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Chemistry of Monocarbon Metallocarboranes Including Polyhedral Rearrangements in Mixed-Metal Bimetallocarboranes

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Abstract: The synthesis and characterization of four isomers of the mixed-metal bimetallocarborane $(C_5H_5)_2CoNiCB_7H_8$ are reported. These species have been found to undergo novel thermal polyhedral rearrangements wherein metal atoms migrate to adjacent polyhedral vertices and remain there, constituting the first example of a thermally stable metal–metal interaction in a metallocarborane. Also described are some brominated derivatives and their thermal rearrangements. A general rearrangement scheme for ten-vertex polyhedra is developed and used in the analysis of polyhedral rearrangements and assignment of structures. In an attempt to synthesize a larger homologue of this mixed-metal species, we have iolated $(\eta\text{-}C_{10}H_8)Co^{III}CB_{10}H_{11}$, the first metallocarborane containing a neutral arene ligand bound to the metal.

The scope of metallocarborane chemistry was recently expanded when we reported[1] the synthesis of the first mixed-metal bimetallocarborane, a monocarbon species containing formal Co(III) and Ni(IV) in the polyhedral framework, $(C_5H_5)_2CoNiCB_7H_8$. Shortly thereafter[2,3] we reported mixed-metal species containing iron and cobalt, $(C_5H_5)_2CoFeC_2B_nH_{n+2}$ (n = 7, 9). To date, these are the only known mixed-metal metallocarboranes. As with the mixed-valence metallocenes,[4] their electrical and magnetic properties are of interest, particularly the aspect of metal-metal interactions within the polyhedron.

Because of the electron-deficient nature of the neutral Co(III)–Fe(III) species above, they are not expected to undergo polyhedral rearrangements.[5] Thus, an attempt to effect a polyhedral rearrangement in $4,5\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}4\text{-}Co\text{-}5\text{-}Fe\text{-}1,8\text{-}C_2B_9H_{11}$ resulted in complete decomposition[3] under the same conditions that $4,5\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}4,5\text{-}Co_2\text{-}1,8\text{-}C_2B_9H_{11}$ did rearrange.[3] It has been previously stated[6] that $\{C_5H_5Ni\}$ is formally isoelectronic with $\{CH\}$ with regard to the number of electrons donated to polyhedral bonding, just as $\{C_5H_5Co\}$ is similar to $\{BH\}$. Therefore, the monocarbon Co–Ni mixed-metal species is similar to a two-carbon carborane, $C_2B_nH_{n+2}$, or a two-carbon cobaltacarborane, $(C_5H_5Co)_xC_2B_nH_{n+2}$, and thus may undergo polyhedral rearrangement. We report here the preparation and novel polyhedral rearrangement of the heterobimetallocarborane $(C_5H_5)_2CoNiCB_7H_8$, along with the first report on the derivative chemistry of a bimetallocarborane including the physical properties of mono- and dibromo-substituted derivatives. We also report that an attempt to synthesize a larger homologue of this bimetallocarborane yielded instead the neutral complex $(\eta\text{-naphthalene})Co^{III}CB_{10}H_{11}$, the first metallocarborane containing a neutral arene ligand bound to the metal.

Results and Discussion

Synthesis and Characterization of the $(C_5H_5)_2$Co-NiCB$_7$H$_8$ Isomers. The anionic metallocarborane[7] $[3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3\text{-}Co\text{-}4\text{-}CB_7H_8]^-$ consumed 3 equiv of sodium naphthalide over a period of several days and was then treated with NaC_5H_5 and Ni(II) in tetrahydrofuran (THF). Whether the reduction/reaction temperature was −78°, 0°, 25°, or reflux, three isomers of $(C_5H_5)_2CoNiCB_7H_8$ were invariably isolated and separated by column and preparative thick-layer chromatography. A fourth isomer appeared consistently when the reaction was performed at −78°, and capriciously when done at 0°. Relative yields

$$[(CH_3)_4N][(C_5H_5)CoCB_7H_8] \xrightarrow[\text{THF}]{3Na^+C_{10}H_8^-} \xrightarrow[\text{NiBr}_2]{C_5H_5^-} \underset{\text{I–IV}}{(C_5H_5)_2CoNiCB_7H_8}$$

of isomers varied with temperature and can be found in the Experimental Section. While I, II, and IV were always observed, III was sometimes not formed in appreciable yield

Table I. 100-MHz ^{1}H NMR Data (in acetone-d_6)

