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Tricarbon Carborane Chemistry. 3. Synthesis of 6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_{10}$ and Studies of Carbon Atom Rearrangements in 11-Vertex Metallatricarbaborane Complexes

Carole A. Plumb and Larry G. Sneddon*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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The ^{13}C-labeled tricarbon carborane anion 6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_9^-$ has been synthesized by the reaction of $CH_3{}^{13}CN$ with the 4,6-$C_2B_7H_{12}^-$ anion. Protonation of the anion then gives the neutral tricarbon carborane 6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_{10}$ (1). ^{13}C–^{13}C and ^{13}C–^{11}B couplings were observed, and their values allow estimations of the cage-carbon bonding interactions. The labeled anion was used to synthesize the labeled metallatricarbaboranes 1-(η-C_5H_5)Fe-2-CH_3-2-^{13}C-2,3,4-$C_3B_7H_9$ (**2**-^{13}C), 1-(η-C_5H_5)Fe-4-CH_3-4-^{13}C-2,3,4-$C_3B_7H_9$ (**3**-^{13}C), *commo-Fe*-(1-Fe-2-CH_3-2-^{13}C-2,3,5-$C_3B_7H_9$)$_2$ (**6**-^{13}C), *commo-Fe*-(1-Fe-5-CH_3-5-^{13}C-2,3,5-$C_3B_7H_9$)$_2$ (**7**-^{13}C), *commo-Fe*-(1-Fe-5-CH_3-5-^{13}C-2,3,5-$C_3B_7H_9$)(1-Fe-4-CH_3-4-^{13}C-2,3,4-$C_3B_7H_9$) (**8**-^{13}C), and *commo-Fe*-(1-Fe-10-CH_3-10-^{13}C-2,3,10-$C_3B_7H_9$)$_2$ (**9**-^{13}C). Studies of the processes by which **2**-^{13}C is converted to **3**-^{13}C and by which **6**-^{13}C is converted to **7**-^{13}C, **8**-^{13}C, or **9**-^{13}C show that the reactions occur by means of cage-carbon skeletal rearrangements, rather than direct methyl migrations.

Introduction

In the two preceding papers[1,2] the syntheses of a series of mono- and bis(cage) metallatricarbaborane complexes derived from the tricarbon carborane anion 6-CH_3-5,6,9-$C_3B_7H_9^-$ were described. An apparent "methyl migration" reaction was observed in the iron and cobalt complexes by which a methyl at the C2 carbon vertex adjacent to the metal "migrated" to the C4(5) carbon position.

$$\underset{\mathbf{2}}{1\text{-}(\eta\text{-}C_5H_5)Fe\text{-}2\text{-}CH_3\text{-}2,3,4\text{-}C_3B_7H_9} \rightarrow \underset{\mathbf{3}}{1\text{-}(\eta\text{-}C_5H_5)Fe\text{-}4\text{-}CH_3\text{-}2,3,4\text{-}C_3B_7H_9} \tag{1}$$

$$\underset{\mathbf{6}}{commo\text{-}Fe\text{-}(1\text{-}Fe\text{-}2\text{-}CH_3\text{-}2,3,5\text{-}C_3B_7H_9)_2} \rightarrow \underset{\mathbf{7}}{commo\text{-}Fe\text{-}(1\text{-}Fe\text{-}5\text{-}CH_3\text{-}2,3,5\text{-}C_3B_7H_9)_2} + \underset{\mathbf{8}}{commo\text{-}Fe\text{-}(1\text{-}Fe\text{-}5\text{-}CH_3\text{-}2,3,5\text{-}C_3B_7H_9)\text{-}(1\text{-}Fe\text{-}4\text{-}CH_3\text{-}2,3,4\text{-}C_3B_7H_9)} \tag{2}$$

$$\underset{\mathbf{11}}{commo\text{-}Co\text{-}(1\text{-}Co\text{-}2\text{-}CH_3\text{-}2,3,5\text{-}C_3B_7H_9)_2} \rightarrow \underset{\mathbf{10}}{commo\text{-}Co\text{-}(1\text{-}Co\text{-}2\text{-}CH_3\text{-}2,3,5\text{-}C_3B_7H_9)\text{-}(1\text{-}Co\text{-}4\text{-}CH_3\text{-}2,3,5\text{-}C_3B_7H_9)} \tag{3}$$

Thus, in each system the methyl group that was originally present at the four-coordinate carbon in 6-CH_3-5,6,9-$C_3B_7H_9^-$ and in **2**, **6**, and **11** was observed to isomerize to the adjacent five-coordinate carbon in complexes **3**, **7**, **8**, and **10**. In this paper, the results of isotopic labeling studies that were used to probe the mechanism of these and other higher temperature rearrangements observed in these complexes are reported.

Experimental Section

Except as described below, the general procedures, materials, and instrumentation for physical measurements are the same as in the preceding two papers.

^{13}C NMR spectra at 125.7 MHz were obtained on a Bruker AM-500 spectrometer equipped with the appropriate decoupling accessories. ^{13}C NMR spectra at 50.3 MHz were obtained on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. INEPT and refocused INEPT ^{13}C NMR experiments were performed with a J = 130 Hz setting at 160.5 MHz.

