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Preliminary communication

Rearrangements of bimetallic cobaltacarboranes

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SUMMARY

The thermal migration of cobalt atoms in cobaltacarboranes is reported and the spectral similarities of the new bimetallic compounds are discussed.

The thermally induced migration of carbon atoms over the surface of a polyhedral cobaltacarborane is now a well established phenomenon[1–3]. However, while it is possible that cobalt atom migration may also be involved in these rearrangements, such a process has not been proven to occur. A study of some bimetallic cobaltacarboranes has established that cobalt atom migrations are possible. Thus the green compound[4] 2,6,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$ (I)** is converted to the red compound II at 280°. The ^{1}H NMR spectrum*** of II indicated that the carborane CH groups were equivalent as were the cyclopentadienyl ligands while the 80.5 MHz ^{11}B NMR spectrum contained three doublets of relative intensity 2/2/2. Assuming that the carbon atoms of I do not migrate to higher coordinate vertices, the structure of II is uniquely defined as 2,7,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$ by the NMR data. The conversion of I to II thus involves the migration of a cobalt atom from a vertex adjacent to cobalt to a vertex separated from cobalt by one boron atom.

The eleven-vertex polyhedral metallocarborane 1,7,2,4-$(C_5H_5)_2Co_2C_2B_7H_9$ (III) rearranges to 1,7,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (IV) at 98° by means of a carbon atom migration. At 150° IV may in turn be rearranged to 1,10,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (V) by means of a cobalt atom migration. The icosahedral species $(C_5H_5)_2Co_2C_2B_8H_{10}$ also

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**The numbers preceding the formulas refer in order to the positions of the heteroatoms (cobalt and carbon) listed in the formulas using the geometries specified in ref. 5.

***The compounds described here were characterized using mass, electronic, ^{1}H and ^{11}B NMR spectral data. The elemental composition has been determined by either chemical analysis or high resolution mass spectrometry.

undergo a variety of thermal rearrangements involving migration of both cobalt and carbon atoms. Hence the red $(C_5H_5)_2Co_2C_2B_8H_{10}$ (VI) can be formed from the red 1,7,2,3-$(C_5H_5)_2Co_2C_2B_8H_{10}$ [6] (VII) at 340° by a carbon atom migration or from the green 1,2,3,6-$(C_5H_5)_2Co_2C_2B_8H_{10}$ [4] (VIII) at 250° by a cobalt atom migration. At 650° VI affords a complex mixture of isomeric products formed by a combination of carbon and cobalt atom migrations; these species are under further investigation.

The bimetallic cobaltacarboranes isolated so far fall into two distinct classes. The class A compounds exhibit an absorption band at longer wavelength than 750 nm in their electronic spectra and are green in color. In contrast, the class B compounds do not exhibit electronic spectral resonances at wavelengths greater than 540 nm and are red or orange in color. X-ray diffraction studies on two class A compounds[7] (*viz.* 2,6,1,10-$(C_5H_5)_2Co_2C_2B_8H_{10}$ and 1,2,3,6-$(C_5H_5)_2Co_2C_2B_8H_{10}$) have established that the cobalt atoms occupy adjacent vertices in these compounds. The structures of two class B compounds (*viz.* 2,7,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$ and 1,12,2,9-$(C_5H_5)_2Co_2C_2B_8H_{10}$) are uniquely defined by the NMR data while the structures of the "canastide" containing species 1,7,2,3-$(C_5H_5)_2Co_2C_2B_8H_{10}$ and of 1,7,2,3-$(C_5H_5)_2Co_2C_2B_3H_4(CH_3)$ are defined by X-ray diffraction studies[8,9]. These four class B compounds thus contain nonadjacent cobalt atoms. In view of these observations it is possible to propose the following generalization: compounds of general formula $(C_5H_5)_2Co_2C_2B_nH_{n+2}$, where n = 6, 7, 8, in which the cobalt atoms occupy adjacent vertices will exhibit an absorption at longer wavelength than ca. 540 nm in their electronic spectra and will be green in color; compounds which do not have an absorption at longer wavelengths than ca. 540 nm and are red or orange in color do not contain cobalt atoms in adjacent vertices.

Although a more extensive comparison is precluded by the absence of electronic spectral data[10], the colors of 1,8,5,6-$(C_5H_5)_2Co_2C_2B_5H_7$ and 2,4,3,10-$(C_5H_5)_2Co_2C_2B_6H_8$ (compounds V and VI in reference 10) indicate they are of class B in accord with their proposed structures. However, the red compound $(C_5H_5)_2Co_2C_2B_4H_6$ (compound IV in reference 10) is also presumably of class B, suggesting that the cobalt atoms occupy nonadjacent rather than adjacent vertices as proposed. Except in this one case the cobaltacarboranes known at present bear out the above generalization, *i.e.*, the structures proposed on the basis of mass, ^1H, and ^{11}B NMR spectral data, or determined by X-ray diffraction methods, conform to the suggested relationship between the electronic spectral data and the relative separation of the cobalt atoms.

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