Complex	Resonance, τ[a] (rel area)	Assignment[b]
I	4.91 (5) s; 3.93 (5) s;	Cp
	1.62 (1) s, br	C–H
Ia[c]	4.60 (5) s; 3.92 (5) s;	Cp
	1.85 (1) s, br	C–H
Ib[c]	4.36 (1) s; 3.94 (1) s	Cp
II	5.10 (5) s; 4.70 (5) s;	Cp
	5.65 (1) s, br	C–H
IIa	5.02 (5) s; 4.63 (5) s;	Cp
	5.64 (1) s, br	C–H
IIb[c]	4.90 (1) s; 4.52 (1) s	Cp
III	4.80 (5) s; 4.29 (5) s;	Cp
	6.39 (1) s, br	C–H
IV	5.10 (5) s; 4.75 (5) s;	Cp
	4.37 (1) s, br	C–H
V[c, d]	2.00 (4) s; 2.36 (1) d;[e] 2.44 (1) d[e]; 2.81 (1) d[e]; 2.90 (1) d[e]	$C_{10}H_8$

[a] Chemical shifts are relative to TMS = τ 10.00; s = singlet, d = doublet, br = broad. [b] Cyclopentadienyl = Cp; carborane C–H = C–H. [c] At 60 MHz. [d] In CD_3CN. [e] J_{H-H} ~3 Hz.

Table II. 80.5-MHz ^{11}B NMR Data (in acetone-d_6)

Complex	Rel areas	Chem shift[a] (J_{B-H}, Hz)
I	1:2:2:2	–41.9 (140), –36.3 (150), –17.5 (150), +2.6 (160)
Ia	1:1:1:1:1:1:1	–43.4 (140), –39.9,[b] –37.9 (165), –18.8, –19.4, +1.1 (165), +3.1 (165)
Ib[c]	1:2:2:2	–39.2 (160), –36.7,[b] –16.5 (145), +3.6 (145)
II	1:2:2:2	–115.8 (160), –3.6 (155), +1.0 (150), +6.2 (140)
IIa	1:1:1:1:1:1:1	–115.8 (175), –5.9,[b] –5.7, –4.1, +0.1, +1.1, +4.2 (165)
IIb[d]	1:2:2:2	–114.1 (155), –6.1,[b] –3.8 (170), +0.8 (150)
III	2:1:2:2	–48.0 (150), –25.1, –24.1, +4.1 (150)
IV	1:1:1:1:1:1:1	–96.0 (160), –34.1 (155), –0.2, +0.4, +7.0 (115), +8.3 (155), +20.5 (155)
V[e]	3:2:1:2:2	–12.8 (145), –6.2 (140), +3.0 (140), +6.2 (150), +13.1 (155)

[a] Realtive to Et_2OBF_3 = 0. [b] Singlet, confirmed from proton-decoupled spectrum. [c] In pyridine. [d] In CH_2Cl_2. [e] In CD_3CN.

with a reaction temperature of 0° and above, but nevertheless could consistently be synthesized in low yield from the pyrolysis of II (vide infra). Due to the solution temperatures required to rearrange the isomers (see Experimental Section), these data are consistent with at least four different reduced species present in solution prior to addition of Ni^{2+}. The change in yields with temperature could indicate that, although the closo neutral products do not rearrange, the formal nido $[C_5H_5Co^{II}CB_7H_8]^{3-}$ reduced species may rearrange. For instance, the reduced species leading to III may easily rearrange at room temperature, explaining why III is only isolated at low temperature.

All four isomers were air stable and gave mass spectra with cutoffs at *m/e* 346 corresponding to the $^{12}C_{11}{}^1H_{18}{}^{11}B_7{}^{59}Co^{60}Ni^+$ ion. The infrared spectra and ^{1}H and ^{11}B NMR spectra are given in Tables I-III. The proposed structures of I-III are given in Figure 1. The structure of IV (Figure 1) has recently been confirmed by a single-crystal X-ray diffraction study[8] (M-M = 2.449 (1) Å). The structure assigned to II was based on the ^{11}B NMR data. If it can be assumed that the very low field resonance at –116 ppm is due to a low-coordinate boron atom adjacent to two metal vertices[9] (the crystal structure of IV and also that of $(C_5H_5Fe)_2C_2B_6H_8$[11a] supports the proposal that this environment may produce a very low field resonance), then the structure of II is uniquely defined, and is formulated[12] as 6,8-(η^5-C_5H_5)$_2$-6-Co-8-Ni-1-CB_7H_8. Possible structures for I and III will be discussed below.

Cyclic voltammetry data (Table IV) was unlike that of the $(C_5H_5Co)_2C_2B_nH_{n+2}$ (n = 5–10) species, which exhibit a reversible one-electron oxidation and a reversible one-electron reduction.[3,10,13] Metallocarboranes I-IV all exhibited a reversible one-electron reduction and an irreversible oxidation. The reduction is presumably to a formal Co(III)-Ni(III) species, but these were not isolated. When generated electrochemically, solutions of the monoanions of I, II, and IV were all green and very air sensitive.

The ^{1}H NMR spectra of these diamagnetic metallocarboranes (Table I) all exhibited the expected two sharp cyclopentadienyl resonances each of area 5 and a broad resonance of area 1 assigned to carborane C-H. The 80.5-MHz ^{11}B NMR spectra (Table II) contained resonances attributable to seven boron atoms; complexes I-III exhibited 1:2:2:2 symmetry, the highest possible symmetry available in a ten-vertex polyhedron containing three different heteroatoms.

