# ORGANOMETALLICS

# Facile Isomerization and Unprecedented Decarbonation of Metallacarboranes with Fluorinated Aryl Substituents<sup>+</sup>

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Supporting Information



We recently described the synthesis and characterization of a series of icosahedral carboranes with fluorinated aryl C substituents,<sup>1</sup> deliberately targeted as potential precursors for supraicosahedral (hetero)carboranes. Of these the most promising compound, on the basis of a combination of NMR spectroscopic, computational, and electrochemical data, was  $1,2-(4'-F_3CC_6F_4)_2-1,2$ -closo- $C_2B_{10}H_{10}$  (I). We now report that reduction and subsequent metalation of I with {CpCo} and {Cp\*Co} fragments affords 4,1,12-CoC<sub>2</sub>B<sub>10</sub> supraicosahedral products which are the result of unprecedented room temperature (or below) isomerization. The {Cp\*Co} reaction additionally results in a monocarbon metallacarborane which is the result of a unique decarbonation reaction.

dimetallacarborane that remarkably has lost a cage C vertex.

Reaction of a THF solution of I, previously reduced with 2 equiv of sodium naphthalenide, with  $Na[C_5H_5]$  and  $CoCl_2$ , followed by aerial oxidation, affords the orange cobaltacarborane 1 as the only isolable product.<sup>2</sup> Compound 1 was initially characterized by microanalysis, mass spectrometry, and <sup>1</sup>H, <sup>11</sup>B and <sup>19</sup>F NMR spectroscopy. Conventionally, reduction and subsequent metalation of 1,2-closo- $C_2B_{10}$  species affords 4,1,6-MC $_2B_{10}$ docosahedral products<sup>3</sup> which are asymmetric in the solid state<sup>4</sup> but  $C_s$  symmetric in solution via a double diamond-square-diamond (DSD) fluxional process that is well understood.<sup>3,5</sup> However, spectroscopic analysis of 1 clearly suggested that it is asymmetric in solution. Thus, in the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum in acetone- $d_6$ are eight resonances with the relative integrals 2:1:1:1:1:1:2 (from high frequency to low frequency) and the <sup>13</sup>C spectrum includes two  $C_{cage}$  resonances at 67.0 and 69.0 ppm. Although initial inspection of the <sup>19</sup>F spectrum suggests only one unique 4'-F<sub>3</sub>CC<sub>6</sub>F<sub>4</sub> substituent, expansion of the multiplet (due to the  $CF_3$  group) centered on -57.3 ppm clearly shows it to be two

overlapping triplets. An X-ray diffraction study<sup>6</sup> ultimately revealed 1 to be the 4,1,12-MC<sub>2</sub>B<sub>10</sub> isomer 1,12-(4'-F<sub>3</sub>CC<sub>6</sub>F<sub>4</sub>)<sub>2</sub>-4-Cp-4,1,12-closo-CoC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (Figure 1). It is well established that 4,1,12-MC<sub>2</sub>B<sub>10</sub> metallacarboranes can be prepared from either 4,1,6-<sup>3,7</sup> or 4,1,10-analogues<sup>8</sup> by thermolysis (the former proceeding via the 4,1,8-isomer), but the direct formation of a 4,1,12-MC<sub>2</sub>B<sub>10</sub> isomer from an *o*-carborane derivative at only room temperature is unprecedented. We suggest that the initial product of reduction and metalation of I is, indeed, a 4,1,6-MC<sub>2</sub>B<sub>10</sub> species but that this spontaneously isomerizes to the thermodynamically preferred 4,1,12-isomer. Although the precise mechanism by which 4,1,6-MC<sub>2</sub>B<sub>10</sub> sequentially isomerizes to 4,1,8- and 4,1,12-forms has not been determined, there is no reason to believe that the same process does not happen here, in which case the barriers to isomerization must be considerably reduced due to either steric or electronic (or both) influences of the fluorinated aryl substituents.9

When I is stoichiometrically reduced (2e) and treated with  $Na[C_5Me_5]$  and  $CoCl_2$ , three compounds are isolated following workup.<sup>11</sup> The major product (24%), 2, was ultimately shown simply to be the modified carborane 1,2-(4'-F<sub>2</sub>{C<sub>5</sub>Me<sub>5</sub>}- $CC_6F_4$ )<sub>2</sub>-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>,<sup>12</sup> but minor products 3 (6%) and 4 (8%) are cobaltacarboranes.

Compound 3 was characterized spectroscopically. Although single crystals of suitable quality for a diffraction study could not be obtained, we confidently identify 3 as  $1,12-(4'-F_3CC_6F_4)_2-4 Cp^*-4,1,12$ -closo- $CoC_2B_{10}H_{10}$ , the simple  $Cp^*$  analogue of 1.