Synthesis of $CH_3{}^{13}CN$. The procedure reported by Ott[3] was altered in order to prepare labeled $CH_3{}^{13}CN$. A solution of methyl iodide (20.45 g, 145.9 mmol) in dimethyl sulfoxide (25.0 mL) was added slowly over 2.5 h to a stirred solution containing 10.0 g of $K^{13}CN$ in dimethyl sulfoxide (25.0 mL). After it was stirred for an additional 30 min, the mixture was vacuum-fractionated through a 0 °C trap. The $CH_3{}^{13}CN$ passing the 0 °C trap was refractionated and then checked for purity by NMR spectroscopy (5.77 g, 7.3 mL, 94% yield).

Synthesis of Na^+(6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_9$)$^-$ (Na^+1$^-$-^{13}C). Under an inert atmosphere, freshly sublimed 4,6-$C_2B_7H_{13}$ (1.0 mmol) and NaH (0.95 mmol), prepared from a 60% dispersion washed free of mineral oil with pentane, were added to a 10-mL two-neck round-bottom flask equipped with a stirbar, septum, and vacuum stopcock. The flask was evacuated and ~7 mL of $CH_3{}^{13}CN$ vacuum-distilled into the flask. The reaction mixture was then stirred at room temperature until evolution of H_2 gas had ceased. Under a N_2(g) flush, a reflux condenser was attached and the solution brought to rolling reflux. After 16 h the reaction mixture was cooled and checked for completion by ^{11}B NMR spectroscopy and then the unreacted $CH_3{}^{13}CN$ recovered by vacuum distillation into the vacuum line. The oily residue containing the Na^+(6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_9$)$^-$ was immediately dissolved in dry THF and filtered.

Synthesis of 6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_{10}$ (1-^{13}C). A solution of 0.88 mmol of Na^+(6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_9$)$^-$ in THF was added to a 25-mL round-bottom flask equipped with a stirbar. The flask was cooled at −10 °C and a 0.8-mL aliquot of a 1 M solution of HCl in Et_2O added dropwise into the stirred reaction mixture, resulting in the formation of a white precipitate. After 15 min the reaction mixture was warmed to room temperature, stirred for 5 min, and then fractionated in vacuo through −23 and −196 °C traps until all volatile materials were removed. Refractionation of the material in the −23 °C trap through a 0 °C trap removed any traces of 4,6-$C_2B_7H_{13}$ present. 6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_{10}$ (1-^{13}C) was isolated in 40% (0.35 mmol) yield in the −23 °C trap.

Syntheses of Ferratricarbaboranes 2-^{13}C and 3-^{13}C. A 0.51-mmol (66-mg) sample of $FeCl_2$ in 15 mL of THF was added to a stirred solution of 1.00 mmol of Na^+(6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_9$)$^-$ in 15 mL of THF. The reaction conditions and separation procedures were the same as those given[1] for the unlabeled

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[1] Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics*, first of two preceding papers in this issue.

[2] Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics*, second of two preceding papers in this issue.

[3] Ott, D. G. *Syntheses of Stable Isotopes of Carbon, Nitrogen, and Oxygen*; Wiley: New York, 1982; p 38.

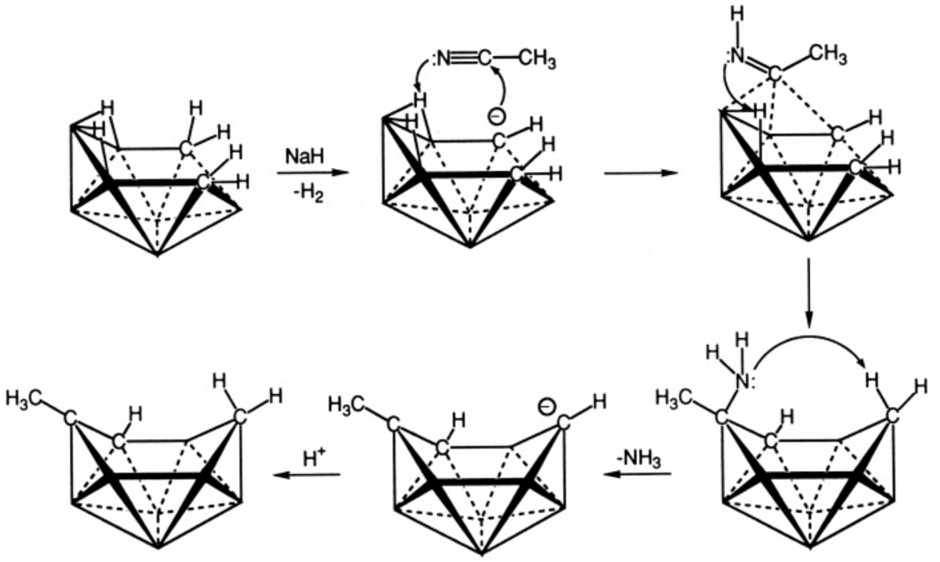

Figure 1. Proposed mechanism of formation of $6\text{-}CH_3\text{-}5,6,9\text{-}C_3B_7H_{10}$.

compounds. A crude yield of 100 mg (39% yield) of blue crystals was recovered and then recrystallized to produce 91 mg of **2**-^{13}C and 8.5 mg of **3**-^{13}C.

