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Preliminary Communication

Steric effects in heteroboranes

Part 8 *. Sterically-induced *Exo*-skeletal isomerisation of di-copper carbametallaboranes: syntheses and crystal structures of $(Ph_3PCu)_2Ph_2C_2B_9H_9$ and $\{(o\text{-tol})_3PCu\}_2Ph_2C_2B_9H_9$

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Abstract

In $(Ph_3PCu)_2Ph_2C_2B_9H_9$ (**Ia**) and $\{(o\text{-tol})_3PCu\}_2Ph_2C_2B_9H_9$ (**Ic**) one copper atom occupies a polyhedral vertex position but is slipped away from the cage carbon atoms (the latter the more so) to relieve phosphine $\cdots$ C_{cage}-phenyl crowding. The second copper atom is *exo*-facially bonded to the B(8)B(9)B(12) triangular face, in contrast to the situation in $(Ph_3PCu)_2C_2B_9H_{11}$, where the *exo*-metal caps the Cu(3)B(4)B(8) triangle. Compounds **Ia**, **Ic** and the related species $(Cy_3PCu)_2Ph_2C_2B_9H_9$ (**Ib**) display fluxionality in solution at room temperature that renders equivalent the two phosphorus nuclei. It is speculated that this fluxional process involves a unique bis(*exo*-metal) *nido* carbaborane.

Key words: Boron; Copper; Carborane; X-ray diffraction; Metallacarborane; Fluxionality

We have previously shown that deliberately producing overcrowding in heteroboranes by the use of sterically bulky C_{cage}-phenyl substituents can have very large effects on both molecular structure and reactivity. For example, the molecule 1,2-Ph_2-3-Cp*-3,1,2-$RhC_2B_9H_9$ [2] is distorted into a novel *pseudocloso* geometry with an open C(1)Rh(3)C(2)B(6) face, and in 7,8-Ph_2-10-(Ph_3PHg)-7,8-*nido*-$C_2B_9H_9$ [3] and 1,2-Ph_2-3-(cod)-3,1,2-$PdC_2B_9H_9$ [4] there are substantially enhanced metal slip distortions [5] relative to those in their non-C_{cage}-phenyl analogues. (In addition, the cod–Pd bonding in the last compound is severly distorted). Moreover, 1-Ph-3,3-$(PhMe_2P)_2$-3,1,2-$PtC_2B_9H_9$ shows remarkably facile polyhedral isomerisation that is sterically-induced, and the bis C_{cage}-phenyl analogue can only be isolated as a C_{cage}-separated isomer [6]. We report here a further possible consequence of overcrowding in heteroboranes, viz. sterically-induced *exo*-skeletal isomerisation.

Reaction of Tl_2[7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] [2] with $0.5[Ph_3PCuBr]_4$ [7], $[Cy_3PCuCl]_2$ [8] or $[(o\text{-tol})_3PCuBr]_2$ [9] gave the complexes $(R_3PCu)_2Ph_2C_2B_9H_9$, **I** (**Ia**, R = Ph; **Ib**, R = Cy, **Ic**, R = *o*-tol), as air-stable white solids in good yield ‡. These three new compounds were characterised by microanalysis and ^1H, ^1H-$\{^{11}B_{selective}\}$, ^{11}B, ^{11}B-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR spectroscopy and, in the cases of **Ia** and **Ic**, by single-crystal diffraction studies.

The ^{11}B NMR spectra of compounds **I** measured at room temperature are consistent with at least time-averaged C_S molecular symmetry. The ^{31}P-$\{^1H\}$ NMR spectra of all three compounds at 298 K show only a single resonance, but whilst this persists for **Ia** down to 215 K, at ca. 235 K (compound **Ib**) and ca. 240 K (compound **Ic**) this single peak gives way to two resonances of approximately equal integral. The process is fully reversible on warming, and clearly shows that in solution at room temperature, a fluxional process renders the two phosphine ligands equivalent.

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* For details of Part 7, see ref. 1.