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**Figure 1.** Molecular structure of **1** with most atoms labeled. B2 lies between C1 and B6, B9 between B5 and C12, and B7 between B3 and B10. Atoms (except H) are shown as 50% probability ellipsoids. Selected distances (Å): Co4-C1 = 2.069(3), Co4-B2 = 2.156(4), Co4-B6 = 2.127(4), Co4-B10 = 2.125(4), Co4-B7 = 2.170(4), Co4-B3 = 2.247(4).

This conclusion is based on the very similar <sup>11</sup>B NMR chemical shift ranges of 1 and 3, +8 to -13 ppm and +9 to -14 ppm, respectively, and the notable absence in 3 of a high-frequency resonance, ca. +21 ppm, characteristic of a 4,1,8-MC<sub>2</sub>B<sub>10</sub> species.<sup>3</sup> The detail of the pattern of the <sup>11</sup>B spectrum of 3 (1:1:1:1:1:2:1:2) is slightly different from that of 1, but in both cases the integral-2 resonances are merely accidental 1 + 1 coincidences.

The third reaction product, compound 4, was fully characterized. Two different {Cp\*Co} fragments are implied by the <sup>1</sup>H NMR spectrum, which also contains resonances attributable to THF but at relatively high frequencies, suggesting a formal  $[C_4H_8O]^+$  unit bound to the cage through a trisubstituted oxygen atom. The <sup>11</sup>B spectrum reveals six resonances (1:1:1:2:2:2) the highest frequency resonance of which is only a singlet, and this suggests the presence of only nine B atoms, one of which does not carry an exo H atom. The exact nature of 4 was established by a crystallographic study (Figure 2).<sup>13</sup>

Compound 4 is the 12-vertex, distorted-icosahedral dimetallamonocarborane 1-(4'-F<sub>3</sub>CC<sub>6</sub>F<sub>4</sub>)-2,8-Cp\*<sub>2</sub>-12-THF-2,8,1-closo-Co<sub>2</sub>CB<sub>9</sub>H<sub>8</sub>, formally a zwitterionic species with charges of 1- on the cage and 1+ on O121. It is related to the reduced precursor I by the following five processes, listed in random order with no implication of a reaction sequence: addition of the first {Cp\*Co} fragment, addition of the second {Cp\*Co} fragment, loss of a {BH} fragment, loss of a { $C(4'-F_3CC_6F_4)$ } fragment, and transformation of  $\{BH\}$  into  $\{B(THF)\}$ . Of these processes the loss of the  $\{C(4'-F_3CC_6F_4)\}$  fragment is the most remarkable. Carbon vertex loss (decarbonation) is rare in carborane chemistry. Štíbr et al. have described the formation of arachnomonocarboranes from  $[7,9-nido-C_2B_{10}H_{12}]^{2-}$  in the presence of Lewis base,<sup>14,15</sup> and Xie has reported decarbonation of supraicosahedral carboranes under similar conditions,<sup>16</sup> but as far as we are aware the formation of a closo metallamonocarborane by decarbonation on metalation of reduced dicarborane is unprecedented.

The 2,8,1- $M_2CB_9$  icosahedral isomer has only been seen once previously, the result of spontaneous direct insertion of a pendant  ${Pt(dppe)}^0$  fragment into an 11-vertex closo MnCB<sub>9</sub> cluster by Stone et al.<sup>17</sup> Current studies are directed toward the synthesis of further homo- and heterobimetallic examples of this cluster



**Figure 2.** Molecular structure of **4** with most atoms labeled. The heteroborane numbering follows the standard convention.<sup>19</sup> Atoms (except H) are shown as 50% probability ellipsoids. Selected distances (Å): Co2-C1 = 2.081(6), Co2-B3 = 2.065(7), Co2-B7 = 2.107(7), Co2-B11 = 2.089(7), Co2-B6 = 2.029(7), Co8-B3 = 2.056(7), Co8-B4 = 2.036(7), Co8-B9 = 2.071(7), Co8-B12 = 2.051(7), Co8-B7 = 2.079(7), B12-O121 = 1.555(7).

architecture by the reduction/metalation approach and toward an understanding of the sequence of events involved in their formation.  $^{18}$ 

# ASSOCIATED CONTENT

**Supporting Information.** CIF files giving crystallographic data for compounds **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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# DEDICATION

<sup>+</sup>In memory of F. Gordon A. Stone, a true giant of organometallic chemistry.