Syntheses of Ferratricarbaboranes 6-^{13}C, 7-^{13}C, 8-^{13}C, and 9-^{13}C. A 1.04-mmol sample of $Na^+(6\text{-}CH_3\text{-}6\text{-}^{13}C\text{-}5,6,9\text{-}C_3B_7H_9)^-$ in THF was added to 0.50 mmol of $FeCl_2$ in 15 mL of THF. The reaction conditions and separation procedures were the same as those given[2] for the unlabeled compounds. A single recrystallization from hexane gave 68 mg of **6**-^{13}C (0.21 mmol, 42%). Subsequent separation of the remaining hexane-soluble material by TLC methods generated 16 mg of **7**-^{13}C (0.05 mmol, 10%) and 26 mg of **8**-^{13}C (0.08 mmol, 16%).

Thermolysis in a sealed 5-mm glass tube under vacuum at 250 °C of 15 mg of **6**-^{13}C produced 9 mg of **9**-^{13}C.

Results

Synthesis and Properties of 6-CH$_3$-6-^{13}C-5,6,9-C$_3$B$_7$H$_{10}$. The synthetic route to *nido*-$6\text{-}CH_3\text{-}5,6,9\text{-}C_3B_7H_{10}$ reported by Kang[4] involves the initial reaction of acetonitrile with *arachno*-$4,6\text{-}C_2B_7H_{12}^-$ to produce $Na^+(6\text{-}CH_3\text{-}5,6,9\text{-}C_3B_7H_9)^-$. The mechanism proposed for this reaction is shown in Figure 1 and is thought to involve an initial nucleophilic attack by the $4,6\text{-}C_2B_7H_{12}^-$ anion at the nitrile carbon followed by reductive deammination, loss of ammonia, and monocarbon insertion into the cage. This sequence predicts that the carbon atom insertion occurs at a site adjacent to one of the two initial cage carbon atoms. This reaction, therefore, offered the opportunity to synthesize a selectively ^{13}C-labeled tricarbon carborane by reaction with labeled acetonitrile, as shown in eqs 4 and 5.

$$4,5\text{-}C_2B_7H_{12}^- + CH_3{}^{13}CN \rightarrow 6\text{-}CH_3\text{-}6\text{-}^{13}C\text{-}5,6,9\text{-}C_3B_7H_9^- + NH_3 \quad (4)$$

$$6\text{-}CH_3\text{-}6\text{-}^{13}C\text{-}5,6,9\text{-}C_3B_7H_9^- + HCl \rightarrow 6\text{-}CH_3\text{-}6\text{-}^{13}C\text{-}5,6,9\text{-}C_3B_7H_{10} \quad (5)$$

The broad-band proton spin-decoupled ^{13}C NMR spectra at 27 and −110 °C of the resulting labeled $6\text{-}CH_3\text{-}6\text{-}^{13}C\text{-}5,6,9\text{-}C_3B_7H_{10}$ product **1**-^{13}C are given in Figure 2. The ^{13}C peak assignments in the figure are consistent with those previously proposed on the basis of ^{13}C NMR studies of unlabeled $6\text{-}CH_3\text{-}5,6,9\text{-}C_3B_7H_{10}$ which had tentatively assigned a weak, broad resonance at 159.5 ppm to the quaternary carbon C6.[4] The ^{13}C NMR spectra in Figure 2 for **1**-^{13}C clearly show that the ^{13}C label is present in this resonance, confirming its assignment to the C6 carbon. The observed enrichment at this position also provides additional support for the nitrile insertion sequence in Figure 1.

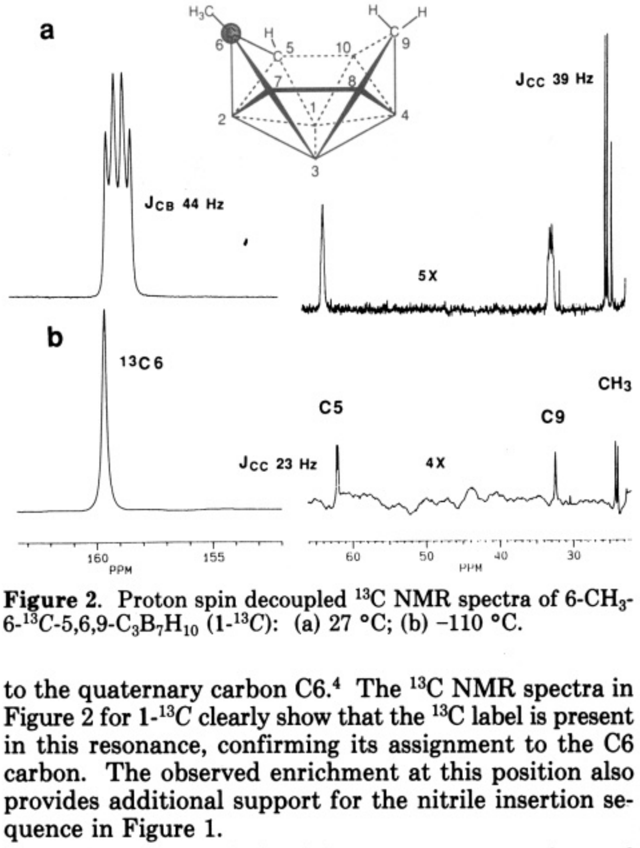

Figure 2. Proton spin decoupled ^{13}C NMR spectra of $6\text{-}CH_3\text{-}6\text{-}^{13}C\text{-}5,6,9\text{-}C_3B_7H_{10}$ (**1**-^{13}C): (a) 27 °C; (b) −110 °C.