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‡ *Compound Ia*: To a slurry of Tl_2[7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (0.50 g, 0.74 mmol) in MeCN (20 cm^3) was added a solution of $[Ph_3PCuBr]_4$ (0.56 g, 0.37 mmol) in CH_2Cl_2 (10 cm^3). After 20 h stirring under N_2 the mixture was filtered through Celite and the volume of the filtrate reduced to ca. 5 cm^3. Addition of Et_2O (10 cm^3) yielded a white precipitate which was isolated by filtration, washed with further Et_2O (10 cm^3) and dried in vacuo. Recrystallisation from CH_2Cl_2/n-hexane afforded colourless crystals. Yield 60%. Calculated for $C_{50}H_{49}B_9Cu_2P_2 \cdot CH_2Cl_2$; 60.0% C, 5.03% H. Found for **1a**; 58.7% C, 5.26% H. NMR (CD_2Cl_2, 298 K): ^1H; δ 7.50–6.55 (m, 40H, C_6H_5) ppm: ^1H-$\{^{11}B_{selective}$, order follows ^{11}B resonances}; δ 2.84 (1H), 1.98 (2H), 1.95 (2H), 1.99 (2H), 1.45 (1H) and 0.95 (1H) ppm. ^{11}B-$\{^1H\}$; δ −10.6 (1B), −18.1 (2B), −19.1 (2B), −24.1 (2B), −34.9 (1B) and −36.3 (1B) ppm. ^{31}P-$\{^1H\}$; δ 6.2 (br) ppm.

Compounds Ib and Ic: These were prepared similarly. For **Ib** yield 58%. Calculated for $C_{50}H_{85}B_9Cu_2P_2$; 61.8% C, 8.8% H. Found for **1b**; 60.2% C, 8.92% H. NMR ($CDCl_3$, 298 K): ^{31}P-$\{^1H\}$; δ 24.2 (br) ppm. For **Ic** yield 61%. Calculated for $C_{56}H_{61}B_9Cu_2P_2$; 65.9% C, 6.22% H. Found for **Ic**; 63.3% C, 6.12% H. NMR ($CDCl_3$, 298 K): ^{31}P-$\{^1H\}$; δ −18.1 (br) ppm.

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Compound **Ia** was obtained as poor quality, single crystals by diffusion of n-hexane into a CH_2Cl_2 solution at ca. 250 K. In contrast, **Ic** was obtained as large, well-formed blocks by the slow evaporation of a CH_2Cl_2 solution. Since Ph_3P and $(o\text{-tol})_3P$ have substantially different cone angles [10] **Ia** and **Ic** could have significantly different molecular structures, and so both were subjected to crystallographic study [‡‡].

Figure 1 shows a molecule of compound **Ia**, and lists important molecular parameters. The structure of **Ic** is similar (Fig. 2) except that the bonding of the $\{Cu(3)P(o\text{-tol})_3\}$ unit to the cage is more distorted (see below). The structure of **Ic** was much more precisely determined than that of **Ia** because of the better quality of the crystals.

In compounds **I** in the solid state one copper atom, Cu(3), completes a very approximately icosahedral $3,1,2\text{-CuC}_2B_9$ polyhedron, with the other, Cu(1), *exo*-facially bonded to the B(8)B(9)B(12) triangular face via three B–H–Cu 3c–2e bonds. In **Ia** Cu(3) is slipped [5] across the C_2B_3 carbaborane ligand face by 0.624 Å towards B(8) to afford Cu(3)–C_{cage} distances of 2.56(3) and 2.68(3) Å, this slip being necessary to avoid over-