Table III. Infrared Spectra

Complex	Frequency, cm^{-1} (Nujol mull)
I	3065 (w), 2530 (vs), 2460 (vs), 1420 (m), 1110 (m), 1085 (w), 1070 (w), 1060 (w), 1020 (m), 1010 (w), 905 (w), 870 (m), 855 (m), 850 (m), 840 (m), 830 (s), 815 (s), 795 (w), 765 (w), 725 (w), 695 (w)
Ia	3050 (w), 2540 (vs), 2495 (vs), 2455 (m), 1410 (m), 1335 (w), 1110 (m), 1090 (m), 1075 (m), 1060 (m), 1015 (m), 905 (w), 855 (m), 835 (s), 815 (s), 800 (w), 745 (m), 740 (m), 715 (m)
Ib	3060 (w), 2530 (vs), 2495 (m), 1410 (m), 1350 (w), 1105 (m), 1095 (m), 1085 (m), 1065 (w), 1015 (m), 960 (w), 915 (w),-905 (w), 890 (w), 860 (m), 850 (m), 835 (s), 825 (s), 815 (m), 760 (m), 750 (s), 745 (s), 705 (s), 690 (s)
II	3075 (w), 2530 (vs), 2470 (s), 1780 (w), 1420 (m), 1340 (w), 1120 (m), 1105 (w), 1080 (w), 1065 (w), 1015 (m), 930 (m), 920 (m), 880 (m), 860 (w), 835 (s), 820 (s), 800 (s), 745 (w), 695 (w)
IIa	3075 (w), 2530 (vs), 2465 (m), 1865 (w), 1790 (w), 1425 (m), 1345 (m), 1125 (m), 1105 (m), 1080 (w), 1065 (w), 1015 (m), 940 (w), 915 (m), 885 (m), 865 (s), 835 (s), 825 (s), 815 (s), 780 (w), 770 (s), 735 (s), 700 (w)
IIb	3040 (w), 2520 (vs), 1415 (m), 1335 (w), 1120 (m), 1115 (m), 1110 (m), 1080 (m), 1065 (w), 1010 (s), 905 (w), 880 (m), 860 (s), 835 (s), 815 (s), 795 (m), 785 (m), 745 (w), 730 (m), 695 (s), 685 (s)
III[a]	3065 (w), 2520 (vs), 1420 (m), 1110 (m), 1080 (m), 1015 (m), 915 (m), 880 (m), 860 (w), 840 (m), 815 (s)
IV	3060 (w), 2520 (vs), 2465 (vs), 1845 (w), 1765 (w), 1415 (m), 1345 (w), 1110 (s), 1065 (w), 1010 (m), 945 (m), 915 (s), 905 (s), 865 (m), 835 (s), 825 (s), 800 (m), 785 (s), 770 (m), 735 (w), 725 (w)
V	2500 (vs), 1625 (w), 1550 (w), 1480 (w), 1400 (w), 1260 (w), 1110 (m), 1045 (w), 1005 (m), 980 (w), 925 (w), 905 (w), 890 (w), 860 (w), 845 (w), 760 (w), 735 (w)

[a] $CHCl_3$ solution vs. $CHCl_3$ standard.

Bromination of I and II. Isolation of B-bromo-substituted derivatives of I as products of the polyhedral expansion reaction most likely arose due to the inadvertent presence of traces of bromine in the nickel reagent, and led us to investigate the reaction of bromine with I and II. We found that I and II readily reacted with 1 or 2 mol of Br_2 in CCl_4 solvent, liberating HBr and cleanly yielding a single isomer of mono- or dibromo-derivative in high yield. Tables I-IV describe the characterization data obtained for these bromo-