It is significant in light of the rearrangements observed in the metallatricarbaborane complexes, outlined in eqs 1–3 and discussed below, that the methyl group in **1**-^{13}C is still attached to the ^{13}C-labeled carbon present at the cage 6-position. Any methyl rearrangement from the labeled carbon would have been detected by loss of coupling between the methyl and the 6-^{13}C carbon. However, in the ^{13}C and ^1H NMR spectra of **1**-^{13}C the methyl carbon and protons appear as the expected doublets arising from $J_{^{13}C-^{13}C}$ (39 Hz) and $^2J_{^{13}C-^1H}$ (6 Hz) couplings with the labeled carbon atom.

In addition to the exopolyhedral methyl group, the $^{13}C6$ carbon atom is directly connected to the three cage atoms B7, B2, and C5. The quartet structure of the 6-^{13}C resonance indicates, however, that it is strongly coupled to only one of the two borons, B7, with $J_{^{13}C-^{11}B} \approx 44$ Hz.[5] As shown

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[4] Kang, S. O.; Furst, G. T.; Sneddon, L. G. *Inorg. Chem.* **1989**, *28*, 2339–2347.

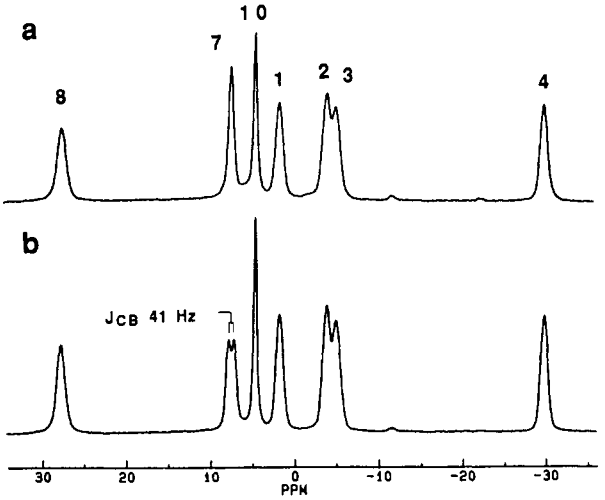

Figure 3. Proton spin decoupled ^{11}B NMR spectra of (a) 6-CH_3-5,6,9-$C_3B_7H_{10}$ (1) and (b) 6-CH_3-6-^{13}*C*-5,6,9-$C_3B_7H_{10}$ (1-^{13}*C*).

in Figure 2, at -110 °C the carbon–boron scalar coupling is quenched[6] and a singlet is observed. Likewise, at -110 °C the C5 resonance at 61.67 ppm appears as a doublet with $J_{^{13}C-^{13}C} \approx 23$ Hz, consistent with its position adjacent to ^{13}C6.

The ^{11}B NMR spectra of both ^{13}C-labeled and unlabeled 6-CH_3-5,6,9-$C_3B_7H_{10}$ are shown in Figure 3. The assignments are consistent with those made previously on the basis of the ^{11}B–^{11}B 2D NMR spectra of *nido*-6-CH_3-5,6,9-$C_3H_7H_{10}$.[4] In agreement with the ^{13}C NMR results discussed above, only one boron resonance, B7, shows the doublet structure expected for coupling with the 6-^{13}C label. The magnitude of this coupling ($J_{^{13}C-^{11}B} \approx 41$ Hz) is typical of that observed between adjacent skeletal carbon and boron atoms in polyhedral boranes.[6] Surprisingly, again no coupling of the 6-^{13}C carbon is observed to the boron atom at the 2-position; however, we have previously noted[7] a similar selective carbon–boron coupling between boron and carbon atoms located on the face of 1,2,8,10-$C_4B_7H_{11}$.

The $^2J_{^{13}C-CH_3}$ and $J_{^{13}C-^{13}C}$ coupling constants reported herein are, to our knowledge, the first values to be reported for the coupling of a cage carbon to either an exopolyhedral carbon or an adjacent cage-carbon atom. In general, carbon–carbon coupling constants have been found to be proportional to bond order and fractional s character.[8] Thus, ^{13}C–^{13}C coupling constants between normal single-bonded sp^3–sp^3-hybridized carbon atoms are typically in the range of ~35–50 Hz, while those in acetylenes can be greater than 200 Hz. The 39-Hz value for $J_{^{13}C6-^{13}CH_3}$ in 6-CH_3-6-^{13}C-5,6,9-$C_3B_7H_{10}$ is consistent with the expected single bond between C6 and CH_3 and falls in the overlapping ranges typically observed for either single-bonded sp^3–sp^3- or sp^2–sp^3-hybridized carbons. The smaller $J_{^{13}C6-C5}$ value of 23 Hz is in agreement with both the lower bond order and lower s character expected for the weaker three-center, two-electron bonding interaction of C6 with both C5 and B2. This value falls between the ranges found for strained-ring compounds, such as cyclopropanes and cyclobutanes, that have reduced s characters in their single bonds.[8,9]

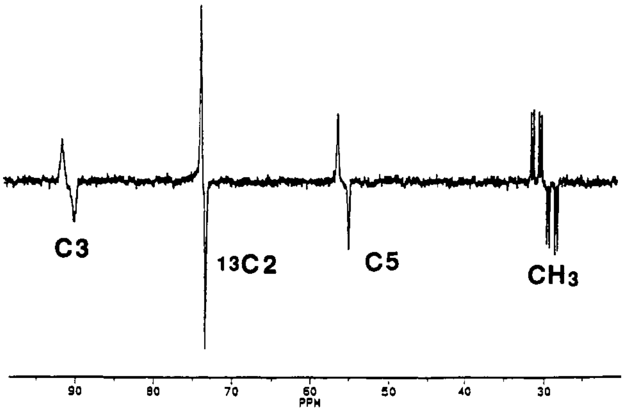

Figure 4. INEPT ^{13}C NMR spectrum of *commo-Fe*-(1-Fe-2-CH_3-2-^{13}*C*-2,3,5-$C_3B_7H_9$)$_2$ (6-^{13}*C*).

