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The First Example of Electrophilic Mercuration of Icosahedral Dicobaltacarborane 3,6-Cp_2-3,6,1,2-$Co_2C_2B_8H_{10}$

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The interaction of equivalent amounts of 3,6-Cp_2-3,6,1,2-$Co_2C_2B_8H_{10}$ **1** and mercury(II) acetate in boiling CH_2Cl_2 followed by treatment with NaCl results in a mixture (1:1.2) of 8- and 9-chloromercury derivatives of dicobaltacarboranes (compounds **2** and **3**). The action of excess $Hg(OAc)_2$ on **1** leads to the tetramercurated compound with substitution in positions 8, 9, 10 and 12 of the carborane icosahedron; the structure of 8-ClHg-3,6-Cp_2-3,6,1,2-$Co_2C_2B_8H_9$ was determined by an X-ray diffraction study.

The exchange of hydrogen atom for mercury as a result of the interaction of aromatic substrates with mercury salts (mercuration) is one of the most widespread reactions in organomercury chemistry. As to mercuration of icosahedral boron-containing clusters, reported studies have dealt mostly with carboranes(12),[1] although the mercuration of $B_{12}H_{12}^{2-}$ anion has also been reported.[2] Only a few examples of mercuration of icosahedral metallacarboranes, *viz*. monocobaltacarboranes[3,4] and 3-Cp-3,1,2-$FeC_2B_9H_{11}$,[5] have been described. It was shown[3–5] that the main products of the mercuration of icosahedral monometallacarboranes are 9-mercurated complexes, in which the mercury atom is bonded to the boron atom that occupies one of the two positions of the C_2B_9 cage most remote from the carbon atom.

No data on the mercuration of icosahedral bimetallacarboranes have as yet been published. In the present communication we report the synthesis and structural characterization of the products of mercuration of 3,6-Cp_2-3,6,1,2-$Co_2C_2B_8H_{10}$ **1**, and on the reactivity of **1** towards such metallating agents as mercury(II) salts and thallium(III) trifluoroacetate.

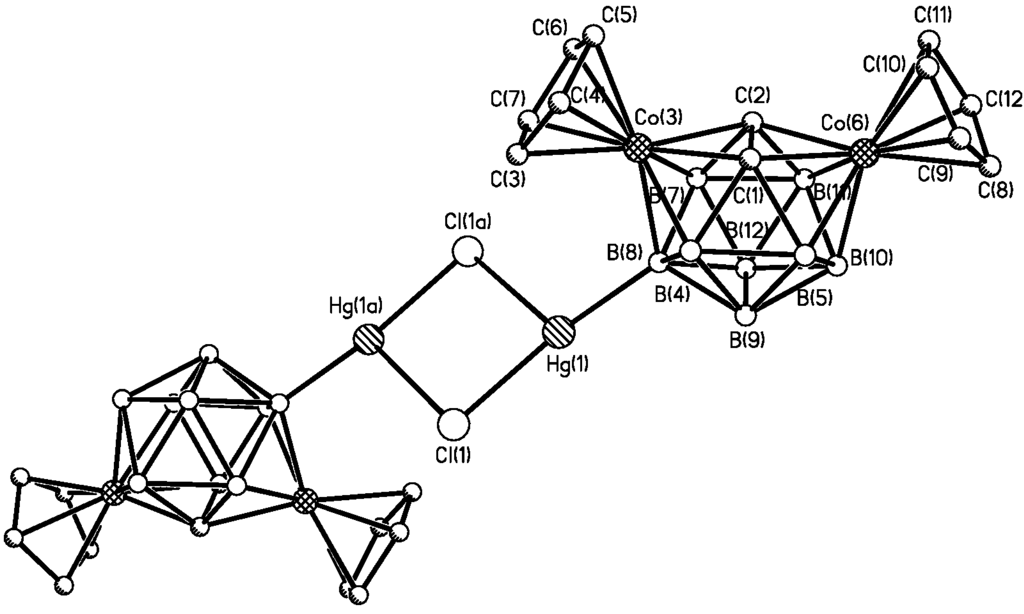

Fig. 1 Structure of dimeric molecular aggregates in the crystal of **2**. Selected interatomic distances, A: Hg(1)–Cl(1) 2.396(6), Hg(l)···Cl(1a) 3.131(6), Hg(1)–B(8) 2.11(2), Co(3)–C(1) 2.01(2), Co(3)–C(2) 2.01(2), Co(3)–B(4) 2.06(2), Co(3)–B(7) 2.03(2), Co(3)–B(8) 2.09(2), Co(6)–C(1) 2.01(2), Co(6)–C(2) 2.00(2), Co(6)–B(5) 2.06(2), Co(6)–B(10) 2.07(2), Co(6)–B(11) 2.05(2), Co–C(Cp) 2.01–2.12.

