $HO(R)C_2B_{10}H_{10}$ (**1**) have received surprisingly little attention, and none has been structurally characterised. In one of the few reported studies of such compounds,[4] it was noted that they are acidic, though the potential interest of the anions $[O(R)C_2B_{10}H_{10}]^-$ (**2**) generated on deprotonation of (**1**) went unremarked. The delocalization of anionic charge into the carborane cage expected in (**2**) allows such anions to be regarded as *nido*-shaped residues $[RCB_{10}H_{10}]^-$ stabilised by pentuply-bridging carbonyl groups (**3**), an environment consistent with the cluster-forming potential of CO units as



(1) (2) (3)

sources of two electrons and three orbitals. Such an environment to our knowledge is without precedent in carbonyl co-ordination chemistry,[5,6] although C-hydroxy,[7] C-diethyl ether,[8] and C-carboxylato[9,10] metallacarboranes formed by migration of carbonyl ligands into cage sites have been reported.

We therefore prepared the C-hydroxy-*ortho* carboranes $HO(R)C_2B_{10}H_{10}$ (R = H, Me, or Ph) by benzoyl peroxide oxidation of the lithiocarboranes[4,11,12] and studied their deprotonation by tertiary amines. In particular, 1,8-*N,N,N′,N′*-tetramethylnaphthalenediamine ('proton sponge'[13]) with 1-HO-2-Ph-$C_2B_{10}H_{10}$ in toluene afforded a crystalline salt (m.p. 146—148 °C) that analysed satisfactorily for $[C_{10}H_6(NMe_2)_2H]^+[O(Ph)C_2B_{10}H_{10}]^-$ (**4**). Its C–O stretching mode, at 1460 cm^{-1}, showed the greatest shift ($\Delta\nu$ 230 cm^{-1}) from that of the parent hydroxycarborane of all the salts studied. *X*-Ray crystallographic analysis established the structure shown in Figure 1, which gives selected bond distances and angles.†

The ionic structure of (**4**) is clearly established by the *X*-ray study, which also reveals the expected μ_5 environment of the CO group, and shows that the methyl groups of the base effectively prevent N—H · · · · O hydrogen bonding between the cation and anion. Strong evidence for delocalization of the anionic charge from the oxygen atom into the carborane cage is provided by the carbon–oxygen bond length, which at 1.245(3) Å is in the region typical of a C=O double bond as in ketones; a C–O single bond would be expected to be *ca.* 1.43 Å long. Interestingly, although within the *nido*-shaped $C(2)B_{10}$ residue the cage C–B and B–B distances lie in the range (1.65—1.85 Å) usual for such icosahedral fragments, the C–C and C–B bonds to the carbonyl carbon atom, C(1), have lengths that show the carbonyl unit to be shifted significantly away from C(2) to a position arguably more aptly described as μ_4, though molecular orbital bond index (MOBI)[14] calculations show that, despite the length [2.001(3) Å] of the C(1)–C(2) distance (*cf.* 1.64 Å in *ortho* carborane[1]), there is nevertheless a significant bonding interaction (bond index 0.33) between these two atoms.

A qualititative explanation of these C–O and C–C distances results from a consideration of the frontier orbitals of the *nido*-shaped $[PhCB_{10}H_{10}]^-$ residue to which the CO unit is co-ordinating. Like a cyclopentadienyl group, such a residue has three orbitals[15,16] (Figure 2, with orbitals labelled as by Mingos[15]) with which to interact with an atom or group located over the pentagonal face, though the presence of the single carbon atom in that face removes the degeneracy of the HOMO e_1 pair by significantly lowering the energy of the one [the $5e_1(x)$ orbital] to which the carbon 2p orbital contributes.