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(2) A dry, oxygen-free THF solution (10 mL) of I (0.40 g, 0.69 mmol) was treated with 1.39 mmol (2.1 equiv) of sodium naphthalenide as a THF solution at 0 °C. NaCp (1.41 mL of a 2.0 M solution in THF, 2.82 mmol) and then  $CoCl_2$  (0.333 g, 3.92 mmol) were added, and the reactants were stirred at room temperature for 18 h. Air was drawn through the mixture for 30 min, and all volatiles were removed in vacuo. The residue was extracted into dichloromethane (20 mL) and the extract filtered. All volatiles were again removed in vacuo. Naphthalene and any

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unreacted carborane were removed by washing with 40–60 °C petroleum ether. Preparative thin-layer chromatography (TLC) with dichloromethane/40–60 °C petroleum ether (2/5) as eluent yielded a single orange band, compound 1 ( $R_f$  = 0.63, 0.054 g, 11%). The yield is increased to 16% if the reaction mixture is heated to reflux before oxidation. Anal. Found: C, 36.0; H, 2.10. Calcd for C<sub>21</sub>H<sub>15</sub>B<sub>10</sub>CoF<sub>14</sub>: C, 36.0; H, 2.16. <sup>1</sup>H NMR (acetone- $d_{6}$ , 298 K):  $\delta$  5.81 (s, C<sub>5</sub>H<sub>5</sub>) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (acetone- $d_{6}$ , 298 K):  $\delta$  7.43 (2B), 4.65 (1B), 3.15 (1B), 0.08 (1B), -4.10 (1B), -5.76 (1B), -9.00 (1B), -13.60 (2B) ppm. <sup>19</sup>F NMR (acetone- $d_{6}$ , 298 K):  $\delta$  -56.3 (m [2 × t on expansion], 6F, CF<sub>3</sub>), -133.5 (app s, 4F, o-F), -142.8 (m, 4F, m-F) ppm. Partial <sup>13</sup>C NMR (acetone- $d_{6}$ , 298 K):  $\delta$  69.0 (br, 1C, C<sub>cage</sub>), 67.0 (br. 1C, C<sub>cage</sub>). EI-MS: envelope centered on m/z 701 (M<sup>+</sup>).

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(6) Crystal data for 1:  $C_{21}H_{15}B_{10}CoF_{14}$ , M = 700.36, monoclinic, *Cc*, a = 24.237(3) Å, b = 12.4207(17) Å, c = 9.0234(12) Å,  $\beta = 105.478(7)^{\circ}$ , V = 2617.9(6) Å<sup>3</sup>, Z = 4,  $D_c = 1.777$  Mg m<sup>-3</sup>,  $\mu = 0.771$  mm<sup>-1</sup>, F(000) = 1376, data to  $\theta_{max} = 25.65^{\circ}$  collected at 100(2) K on a Bruker X8 diffractometer using Mo K $\alpha$  radiation, 4860 independent reflections out of 17 205 measured,  $R_{int} = 0.0499$ , R1 = 0.0376, wR2 = 0.0603, S = 1.022for 4115 data with  $I > 2\sigma(I)$ , absolute structure parameter 0.251(12).

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(9) It is well-established in icosahedral metallacarborane chemistry that steric crowding can lead to low-temperature isomerizations,<sup>10</sup> and clearly 1,6-(4'-F<sub>3</sub>CC<sub>6</sub>F<sub>4</sub>)<sub>2</sub>-4-Cp-4,1,6-*closo*-CoC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> would be somewhat more sterically crowded than 4-Cp-4,1,6-*closo*-CoC<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (circumstantial evidence of this is that in 1 the Cp ligand leans away from the C<sub>7</sub>F<sub>7</sub> substituent on C1, making a dihedral angle of 10.9° with the BSB8B13C12B9 reference plane, whereas the equivalent angle to the BSB8B13B12B9 plane in 4-Cp-4,1,6-*closo*-CoC<sub>2</sub>B<sub>10</sub>H<sub>12</sub><sup>4</sup> is only 4.3°). On the other hand, it is not intuitively obvious that 1 would be any less sterically crowded than the putative 1,8-(4'-F<sub>3</sub>CC<sub>6</sub>F<sub>4</sub>)<sub>2</sub>-4-Cp-4,1,8-*closo*-CoC<sub>2</sub>B<sub>10</sub>H<sub>10</sub> species from which it presumably forms.

(10) E.g.: Baghurst, D. R.; Copley, R. C. B.; Fleischer, H.; Mingos, D. M. P.; Kyd, G. O.; Yellowlees, L. J.; Welch, A. J.; Spalding, T. R.; O'Connell, D. J. Organomet. Chem. **1993**, 447, C14–C17.