We surmised that the introduction of two CpCo moieties into the icosahedral cage would, firstly, make mercuration possible under milder conditions as compared with those required for carboranes(12) and, secondly, increase the probability of mercuration of the B–H bond at position 8 of the icosahedral cage. We did indeed find that interaction of equivalent amounts of **1** and mercury(II) acetate under mild conditions[†] affords two monomercurated complexes **2** and **3** in the ratio 1:1.2 (Scheme 1), which contain mercury atoms bonded to boron atoms in positions 8 and 9, respectively. The structure of **2** was determined by means of ^{1}H and ^{11}B NMR spectroscopy and X-ray diffraction studies[‡] and the structure of **3** was deduced from the NMR data.[§]

The molecular structure of **2** is shown in Fig. 1. The metallacarborane cage is considerably distorted from an ideal icosahedron due to the presence of two metal atoms in the icosahedron. The edges involving Co atoms are naturally much longer than other interatomic distances in the cage, which results in significant angular changes. In particular, the dihedral angle between the triangular planes Co(3)C(1)C(2) and Co(6)C(1)C(2) is decreased to 11.2° as compared to the corresponding angles $\sim 40°$ in the ideal icosahedron. The Hg(1)–B(8) bond length of 2.11(2) A is almost equal to the Hg–B bond length [2.13(1) A] reported in the structure of (*m*-carboran-9-yl)(diisopropoxy-phosphoryl)mercury.[8] An important feature of structure **2** is the non-bonded Hg···Cl interaction at 3.131(6) A, which is quite typical of organic derivatives of mercury.[9] This interaction links the molecules of **2** into centrosymmetric dimers in the crystal.

Mercuration of **1** under more severe electrophilic conditions [excess Hg(OAc)$_2$, AcOH] results in the formation of the polymercurated complex **4**, containing four mercury atoms per molecule of substrate. On the basis of the NMR data[¶] it was concluded that the mercury atoms in **4** are bonded to the boron atoms at positions 8,10 and 9,12 of the metallacarborane cluster.

Previously, we reported that thallium(III) trifluoroacetate (TTFA)[10] and thallium(III) acetate sesquihydrate in trifluoroacetic acid (TFA)[11] are convenient thallating reagents for the thallation of *o*- and *m*-carboranes. However, we found that the reaction of **1** with TTFA in TFA results in oxidation of

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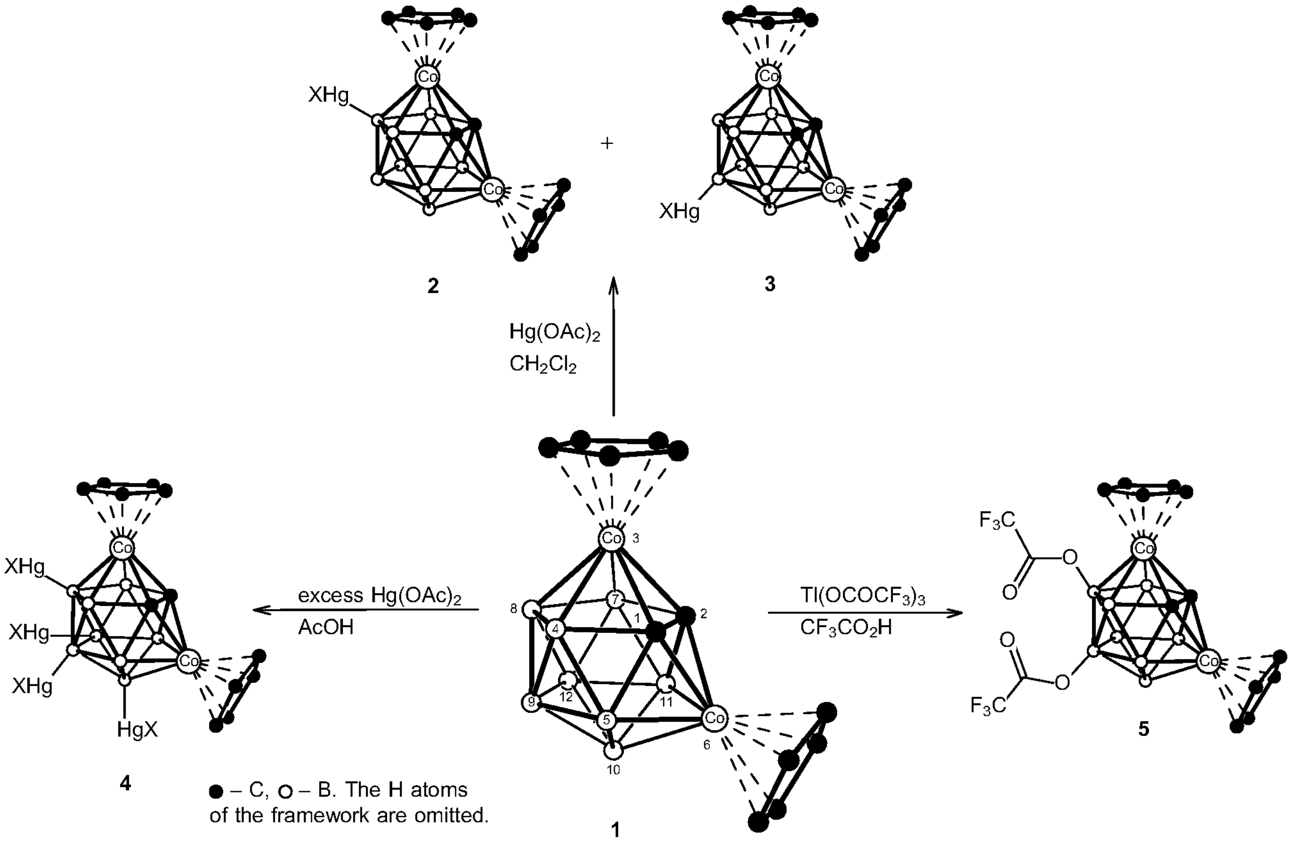
[†] *Typical procedure*: powdered mercury(II) acetate (1 mmol) was added to solution of **1** (1 mmol) in CH$_2$Cl$_2$ and the resulting mixture was stirred in boiling solvent until complete disappearance of starting Hg(OAc)$_2$ (Gilman test). The solution was then evaporated and the resulting residue was washed with water, dissolved in THF and the THF solution poured into an aqueous solution of NaCl (5 g). The precipitate formed was filtered off, dried *in vacuo*, dissolved in CH$_2$Cl$_2$ and separated by column chromatography on silica gel. M.p.: **2** 310 °C (decomp.), **3** 327 °C (decomp.).