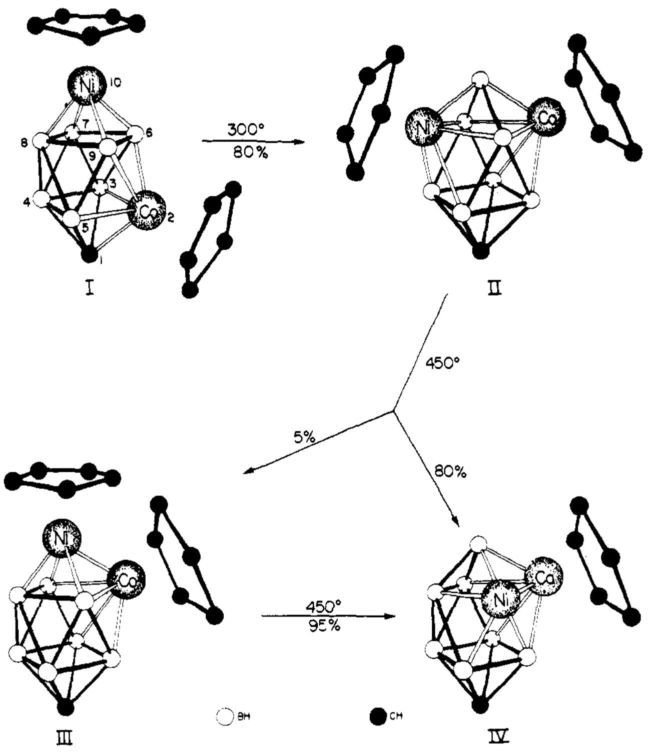

Figure 1. The proposed rearrangement scheme for the $(C_5H_5)_2CoNiCB_7H_8$ isomers. A cyclopentadienyl ring has been omitted from IV for clarity.

Table IV. Electronic Spectra and Electrochemical Data

Complex	λ_{max}, nm (log ϵ)^a	$E_{p/2}$ (V) vs. SCE^b
I	700 (2.79), 623 (2.79), 502 (2.92), 365 (4.03), 307 (4.13), 224 (4.23)	−0.80
Ia	709 (2.91), 600 (sh, 2.92), 500 (sh, 3.10) 380 (3.94), 310 (4.14)	−0.67
Ib^c	718 (3.03), 512 (sh, 3.18), 390 (4.11), 322 (4.18)	----
II	584 (2.63), 500 (2.65), 325 (sh, 4.08) 272 (4.51), 217 (4.40)	−0.98
IIa	611 (2.55), 387 (sh, 3.57), 330 (sh, 4.11), 291 (4.28), 271 (4.30)	----
IIb^{c,d}	654 (2.49), 455 (sh, 3.30), 400 (3.64), 331 (4.29), 307 (sh, 4.25), 271 (4.21), 248 (4.23)	−0.73
III	555 (3.05), 460 (sh, 3.08), 375 (sh, 3.52), 290 (4.38), 268 (sh, 4.36), 223 (4.45)	−0.86
IV	499 (2.79), 366 (3.68), 320 (sh, 4.89), 270 (4.31), 253 (4.33)	−0.90
V	465 (2.44), 270 (4.38)	−0.62 −1.31^e

^{a} Measured in spectroquality CH_3CN, except where noted. ^{b} Cyclic voltammetry in CH_3CN with 0.1 M $(C_2H_5)_4N^+PF_6^-$ supporting electrolyte, platinum button electrode; one-electron reversible reductions except where noted. ^{c} Electronic spectrum in spectroquality CH_2Cl_2. ^{d} Cyclic voltammogram measured in CH_2Cl_2. ^{e} Quasi-reversible reduction.

metallocarboranes. Monobromination of both I and II re-

$$\mathrm{I} \xrightarrow{Br_2} \mathrm{Ia} \xrightarrow{Br_2} \mathrm{Ib}$$

$$\mathrm{II} \xrightarrow{Br_2} \mathrm{IIa} \xrightarrow{Br_2} \mathrm{IIb}$$

moved the symmetry of these species, while dibromination restored the symmetry (Table II), indicating that the two Br substituents enter at magnetically equivalent boron atoms. The 80.5-MHz ^{11}B NMR spectra (Table II) exhibited the singlets expected for terminally substituted boron atoms. Limited solubility precluded the observation of carborane C-H resonances in Ib and IIb. However, the ^{11}B NMR spectra confirmed that substitution took place exclusively at boron.

Complexes Ib and IIb were unreactive in the presence of excess bromine, hence no evidence was found for the formation of tribromo derivatives. The reactivity of I and II toward bromine is in general agreement with previous studies on the bromination of metallocarboranes.[14]

Rearrangements of $(C_5H_5)_2CoNiCB_7H_8$ and Its Derivatives. It was found that I slowly rearranged in heptane at reflux to II, or alternately, rearranged to II in higher yield when sublimed through a long quartz tube heated to about 300°. An attempted rearrangement of II in cyclooctane solution at 140° or in a sealed, evacuated tube at 205° only resulted in decomposition. However, when sublimed through the tube heated to 450°, II rearranged in high yield to a mixture of III and IV. Also at this latter temperature, III rearranged quantitatively to IV. In addition, Ia rearranged in high yield to IIa (300°, quartz tube), and Ib similarly to IIb. At lower temperatures no rearrangements occurred; for example, I was recovered pure upon sublimation through the hot zone at 200°, and II was also unchanged at a temperature of 300°. We found no evidence for any degree of reversibility in the polyhedral rearrangements reported here.