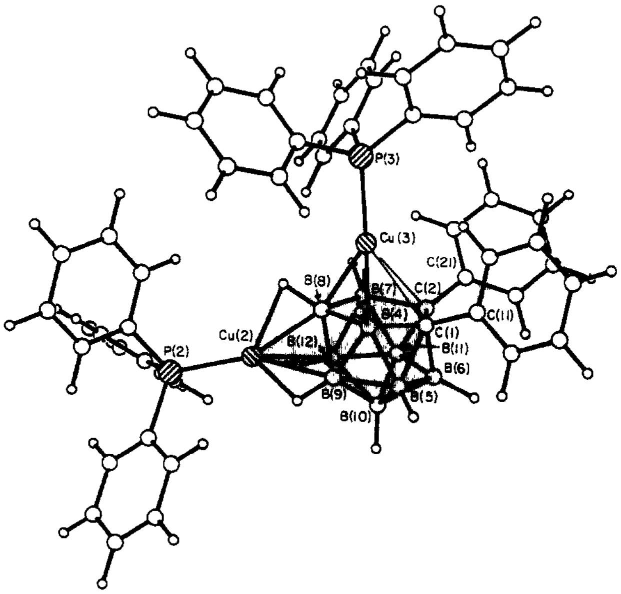

Fig. 1. Molecular structure of **Ia** with key atoms identified. Important molecular parameters (Å and °): Cu(3)–P(3) 2.183(10); Cu(3)–C(1) 2.56(3); Cu(3)–C(2) 2.67(3); Cu(3)–B(8) 2.07(4); Cu(3) ··· H(8) 2.35; C(1)–C(2) 1.65(4); Cu(2)–P(2) 2.128(10); Cu(2)–B(8) 2.17(4); Cu(2)–H(8) 2.07; Cu(2) ··· Cu(3) 4.159(6). $\theta_{\text{ring of C(11)}}$ [15] 23.5°; $\theta_{\text{ring of C(12)}}$ 23.7°.

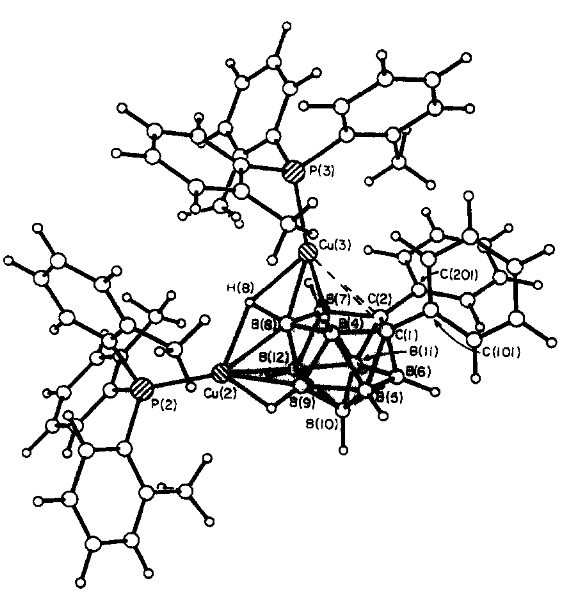

Fig. 2. Molecular structure of **Ic**, key atoms identified. Important molecular parameters (Å and °): Cu(3)–P(3) 2.2198(21); Cu(3) ··· C(1) 2.983(6); Cu(3) ··· C(2) 2.943(6); Cu(3)–B(8) 2.034(8); Cu(3)–H(8) 2.07; C(1)–C(2) 1.609(9); Cu(2)–P(2) 2.1753(22); Cu(2)–B(8) 2.207(8); Cu(2)–H(8) 2.08; Cu(2) ··· Cu(3) 4.030(1). $\theta_{\text{ring of C(101)}}$ 12.2°, $\theta_{\text{ring of C(201)}}$ 49.8°.

[‡‡] All measurements were carried out at 291 ± 1 K using an Enraf–Nonius CAD4 diffractometer operating with graphite-monochromated Mo Kα X-radiation ($\lambda_{bar} = 0.71069$ Å).

Compound Ia: $C_{50}H_{49}B_9Cu_2P_2 \cdot CH_2Cl_2$, $M = 1021.20$, monoclinic, space group $P2_1/c$, $a = 11.348(7)$, $b = 20.252(10)$, $c = 23.169(17)$ Å, $\beta = 103.38(5)°$, $V = 5180.2(21)$ Å^3, from the least-squares refinement of 25 centred reflections ($7 < \theta < 9°$), $Z = 4$, $D_{calc} = 1.309$ g cm^{-3}, μ(Mo Kα) = 10.21 cm^{-1}, $F(000) = 2096$. 6714 intensity data were collected for $1 \le \theta \le 23°$ by $\omega - 2\theta$ scans (ω scan width $0.8 + 0.34 \tan \theta$) over ca. 136 X-ray hours. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares. Using 2202 data for which $F \ge 4.0\sigma(F)$, empirically corrected for absorption, refinement converged at $R = 0.1332$, $R_w = 0.1443$, $S = 1.207$ for a model with anisotropic Cu and P atoms, phenyl rings constrained to rigid planar hexagons and all H atoms set in idealised positions. We ascribe the high residuals primarily to poor crystal quality. Maximum residue in final ΔF synthesis 0.89 eÅ^{-3}.