Syntheses and Properties of Labeled Ferratricarbaborane Complexes. The ^{13}C-labeled 6-CH_3-6-^{13}*C*-5,6,9-$C_3B_7H_9^-$ anion was reacted according to the following equations to yield the indicated labeled metallatricarbaborane complexes:

$$\mathrm{Na^+(6\text{-}CH_3\text{-}6\text{-}^{13}\mathit{C}\text{-}5,6,9\text{-}C_3B_7H_9)^-} \xrightarrow[-\mathrm{NaI},\ -2\mathrm{CO}]{(\eta\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2I}}$$
$$\underset{\mathbf{2}\text{-}^{13}\mathit{C}}{1\text{-}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Fe\text{-}2\text{-}CH_3\text{-}2\text{-}^{13}\mathit{C}\text{-}2,3,4\text{-}C_3B_7H_9}} +$$
$$\underset{\mathbf{3}\text{-}^{13}\mathit{C}}{1\text{-}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Fe\text{-}4\text{-}CH_3\text{-}4\text{-}^{13}\mathit{C}\text{-}2,3,4\text{-}C_3B_7H_9}} \quad (6)$$

$$\mathrm{2Na^+(6\text{-}CH_3\text{-}6\text{-}^{13}\mathit{C}\text{-}5,6,9\text{-}C_3B_7H_9)^-} \xrightarrow[-2\mathrm{NaCl}]{\mathrm{FeCl_2}}$$
$$\underset{\mathbf{6}\text{-}^{13}\mathit{C}}{\mathit{commo\text{-}Fe}\text{-}\mathrm{(1\text{-}Fe\text{-}2\text{-}CH_3\text{-}2\text{-}^{13}\mathit{C}\text{-}2,3,5\text{-}C_3B_7H_9)_2}} +$$
$$\underset{\mathbf{7}\text{-}^{13}\mathit{C}}{\mathit{commo\text{-}Fe}\text{-}\mathrm{(1\text{-}Fe\text{-}5\text{-}CH_3\text{-}5\text{-}^{13}\mathit{C}\text{-}2,3,5\text{-}C_3B_7H_9)_2}} +$$
$$\underset{\mathbf{8}\text{-}^{13}\mathit{C}}{\mathit{commo\text{-}Fe}\text{-}\mathrm{(1\text{-}Fe\text{-}5\text{-}CH_3\text{-}5\text{-}^{13}\mathit{C}\text{-}2,3,5\text{-}C_3B_7H_9)\text{-}(1\text{-}Fe\text{-}4\text{-}CH_3\text{-}4\text{-}^{13}\mathit{C}\text{-}2,3,4\text{-}C_3B_7H_9)}} \quad (7)$$

$$\mathbf{6}\text{-}^{13}\mathit{C} \rightarrow \underset{\mathbf{9}\text{-}^{13}\mathit{C}}{\mathit{commo\text{-}Fe}\text{-}\mathrm{(1\text{-}Fe\text{-}10\text{-}CH_3\text{-}10\text{-}^{13}\mathit{C}\text{-}2,3,10\text{-}C_3B_7H_9)_2}} \quad (8)$$

The complexes were isolated in a manner similar to that described for the unlabeled compounds.[1,2] The ^{11}B NMR spectra of all complexes were identical with those observed for the unlabeled compounds; thus, in contrast to the spectra of **1**, ^{11}B–^{13}C couplings could not be observed. The ^1H and ^{13}C NMR spectra of **7**-^{13}*C* were, as observed for the unlabeled compound **7**, broad and uninterpretable, suggesting that the compound is fluxional in solution, as discussed in the preceding paper.[2] The proton NMR spectra of the other compounds were identical with the spectra of the unlabeled compounds, with the exception that the methyl proton resonances in all labeled compounds appeared as doublets owing to $^2J_{^{13}C-^1H}$ coupling.

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(5) The line shape of the ^{13}C resonances from carbons coupled to boron may vary considerably due to partial decoupling by boron quadrupolar relaxation effects. Theoretical calculations of the line shape of the predicted quartet have shown that the separation between the two central resonances can be considered an upper limit to J_{BC}. See: (a) Hall, L. W.; Lowman, D. W.; Ellis, P. D.; Odom, J. D. *Inorg. Chem.* **1975**, *14*, 580–583. (b) Pople, J. A. *Mol. Phys.* **1958**, *1*, 168. (c) Bacon, R.; Gillespie, R. J.; Quail, J. W. *Can. J. Chem.* **1963**, *41*, 3603. (d) Suzuki, M.; Kubo, R. *Mol. Phys.* **1963**, *7*, 201. (e) Zozulin, A. J.; Jakobsen, H. J.; Moore, T. F.; Garber, A. R.; Odom, J. D. *J. Magn. Reson.* **1980**, *41*, 458–466. For the C6 quartet resonance, the separation between the inner two peaks was 47 Hz, while the outer to inner peak separations were 43 and 42 Hz.