Little is known about the thermal rearrangements of ten-vertex polyhedra; the few studies[15] performed, though, support the "diamond-square-diamond" (dsd) mechanism shown in Figure 2. Other rearrangement mechanisms are possible and would include rotation of four- or five-membered belts, or rotation of triangular faces on the polyhedron. The dsd model is used here for three reasons: it is the only mechanism yet proposed for rearrangements within a ten-vertex polyhedron, it requires the least amount of bond-breaking and atomic motion,[15a] and it is substantiated by the facile and quantitative conversion of 2,3-$B_{10}H_8[N(CH_3)_3]_2$ to the 1,6 isomer.[15b] The arguments following can then be viewed as further supporting evidence for the dsd mechanism, rather than the mechanism being a necessary criterion.

The rearrangement shown in Figure 2 corresponds to what we shall designate a "one-step" process. Two such successive rearrangements are required, for example, for the 1,2- → 1,6-$C_2B_8H_{10}$ or 1,6- → 1,10-$C_2B_8H_{10}$ rearrangements[16] and these carborane rearrangements are formal "two-step" processes. When three heteroatoms are incorporated into a ten-vertex system (such as in the hypothetical $C_3B_7H_{10}^+$, $C_5H_5CoC_2B_7H_9$, or complexes I-IV), the number of possible isomers increases as do possible interconversions. A scheme using the above rearrangement mechanism (Figure 2) which depicts these possible isomeric rearrangements is shown in Figure 3. The three equivalent heteropositions have been given numbers corresponding to their positions in the polyhedron.[12] This scheme can be used for metallocarboranes I-IV if one labels different heteroatoms and carefully follows their movement about the polyhedron, but it must be emphasized that it only gives theoretical rearrangement possibilities, and clearly must be used in conjunction with the known stability parameters for carboranes and metallocarboranes. For instance, 1,2,10 → 1,6,8 conversion passes through a 2,3,8 isomer, but may not stop there because it contains no apical heteroatoms (i.e., carbon has not been observed to migrate from a low-coordinate to a high-coordinate position).

There are four reasonable possibilities[17] for the structure of isomer I: 2,10-(η^5-C_5H_5)$_2$-2-Co-10-Ni-1-CB_7H_8, 2,10-(η^5-C_5H_5)$_2$-2-Co-10-Ni-4-CB_7H_8, 2,4-(η^5-C_5H_5)$_2$-2-Co-4-Ni-1-CB_7H_8, or 1,4-(η^5-C_5H_5)$_2$-1-Ni-4-Co-2-CB_7H_8. Of these four possibilities, we feel the 1-Ni-2-C-4-Co is less likely for the following reasons. (1) Assuming the dsd rearrangement mechanism, to obtain II from this isomer requires a four-step dsd rearrangement process[19] (Figure 3). Since the II → III and III → IV conversions can be regarded as formal two-step rearrangements (vide infra), and since the I → II rearrangement is most facile, it seems likely that this latter rearrangement would also only require a two-step mechanism. (2) Bromination of this isomer might be expected to introduce Br to the magnetically unique boron atom.[20] (3) The presence of high-coordinate carbon in the products is unlikely since carbon prefers the low-coordinate position and is low coordinate in the starting material. Consequently, we believe that carbon would remain low coordinate in the product. In addition, the low field chemical shift of the carborane C–H resonance in the ^{1}H NMR spectrum is consistent with a low-coordinate position for the carbon atom.[21] (4) The 1-Ni-2-C-4-Co isomer contains a metal–metal "bond", and its rearrangement to II would not be consistent with the established preference for a metal–metal "bond" in this metallocarborane. We consider the 1-C-2-Co-4-Ni isomer less likely for reasons 1 and 2. Reason 3 is not congruent with the 2-Co-4-C-10-Ni isomer. Therefore we favor 2,10-(η^5-C_5H_5)$_2$-2-Co-10-Ni-1-CB_7H_8 as the structure of I.

The rearrangement results concerning the symmetrically dibrominated derivatives are also in agreement with our proposal for the structure of I. If one considers the three possible symmetric structures for IIb (assuming the positions of carbon, cobalt, and nickel are correct), and performs a two-step "reverse rearrangement" in every possible way (using the dsd mechanism), there are only two structures for IIb which will yield a symmetric structure for Ib. These two rearrangements are depicted below.

$$2,4\text{-}Br_2\text{-}3,10\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}3\text{-}Co\text{-}10\text{-}Ni\text{-}1\text{-}CB_7H_6 \rightarrow 2,3\text{-}Br_2\text{-}6,8\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}6\text{-}Co\text{-}8\text{-}Ni\text{-}1\text{-}CB_7H_6 \tag{1}$$

$$1,8\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}1\text{-}Ni\text{-}8\text{-}Co\text{-}2,3\text{-}Br_2\text{-}6\text{-}CB_7H_6 \rightarrow 2,3\text{-}Br_2\text{-}6,8\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}6\text{-}Ni\text{-}8\text{-}Co\text{-}1\text{-}CB_7H_6 \tag{2}$$