[‡] *Crystal data for* **2**: C$_{12}$H$_{19}$B$_8$ClCo$_2$Hg·0.5CH$_2$Cl$_2$, monoclinic, space group $P2_1/n$, at 193 K $a = 6.845(3)$, $b = 21.848(8)$, $c = 12.827(4)$ A, $\beta = 98.79(2)°$, $D_c = 2.260$ g cm^{-3}, $Z = 4$, $F(000) = 1208$. 3391 independent reflections were measured with a Syntex P2$_1$ automated diffractometer (193 K, λMoKα graphite monochromator, θ/2θ-scan, $2\theta \leqslant 50°$, absorption correction using the DIFABS method[6]). The structure was determined by direct methods and refined by a full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms. All hydrogen atoms and the solvating CH$_2$Cl$_2$ molecule (which was disordered over two positions, related by the inversion centre), were located in the difference Fourier synthesis. Hydrogen atoms were refined in the final cycles in the riding model approximation with a common $U_{\text{iso}} = 0.10(2)$ A^2. The refinement converged at $R = 0.0803$, $R_w = 0.0967$ for 2470 reflections with $F^2 \geqslant 3\sigma$. All calculations were carried out using the SHELXTL PLUS program package[7] on an IBM PC computer. Atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (see Notice to Authors, *Mendeleev Commun.*, 1994, issue 1).

[§] *NMR data* [chemical shifts δ in ppm, *J*(BH) coupling constants in Hz; assignment] for **2** ^{1}H ([^{2}H$_6$]DMSO): 5.76 (Cp), 5.59 (Cp), 5.33 ($J_{^1\text{H}-^{199}\text{Hg}} = 75$; C–H$_{\text{carb}}$); ^{11}B ([^{2}H$_6$]DMSO): 25.62 ($J_{^{11}\text{B}-^{199}\text{Hg}} = 2214$; B8), 21.87 (151; B10), −1.47 (149; B4,5,7,11), −7.6 (134; B9,12); for **3** ^{11}B ([^{2}H$_6$]DMSO): 18.05 (80; B8,10), −2.15 (130; B4,5,7,11), −4.06 ($J_{^{11}\text{B}-^{199}\text{Hg}} = 2296$), −9.06 (154; B12).



Scheme 1

the B–H bonds at positions 8 and 10 in **1**, and the corresponding bis(trifluoroacetate) **5**[¶] is formed.

Thus, novel polymetallacarborane clusters containing mercury atoms bonded to boron atoms by σ-bonds and two cobalt atoms bound to the carborane framework *via* π-bonds have been prepared.

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[¶] *NMR data* [chemical shifts δ (^{1}H and ^{11}B) in ppm, J(BH) coupling constants in Hz; assignment] for **4** ^{1}H ([^{2}H$_6$]DMSO): 5.96 (Cp), 5.27 (CH$_{\text{carb}}$); ^{11}B{^{1}H} ([^{2}H$_6$]DMSO): 25.92 ($J_{^{11}\text{B}-^{199}\text{Hg}} = 2587$; B8,10), −0.13 (B4,5,7,11), −2.02 ($J_{^{11}\text{B}-^{199}\text{Hg}} = 2441$; B9,12); for **5** ^{1}H: 5.56 (Cp), 5.13 (CH$_{\text{carb}}$); ^{11}B: 25.66 (0; B8,10), −5.86 (153; B4,5,7,11), −10.48 (148; B9,12). IR for **5** (CH$_2$Cl$_2$, ν/cm^{-1}): 1680–1780 (C=O); 2580–2615 (B–H$_{\text{carb}}$).