(6) (a) Wrackmeyer, B. *Prog. NMR Spectrosc.* **1979**, *12*, 227–259. (b) Gragg, B. R.; Layton, W. J.; Niedenzu, K. *J. Organomet. Chem.* **1977**, *132*, 29–36.

(7) Astheimer, R. J.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 1928–1934.

(8) Krivdin, L. B.; Kalabin, G. A. *Prog. NMR Spectrosc.* **1989**, *21*, 293–448.

(9) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 6021–6025.

Table I. ^{13}C and ^{1}H NMR Data[a,b]

compd	nucleus	δ (mult, *J* (Hz), assign)
$6\text{-}CH_3\text{-}6\text{-}^{13}C\text{-}5,6,9\text{-}C_3B_7H_{10}$ (**1**-^{13}C)	$^{13}C^{c}$	27 °C: 158.97 (q, J_{BC} ~44, ^{13}C6), 62.13 (br s, C5), ~32 (m, C9), 23.60 (d, J_{CC} 39, CH_3)
	$^{13}C^{c}$	–85 °C: 159.40 (s, ^{13}C6), 61.67 (d, J_{CC} 24, C5), 32.01 (m, C9), 23.67 (d, J_{CC} 39, CH_3)
$1\text{-}(\eta\text{-}C_5H_5)Fe\text{-}2\text{-}CH_3\text{-}2\text{-}^{13}C\text{-}2,3,4\text{-}C_3B_7H_9$ (**2**-^{13}C)	$^{13}C^{d}$	79.33 (m, J_{CH} 192, Cp), 70.99 (d, J_{CH} 195, C3), 64.20 (m, 28, ^{13}C2), 33.81 (d, J_{CH} 182, C4), 30.83 (d of q, J_{CC} 45, J_{CH} 129, CH_3)
	$^{13}C^{e}$	79.16 (m, Cp), 70.99 (br s, C3), 64.37 (br s, ^{13}C2), 33.87 (br s, C4), 30.82 (d, J_{CC} 47, CH_3)
	^{1}H	6.50 (br s, CH), 3.84 (s, Cp), 2.57 (d, J_{CH} 5, CH_3), 0.71 (br s, CH)
$1\text{-}(\eta\text{-}C_5H_5)Fe\text{-}4\text{-}CH_3\text{-}2,3,4\text{-}C_3B_7H_9$ (**3**)	$^{13}C^{d,f}$	78.46 (m, J_{CH} 179, Cp), 77.58 (br d, J_{CH} 151, C3), 56.95 (br d, J_{CH} 209, C2), 42.78 (s, C4), 26.29 (q, J_{CH} 130, CH_3)
	$^{13}C^{e,f}$	78.44 (m, Cp), 77.90 (br s, C3), 57.07 (br s, C2), 26.29 (s, CH_3)
$1\text{-}(\eta\text{-}C_5H_5)Fe\text{-}4\text{-}CH_3\text{-}4\text{-}^{13}C\text{-}2,3,4\text{-}C_3B_7H_9$ (**3**-^{13}C)	$^{13}C^{d}$	42.78 (s, ^{13}C4)[g]
	^{1}H	6.89 (br s, CH), 5.49 (br s, CH), 3.82 (s, Cp), 0.88 (d, J_{CH} 5, CH_3)
commo-Fe-$(1\text{-}Fe\text{-}2\text{-}CH_3\text{-}2\text{-}^{13}C\text{-}2,3,5\text{-}C_3B_7H_9)_2$ (**6**-^{13}C)	$^{13}C^{d}$	90.92 (br s, J_{CH} 171, C3), 73.63 (m, 62, ^{13}C2), 55.62 (br d, J_{CH} 188, C5), 29.81 (d of q, J_{CC} 43, J_{CH} 130, CH_3)
	$^{13}C^{c}$	90.76 (br s, C3), 73.61 (m, 25, ^{13}C2), 55.61 (br s, C5), 29.81 (d, J_{CC} 43, CH_3)
	^{1}H	6.56 (br s, C3H), 2.01 (d, J_{CH} 5, CH_3), 1.55 (s br, C5H)
commo-Fe-$(1\text{-}Fe\text{-}5\text{-}CH_3\text{-}5\text{-}^{13}C\text{-}2,3,5\text{-}C_3B_7H_9)$-$(1\text{-}Fe\text{-}4\text{-}CH_3\text{-}4\text{-}^{13}C\text{-}2,3,4\text{-}C_3B_7H_9)$ (**8**-^{13}C)	$^{13}C^{d}$	95.27 (d, J_{CH} 178, C3), 66.81 (d, J_{CH} 189, C2), 55.09 (m, 22, ^{13}C5), 23.99 (d of q, J_{CC} 41, J_{CH} 132, CH_3)
	$^{13}C^{e}$	95.25 (s, C3), 66.73 (s, C2), 55.08 (s, ^{13}C5), 23.99 (d, J_{CC} 42, CH_3)
	^{1}H	6.05 (br s, C3H), 5.41 (s, C2H), 0.93 (d, J_{CH} 5, CH_3)
commo-Fe-$(1\text{-}Fe\text{-}10\text{-}CH_3\text{-}10\text{-}^{13}C\text{-}2,3,10\text{-}C_3B_7H_9)_2$ (**9**-^{13}C)	$^{13}C^{d,f}$	68.50 (d, J_{CH} 181, CH (2 or 3)), 67.78 (d, J_{CH} 187, CH (2 or 3)), 42.13 (d, J_{CH} 31, C10H), 18.75 (d, J_{CH} 132, CH_3)
	$^{13}C^{e}$	42.10 (s, ^{13}C10), 18.72 (d, J_{CH} 42, CH_3)
	^{1}H	5.79 (br s, CH), 5.55 (br s, CH), 1.12 (d, J_{CH} 5, CH_3)

[a] ^{13}C at 125.8 MHz; ^{1}H at 500 MHz. [b] In C_6D_6. [c] Broad-band proton decoupled. [d] INEPT. [e] Refocused INEPT. [f] Natural abundance. [g] Owing to limited sample size, the remaining resonances were too weak to be observed.