This gives two possibilities for the structure of I, 1-C-2-Co-10-Ni and 2-Co-4-C-10-Ni. Noticing that increasing bromination of I significantly shifted only one of the cyclopentadienyl resonances in the ^{1}H NMR spectra, we synthesized $(C_5H_5Co)(C_5H_4CH_3Ni)CB_7H_8$ to allow assignment of the cyclopentadienyl resonances, and found it was the Co-C_5H_5 resonance (τ 4.91) that is moved downfield in Ia and Ib with respect to I (Table I). Thus, it seems likely that the Br substituents are on boron atoms adjacent to cobalt rather than nickel, which is consistent with only the first possibility immediately above. It must be emphasized that these data are not conclusive,[24] but they favor one possibility over another. Thus, the proposed structures for Ib and IIb appear in eq 1 above. The proposed structure of I contains the carbon atom adjacent to cobalt, whereas it was not adjacent to cobalt in the starting material.[7b] Although the migration of carbon away from cobalt is thermodynamically favored in closo-metallocarboranes,[10b,27] little is known about the complex rearrangements which carboranes and metallocarboranes may undergo upon reduction.[28]

When sublimed through a hot tube at temperatures from 380 to 450°, II rearranged in high yield to a mixture of III and IV, the highest yield of III (15%) occurred at 380° and 30% of the II isomer was recovered. At 450°, the yield of III was 5% and that of IV was 90%. Also at this latter temperature, III rearranged to IV in 95% yield. Isomer IV was recovered in high yield when sublimed through the tube at 600°, clearly identifying it as the thermally most stable isomer. It is likely that III represents a high energy intermediate in the II → IV rearrangement because the II → III and III → IV rearrangements can occur by a two-step dsd mechanism, but the II → IV rearrangement requires at least three steps, and may pass through a 1,2,10 intermediate according to the rearrangement diagram (Figure 3). The III → IV barrier could be quite low, as this conversion did occur in moderate yield at 350°.

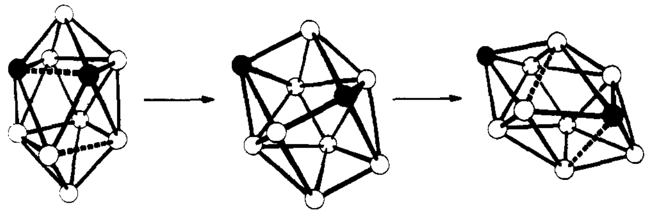

Figure 2. The proposed dsd rearrangement mechanism for a ten-vertex polyhedron, illustrating the conversion of a 2,3 isomer to a 1,6 isomer (from ref 20a).

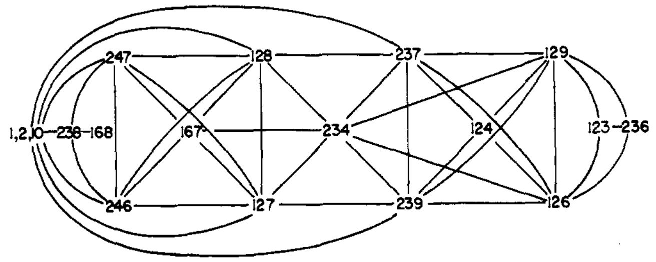

Figure 3. The possible interrearrangements of a ten-vertex polyhedron containing three equivalent heteropositions. A line connecting two isomers denotes a "one-step" reversible rearrangement. Mirror images of optically active species have not been included.

The structure proposed for III is shown in Figure 1 and contains a metal–metal bond. This is the only reasonable structure for III because (a) the II → IV conversion established that the migration of metals to adjacent vertices was favored, (b) the symmetry in the ^{11}B NMR spectrum with the unique resonance not at lowest field suggests that both apices are not boron, and (c) the striking color change in going from II → III (green → red) suggests also that the metals are adjacent[29] in III. The III → IV rearrangement establishes the preference of nickel for the higher coordinate position within the polyhedron, despite the decrease in the nickel–carbon separation.[31] This is an interesting result in view of the polyhedral rearrangement observed in the related complex $[2\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}NiB_9H_9]^-$, which undergoes quantative conversion to the 1-isomer,[18] and seems to be an indication of the ability of metal–metal interactions in metallocarboranes to significantly alter the properties of the transition metals involved. The presence of a low-coordinate NiC_5H_5 vertex in I and III is not unprecedented since we have recently confirmed this bonding mode in the closely related metallocarboranes[18,22] 10-(η^5-C_5H_5)-10-Ni-1-CB_8H_9 and $[1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-}NiB_9H_9]^-$

The presence of metal–metal bonds in metallocarboranes has recently been established,[33] but the existence of a thermally stable metal–metal bond is unprecedented in metallocarborane chemistry.[40] Rearrangement studies performed on systems of the general formula $(C_5H_5Co)_2C_2B_nH_{n+2}$ (n = 6–10) have shown in every case that the thermally most stable isomer contains nonadjacent metal vertices.[11b] In-