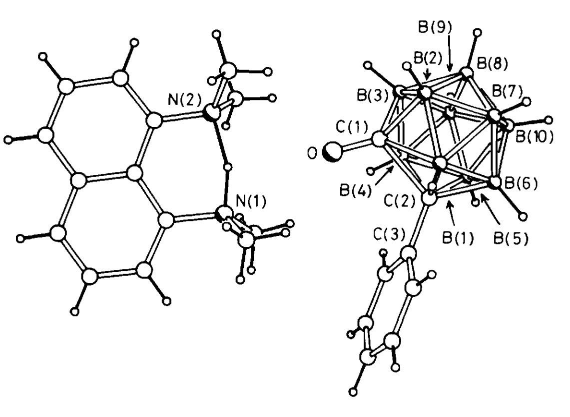


Figure 1. Structure of (**4**). Selected interatomic distances (Å): C(1)–O, 1.245(3); C(1)–C(2), 2.001(3); C(1)–B(1), 1.822(5); C(1)–B(2), 1.684(3); C(1)–B(3), 1.683(4); C(1)–B(4), 1.813(4); C(2)–B(1), 1.697(5); B(1)–B(2), 1.771(4); B(2)–B(3), 1.801(6); B(3)–B(4), 1.770(5); B(4)–C(2), 1.686(4); C(2)–C(3), 1.502(4); N(1)–H, 1.222(32); N(2)–H, 1.519(25); O · · · · H, 2.603(60); N(1) · · · · O, 3.115(12); N(2) · · · · O, 3.208(12). Selected bond angles (°): O–C(1)–C(2), 117.7(2); O–C(1)–B(1), 119.7(2); O–C(1)–B(2), 130.0(3); O–C(1)–B(3), 130.3(3); O–C(1)–B(4), 120.1(3); C(1)–C(2)–C(3), 117.3(2); B(1)–C(2)–B(4), 108.1(2); C(2)–B(1)–B(2), 110.0(2); C(2)–B(4)–B(3), 110.6(3); B(1)–B(2)–B(3), 105.5(3); B(2)–B(3)–B(4), 105.2(2).

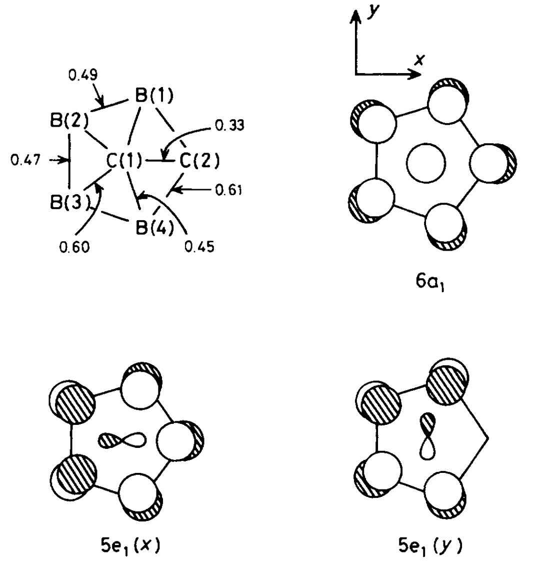


Figure 2. Orbitals involved in bonding the carbonyl carbon atom, C(1), to the rest of the carborane icosahedron, and calculated bond indices for the bonds to C(1) and around the face of the icosahedral residue, C(2)B(1)B(2)B(3)B(4).

The $6a_1$ orbital functions as the one into which the lone pair electrons on the carbon of the μ_5 carbonyl group are formally donated. Back π-bonding from the $5e_1(x)$ and $5e_1(y)$ orbitals to the carbonyl group's π^* orbitals is expected to leave the CO unit slightly negatively charged, though with less than the full charge on oxygen that (**2**) implies. The lower energy of the $5e_1(x)$ orbital makes it far less effective than $5e_1(y)$ at back π-bonding, so the carbonyl ligand shifts from the pseudo five-fold axis of the carborane cage away from C(2) to a

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†*Crystal data* for (**4**): $C_{22}H_{34}B_{10}N_2O$, M = 450.62, monoclinic, space group $P2_1/c$, a = 10.4583(6), b = 25.043(2), c = 11.1044(7) Å, β = 116.067(5)°, U = 2612.5 Å^3, Z = 4, D_c = 1.146 g cm^{-3}, μ(Cu-K_α) = 0.44 mm^{-1}; R = 0.058 for 2600 unique reflections with $F > 3\sigma(F)$ and $2\theta \leq 115°$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

position more appropriate for strong interaction with the $5e_1(y)$ orbital. The bond indices calculated for the bonds to C(1) broadly support this bonding picture (Figure 2), though the C–O bond has a lower index than expected (1.20), emphasising the carbocationic nature of C(1) [the total valencies of C(1) and C(2) are 3.76 and 3.95 respectively].

Corollaries of this treatment are that a related anion 1,7-$[OCB_{10}H_{10}CR]^-$ prepared from the hydroxy-*meta*-carborane 1,7-$HOCB_{10}H_{10}CR$, in which the open face of the *nido* $[RCB_{10}H_{10}]^-$ residue would contain only boron atoms, would be expected to show only very slight displacement of the μ_5-CO group from the pseudo-five-fold axis, while in anions 1,12-$[OCB_{10}H_{10}CR]^-$ or $[OCB_{11}H_{11}]^{2-}$ (prepared from the hydroxy-*para*-carborane 1,12-$HOCB_{10}H_{10}CR$ or mono-carba species $[HOCB_{11}H_{11}]^-$ respectively) the CO groups would be fully μ_5, lying on the five-fold axes of the *nido* residues. There are also interesting implications for the deprotonation of B-hydroxy species,[17] and the possibility of direct elimination of carbon monoxide from (**4**).

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