The ^{13}C NMR spectra for the compounds are summarized in Table I. Comparison of the natural-abundance and labeled spectra, coupled with knowledge of their X-ray-determined structures, permitted assignment of the ^{13}C resonances in both the mono- and bis(cage) complexes. Due to the absence of an NOE enhancement, the methyl-substituted cage carbons are difficult to see in the spectra of the unlabeled compounds; however, they are readily observed in the spectra of the ^{13}C-enriched samples. Thus, the intense resonances at 64.2 and 42.83 ppm in the spectra of **2**-^{13}C and **3**-^{13}C were assigned to the C2 and C4 positions, respectively, while the labeled resonances in the bis(cage) compounds occur at 73.6 ppm (C2) in **6**-^{13}C, 55.6 ppm (C4(5)) in **8**-^{13}C, and 42.1 ppm in **9**-^{13}C (C10). As illustrated in the spectrum for compound **6**-^{13}C shown in Figure 4, the remaining cage-carbon resonances in each compound appear as doublets in their INEPT ^{13}C NMR spectra, which is consistent with the presence of a hydrogen substituent at each of these carbons. In agreement with previously noted trends,[10] the resonances for the four-coordinate carbons (C2 and C3) adjacent to the iron atoms in each compound appeared at lower field (>56 ppm), while those of the five-coordinate C4(5) and C10 (**10**) carbons were at higher fields. The resonances arising from the methyl carbon in all labeled compounds were observed as doublets with a $J_{^{13}C-^{13}C}$ values of ~40–50 Hz in their broad-band proton-decoupled or refocused-INEPT spectra.

Discussion

In principle, the rearrangements in eqs 1–3 could occur by two distinct types of mechanisms. One type of mechanism might involve a direct methyl migration, perhaps metal-mediated, from the C2 cage vertex to the C4(5) cage vertex. Reversible metal–ring alkyl migrations have, in fact, previously been observed in bis(cyclopentadienyl)molybdenum complexes.[11] Alternatively, the isomerization may not involve a "migration" but instead a skeletal rearrangement of the carbon atoms in the polyhedral framework in which the methyl–C2 bond stays intact as the C2 moves to the C4(5) position. Since in a migration mechanism the methyl transfers from one carbon to another, but in a skeletal rearrangement mechanism the methyl stays on the original cage carbon, a study of the rearrangement reactions of the ^{13}C-labeled analogues of compounds **2**–**9** should, in fact, distinguish between these two mechanisms. For example, as illustrated for the ferratricarbaborane cage shown in Figure 5, if a direct shift mechanism (A) is operative, then upon isomerization the labeled carbon will remain in the 2-vertex, but if the isomerization occurs by a cage-skeletal rearrangement (B), then the methyl and labeled cage atom will migrate together.

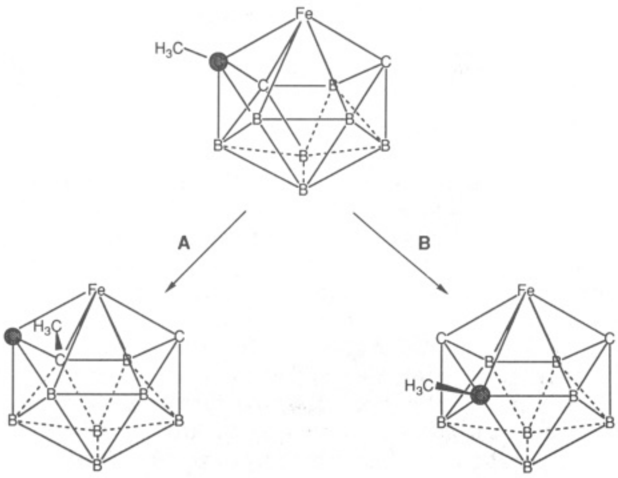

Figure 5. Predicted results of ^{13}C migrations if isomerization occurs by either (A) a direct methyl shift or (B) a cage-carbon rearrangement.

Examination of both the ^{1}H and ^{13}C NMR spectra of isomers **3**, **8**, and **9** demonstrated that both the labeled cage carbon and its attached methyl substituent rearrange

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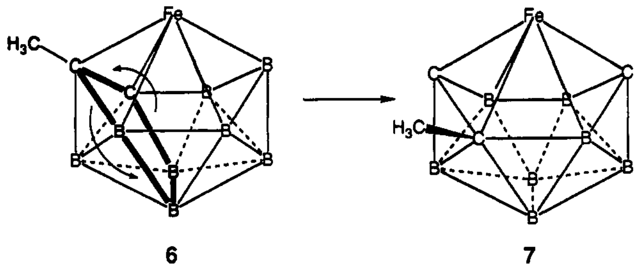

Figure 6. Pentagonal-belt rotation isomerization mechanism.

during the isomerization and that the methyl-^{13}C bond is retained. Thus, according to the ^{13}C NMR spectra, the labeled carbon in each compound was observed to have isomerized from the C2 to the C4(5) resonance. Furthermore, in both the ^{1}H and ^{13}C NMR spectra of the rearranged products the methyl protons and carbons appeared as doublets owing to $^{2}J_{^{13}C-CH_3}$ and $J_{^{13}C-^{13}C}$ couplings, respectively. Therefore, it must be concluded that the observed isomerization does not result from a methyl-migration reaction, but instead the process involves the movement of the C2 skeletal carbon along with its methyl substituent to the cage 4(5)-vertex.