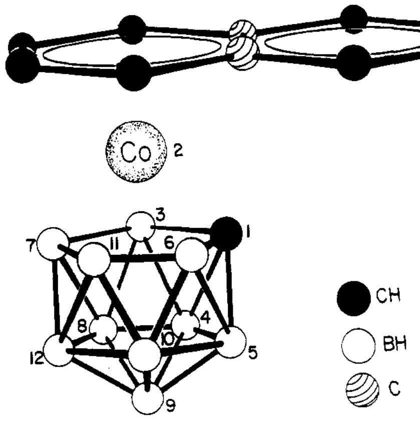

Figure 4. The proposed structure of V, (η-$C_{10}H_8$)$Co^{III}CB_{10}H_{11}$.

deed, in the case of the bimetallocarborane $(C_5H_5Co)_2C_2B_6H_8$, which is isoelectronic with $(C_5H_5)_2CoNiCB_7H_8$, it has been shown[11b] that thermal rearrangement results in cleavage of the metal-metal bond, with the metals migrating to nonadjacent polyhedral vertices. Purely electrostatic arguments would seem to support nonadjacent metal vertices, just as nonadjacent carbon vertices are favored due to carbon's net electropositive character when compared to that of boron.

It is evident from this work that the nature of metal-metal interactions in metallocarboranes may be highly varied and dependent upon the metallic species involved; drastic changes in chemical properties can result from small differences in isoelectronic molecules. Clearly the factors affecting the stability of metal-metal bonds in metallocarboranes are not yet clear, and further work is in progress to elucidate the nature of these metal-metal interactions.

Preparation of (η-naphthalene)$Co^{III}CB_{10}H_{11}$. The anionic metallocarborane[32] $[2\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1\text{-}CB_{10}H_{11}]^-$ consumed 3 equiv of sodium naphthalide and was then treated with $C_5H_5^-$ and Ni(II). The reaction mixture was air oxidized and chromatographed on silica gel. The only neutral product formed in appreciable yield was the orange, air stable, and diamagnetic metallocarborane $2\text{-}(\eta^6\text{-}C_{10}H_8)\text{-}2\text{-}Co\text{-}1\text{-}CB_{10}H_{11}$ (V), whose proposed structure[34] is shown in Figure 4. Because of the similarity in the ^{11}B NMR spectra of $[C_5H_5CoCB_{10}H_{11}]^-$ and V, it is quite likely that the carborane cage is also π-bonded to cobalt in V. The electronic requirements of cobalt then lead to the proposed structure, in which cobalt(III) is π-bound to one of the naphthalene rings. The symmetry in the ^{11}B NMR spectrum implies that the structure must be locked into the configuration shown in Figure 4 *or* rapid rotation of the naphthalene or carborane ligand occurs. The ^{11}B NMR, ^1H NMR, and ir data for V are presented in Tables I-III. The mass spectrum contained a parent envelope with a cutoff at *m/e* 320 corresponding to the $^{12}C_{11}{}^1H_{19}{}^{11}B_{10}{}^{59}Co^+$ ion (calcd 320.1749, found 320.1747), with large peaks also at *m/e* 128 ($C_{10}H_8$) and *m/e* 187 ($CoC_{10}H_8$). The cyclic voltammogram (Table IV) showed a reversible reduction (−0.62 V) and a quasi-reversible reduction (−1.31 V). The former is likely the Co(III)-Co(II) couple, while the latter may correspond to reduction of the naphthalene ligand. Unlike $[C_5H_5CoCB_{10}H_{11}]^-$, no oxidation was observed.[32]

The existence of naphthalene as a ligand to transition metals has been established.[35] However, V represents the first metallocarborane containing a neutral arene π-bound to the metal. We are presently investigating the possibility of synthesizing other such neutral π-arene complexes along with a study of their reactivity toward displacement of the arene ligand by other neutral ligands such as phosphines or olefins.

Conclusions

The synthesis of the mixed-metal metallocarboranes reported here is a continuation of our studies with monocarbon metallocarboranes and was prompted by a consideration of the electronic requirements of metallocarboranes.[5] Specifically, it has been suggested[5,6] that $\{NiC_5H_5\}$ should resemble {CH} in a polyhedral metallocarborane environment. The results of our studies show this to be the case, as evidenced by the high stability of these metallocarborane complexes. However, the nickel vertex did not behave here as a carbon vertex with respect to polyhedral rearrangement, and when given a choice preferred a five- over a four-coordinate vertex and preferred a position adjacent to a metal.

The preference for metal-metal interactions in these complexes containing *formally* high-valent metals seems puzzling, as bonds are usually favored between formally low-valent metals.[36] However, the metal-metal interactions in polyhedral metallocarboranes are likely to involve more complex bonding modes than found in simple organometallic complexes such as $Mn_2(CO)_{10}$. It is evident from this study that the carborane framework is able to significantly alter the chemical properties of transition metals, although further work is required before any generalizations can be advanced.