Compound Ic: $C_{56}H_{61}B_9Cu_2P_2 . 0.42CH_2Cl_2$, $M = 1020.43$, triclinic, space group $P\bar{1}$, $a = 14.246(6)$, $b = 15.102(6)$, $c = 15.692(11)$ Å, $\alpha = 116.10(6)$, $\beta = 104.43(5)$, $\gamma = 97.74(3)°$, $V = 2818(3)$ Å^3, from the least-squares refinement of 25 centred reflections ($10 < \theta < 12°$), $Z = 2$, $D_{calc} = 1.202$ gcm^{-3}, μ(Mo Kα) = 8.46 cm^{-1}, $F(000) = 1060$. (M, D_{calc}, μ and $F(000)$ calculated assuming no solvate.) 10447 data were collected for $1 \le \theta \le 25°$ by ω-2θ scans (ω scan width as for **Ia**) over ca. 229 X-ray hours. The structure was solved by direct methods and developed by full-matrix least-squares refinement and ΔF syntheses. Using 7131 data [$F \ge 2.0\sigma(F)$] empirically corrected for absorption, anisotropic thermal parameters for all non-H atoms, aromatic rings treated as regular hexagons and all H atoms set in idealised positions, refinement in two blocks converged at $R = 0.0792$, $R_w = 0.1105$, $S = 1.200$. A molecule of CH_2Cl_2 of solvation (42% occupancy) cocrystallises with **Ic** and maximum residues in the final ΔF synthesis (ca. 1.10 eÅ^{-3}) are located near the Cl atoms.

For both compounds tables of atomic coordinate, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

crowding between the P(3) phosphine and C_{cage}-phenyl groups. In **Ic** (in which the phosphine ligands are larger) the slip of Cu(3) is much more severe, 1.004 Å [11], resulting in substantially longer Cu(3)–C_{cage} connectivities [2.983(6) and 2.943(6) Å] and necessitating interaction between Cu(3) and the B(8)H(8) unit, not merely B(8). Unfortunately, even the diffraction data from **Ic** were not of sufficient quality to merit positional refinement of the cage H atoms, but in its idealised location, 1.16 Å from B(8) and radial to the C_2B_9 cluster, H(8) is 2.08 Å from Cu(2) and 2.07 Å from Cu(3).

The structures of compounds **I** may be compared with that of $(Ph_3PCu)_2C_2B_9H_{11}$, **II**, previously studied by Hawthorne et al. [12]. In **II**, which contains no C_{cage}-phenyl substituents, the cluster copper atom Cu(3) is barely slipped across the carbaborane face (0.248 Å) and the *exo*-skeletal copper caps the Cu(3)B(4)B(8) triangle, thereby directly linking the two copper atoms, Cu–Cu 2.576(1) Å. In **I** the cage phenyl groups clearly push the vertex copper back beyond the point where the bonding of Cu(2) to a CuB_2 face can be sustained and the B(4)B(7)B(8) triangle is capped; thus molecular overcrowding results in *exo*-skeletal isomerisation.

In compound **II** in solution at room temperature the two phosphorus nuclei in the molecule undergo rapid exchange. Although this is arrested below ca. 250 K, a second dynamic process, interpreted as involving the *exo*-skeletal $\{CuPPh_3\}$ unit flipping between Cu(3)-B(4)B(8) and Cu(3)B(7)B(8) faces, still operates down to 203 K, affording this carbadicupraborane time-averaged C_S molecular symmetry. In compounds **I** there is also a dynamic process which results in equivalence of the two phosphine ligands (arrested at low temperatures for **Ib** and **Ic**) but we cannot distinguish between interchange of $\{CuPR_3\}$ units and simple interchange of phosphine ligands. However, the evidence of Hawthorne et al. for $\{CuPR_3\}$ mobility in **II** is persuasive, and in as much as it would apply to **I** suggests an intermediate in which $\{CuPR_3\}$ units are simultaneously bound to B(4)B(8)B(9) and B(7)B(8)B(12) triangular faces. The possibility of isolating such a novel bis(*exo*-skeletal metal) *nido* species [13] by the use of C_{cage} substituents that are even more sterically demanding than phenyl groups is currently under investigation [14].

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