(11) I (0.50 g, 0.87 mmol) in THF (10 mL) was treated with 1.82 mmol (2.1 equiv) of sodium naphthalenide. NaCp\* (5.20 mL of a 0.5 M solution in THF, 2.60 mmol) and CoCl<sub>2</sub> (0.293 g, 3.45 mmol) were added and the reactants stirred at room temperature for 18 h. After 30 min of aerial oxidation volatiles were removed and the residue was washed with 40-60 °C petroleum ether. Column chromatography on silica with dichloromethane/40–60 °C petroleum ether (1/1) as eluent afforded pale yellow 2 (0.169 g, 24%) and an orange mixture that was separated by preparative TLC, with dichloromethane/40-60 °C petroleum ether (2/3) as eluent, to yield 3 ( $R_f = 0.75, 0.037$  g, 6%) and 4  $(R_f = 0.27, 0.058 \text{ g}, 8\%)$ . Data for 2 are as follows. Anal. Found: C, 53.0; H, 4.85. Calcd for C<sub>36</sub>H<sub>40</sub>B<sub>10</sub>F<sub>12</sub>: C, 53.5; H, 4.98. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  1.85 (s, 12H, C<sub>5</sub>Me<sub>5</sub>), 1.46 (s, 12H, C<sub>5</sub>Me<sub>5</sub>), 1.25 (s, 6H, C<sub>5</sub>Me<sub>5</sub>) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  –1.97 (2B), –9.89 (8B) ppm. NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  -94.92 (m, 4F, CF<sub>2</sub>), -135.29 (m, 4F, o-F), -138.03 (m, 4F, m-F) ppm. EI-MS: envelope centered on m/z 809 (M<sup>+</sup>). Data for 3 are as follows. Anal. Found: C, 41.2; H, 3.28. Calcd for  $\begin{array}{l} C_{26}H_{25}B_{10}\text{CoF}_{14}: \text{ C, 40.5; H, 3.27. }^{1}\text{H NMR} (\text{CDCl}_{3}, 298 \text{ K}): \delta 1.71 \\ (\text{s, } C_{5}Me_{5}) \text{ ppm. }^{11}\text{B}\{^{1}\text{H}\} \text{ NMR} (\text{CDCl}_{3}, 298 \text{ K}): \delta 8.78 (1B), 4.73 (1B), \end{array}$ 1.93 (1B), 0.12 (1B), -2.21 (1B), -7.98 (2B), -9.76 (1B), -14.00 (2B) ppm. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  –56.55 (m, 6F, CF<sub>3</sub>), –131.31 (m, 4F, o-F), -141.26 (m, 4F, m-F) ppm. EI-MS: envelope centered on *m*/*z* 771 (M<sup>+</sup>). Data for 4 are as follows. Anal. Found: C, 48.6; H, 5.83. Calcd for C<sub>32</sub>H<sub>46</sub>B<sub>9</sub>Co<sub>2</sub>F<sub>7</sub>O: C, 48.4; H, 5.83. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  4.33 (M, 4H, THF), 2.11 (m, 4H, THF), 1.76 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.48

(s, 15H,  $C_5Me_5$ ) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  27.15 (1B, B12), 19.17 (1B, 17.32 (1B), 4.04 (2B), 0.57 (2B), -18.74 (2B) ppm. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  -56.07 (m, 3F,  $CF_3$ ), -120.05 (m, 2F, *o*-F), -144.39 (m, 2F, *m*-F) ppm. EI-MS: envelopes centered on *m*/*z* 795 (M<sup>+</sup>) and 723 (M<sup>+</sup> – THF).

(12) Crystal data for 2:  $C_{36}H_{40}B_{10}F_{12}$ , M = 808.78, triclinic,  $P\overline{I}$ , a = 14.5973(13) Å, b = 16.0164(14) Å, c = 18.3603(16) Å,  $\alpha = 70.015(4)^{\circ}$ ,  $\beta = 79.973(4)^{\circ}$ ,  $\gamma = 89.535(4)^{\circ}$ , V = 3966.3(6) Å<sup>3</sup>, Z = 4,  $D_c = 1.354$  Mg m<sup>-3</sup>,  $\mu = 0.113$  mm<sup>-1</sup>, F(000) = 1656,  $\theta_{max} = 25.49^{\circ}$ , 100(2) K,  $18\ 020/69\ 711$  reflections,  $R_{int} = 0.0605$ , R1 = 0.0835, wR2 = 0.2115, S = 1.146 for 14 072 data with  $I > 2\sigma(I)$ .

(13) Crystal data for 4:C<sub>32</sub>H<sub>46</sub>B<sub>9</sub>Co<sub>2</sub>F<sub>7</sub>O, M = 794.84, orthorhombic, *Pbca, a* = 12.8521(5) Å, *b* = 16.2817(6) Å, *c* = 33.9667(12) Å, *V* = 7107.7(5) Å<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 1.486 Mg m<sup>-3</sup>,  $\mu$  = 0.998 mm<sup>-1</sup>, *F*(000) = 3264,  $\theta_{max}$  = 25.68°, 100(2) K, 6737/39 726 reflections, *R<sub>int</sub>* = 0.1167, R1 = 0.0899, wR2 = 0.1459, *S* = 1.422 for 4792 data with *I* > 2 $\sigma$ (*I*).

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