The question then arises as to what type of skeletal rearrangement process will enable this change. All isolated isomers retain two carbons in the four-coordinate cage positions and the metal atom in the six-coordinate position. These positions are, in fact, predicted to be the thermodynamically favored cage sites for these atoms.[12] Thus, isomerizations through other intermediates in which the carbons or metals occupy other cage sites, while perhaps possible, are unlikely. A process that is in agreement with this conclusion and which can account for the observed isomerization in a straightforward manner is the belt-rotation mechanism, which was one of the original mechanisms[13] proposed to explain the fluxional behavior observed in the parent 11-vertex borane anion *closo*-$B_{11}H_{11}^{2-}$. As illustrated in Figure 6, a single rotation of the five-atom pentagonal C2–B4–B10–B11–C5 ring in the direction shown will result in an isomerization of the methyl-substituted C2 carbon to the cage 4(5)-vertex position. This sequence again has the advantage that the metal always stays in the six-coordinate site and carbon atoms always occupy both four-coordinate sites.

As described in the preceding paper,[2] other skeletal rearrangements were observed in the metallatricarbaborane complexes at higher temperatures. Thermolysis of 6 at 230 °C produced a mixture of 7 and 8, and thermolysis of pure samples of either 7 or 8 produced mixtures of the two compounds. These observations suggest that the last two isomers are in equilibrium at these temperatures:

$$\underset{7}{\textit{commo-Fe}\text{-}(1\text{-Fe-5-CH}_3\text{-2,3,5-C}_3\text{B}_7\text{H}_9)_2} \rightleftharpoons \underset{8}{\textit{commo-Fe}\text{-}(1\text{-Fe-5-CH}_3\text{-2,3,5-C}_3\text{B}_7\text{H}_9)\text{-}(1\text{-Fe-4-CH}_3\text{-2,3,4-C}_3\text{B}_7\text{H}_9)}$$

In both 7 and 8 the methyl group is present at the C4(5) positions. The two isomers differ in that both of the cages of 7 are of the same enantiomeric form (*RR*) while in 8 the complex is formed from two different anion enantiomers (*RS*). Thus, the interconversion of 7 and 8 involves the isomerization of one of the cages of a complex from one enantiomeric form to another. A skeletal rearrangement in which the methyl group on one side (e.g. C4) of the cage isomerizes to the opposite side (C5) would in fact generate the opposite enantiomer.

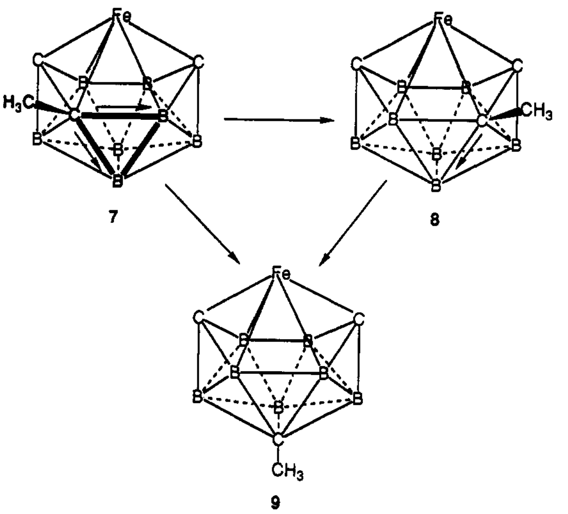

Figure 7. Triangular-face rotation mechanism.

The belt-rotation mechanism cannot account, however, for the interconversion observed between 7 and 8 or for the formation of the final isomer 9 that is formed upon heating 6, 7, or 8 to higher temperatures. The fact that these interconversions occur at higher temperatures also suggests a different rearrangement process. A simple triangular-face rotation mechanism can be invoked to account for both of these transformations. Thus, a single clockwise rotation of the triangular C4, B7, B10 face, as illustrated in Figure 7, in effect accomplishes the transformation of 7 to 8. A second rotation of this face results in the production of 9.

It should be noted that although the above isomerizations can be rationalized on the basis of *formal* pentagonal- and triangular-face rotations, the actual processes by which these rotations may be accomplished may be much more complex. For example, Gaines[14] has recently discussed the various mechanisms, including both pentagonal-belt and triangular-face rotations, that have been proposed to account for the isomerization reactions of $C_2B_{10}H_{12}$ and has shown that equivalent processes can be achieved through nido-cage intermediates. Likewise, Grimes[15] has previously proposed similar mechanisms to account for isomerizations in 12-vertex C_4B_8-cage systems. Open-cage structures could indeed be important transition states or intermediates in the isomerizations reported herein. In fact, the skeletal distortions producing the open quadrilateral faces with elongated iron-C4(5) bonding interactions observed in compounds 6–8 may be related to these required geometries.

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