In addition, the existence of complex V establishes a new area of metallocarborane chemistry, and may lead to novel significant uses of monocarborane ligands in future work.

Experimental Section

Physical Measurements. Ultraviolet-visible spectra were measured with a Cary 14 spectrophotometer. Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Proton NMR spectra were obtained on Varian A-60D or HA-100 spectrometers. The 80.5-MHz ^{11}B NMR spectra were obtained with an instrument designed by Professor F. A. L. Anet of this department. Electrochemical data were obtained on an instrument described previously.[37] Mass spectra were measured using an Associated Electrical Industries MS-9 spectrometer.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Melting points were taken in evacuated capillaries and are uncorrected.

Materials. $[(CH_3)_4N][3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3\text{-}Co\text{-}4\text{-}CB_7H_8]$, $[(CH_3)_4N][2\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1\text{-}CB_{10}H_{11}]$, and the Ni(II) reagent, $NiBr_2\cdot 2C_2H_4(OCH_3)_2$, were prepared according to literature methods.[7a,32,38] Tetrahydrofuran (THF) was distilled from lithium aluminum hydride and stored under nitrogen prior to use. Heptane was freshly distilled from CaH_2 under nitrogen. All other solvents were reagent grade and used without further purification. Naphthalene and Spectroquality acetonitrile were obtained from Matheson Coleman and Bell. Sodium hydride, as a 50% dispersion in mineral oil, was obtained from ROC/RIC Chemical Corp. Dicyclopentadiene was obtained from Aldrich Chemical Co. and converted to cyclopentadiene immediately prior to use. THF solutions of sodium cyclopentadienide were prepared as previously described[39] and immediately used. Sodium metal was purchased from Allied Chemical Co. Silica gel powder, 60-200 mesh, was obtained from J. T. Baker Chemical Co. for use in column chromatography. Preparative thick-layer chromatography was performed with Chrom AR Sheet 1000 purchased from Mallinckrodt Chemical Co.

The apparatus for thermal rearrangements was constructed as follows. A chromel-alumel thermocouple was placed near the middle of a 3/4 × 24 in. quartz Vycor tube and wrapped with heating tape, followed by asbestos. The temperature was read with the use of a potentiometer. To the top was attached a cold finger cooled to 0°, and to the bottom could be attached a small round-bottom flask containing the material to be sublimed. The entire apparatus was connected to a vacuum line and evacuated to $<10^{-4}$ mm pressure.

Once isolated by thick-layer chromatography, metallocarboranes were identified by comparison of ir, ^1H, and ^{11}B NMR spectra with known samples.

Polyhedral Expansion of $[C_5H_5CoCB_7H_8]^-$ at −78°. $[(CH_3)_4N][C_5H_5CoCB_7H_8]$ (0.67 g, 2.25 mmol) was converted to the Na^+ salt by the addition of $NaB(C_6H_5)_4$ in $CH_3CN–H_2O$ solution. Addition of a large excess of H_2O followed by filtration of the colorless precipitate yielded a solution of $Na^+C_5H_5CoCB_7H_8^-$ which was reduced in volume and vacuum dried to remove solvents. Nitrogen was admitted to the residue followed by 80 ml of THF, 0.2 g of naphthalene, and sodium metal (0.155 g, 6.75 mmol). The solution was cooled to −78° and stirred for 14 days, after which was added a THF solution of 8 mmol of NaC_5H_5 followed by $NiBr_2{\cdot}2C_2H_4(OCH_3)_2$ (2.8 g, 7 mmol). After 3 hr at −78°, the solution was warmed to 25° over a 2-hr period. The nitrogen inlet was removed and O_2 was bubbled through the solution for 20 min. The resulting green solution was filtered through Celite and added to 12 g of silica gel and the solvent removed on a rotary evaporator. The remaining solid was chromatographed on a 5 × 50 cm column of silica gel in hexane. Initial faint yellow bands were observed but not characterized. The following bands are in order of elution in hexane.

(a) $(C_5H_5)_2CoNiCB_7H_8$, II. A small green band was eluted; slow evaporation of the hexane solution yielded 3 mg (<1%) of dark green crystalline II, mp 199°. Anal. Calcd for $(C_5H_5)_2CoNiCB_7H_8$: C, 38.46; H, 5.28; B, 22.02; Co, 17.15; Ni, 17.09. Found: C, 38.44; H, 5.62; B, 22.31; Co, 17.15; Ni, 17.30.

(b) $(C_5H_5)_2CoNiCB_7H_8$, III. Next was eluted a small red band, partially overlapped with the following band. Thick-layer chromatography allowed the separation of 26 mg (3%) of red-black crystals of III, mp 201°. Anal. Calcd for $^{12}C_{11}{}^{11}B_7{}^1H_{18}{}^{59}Co^{64}Ni^+$: 350.0671. Found: 350.0676.

(c) $(C_5H_5)_2CoNiCB_7H_8$, I. Use of thick-layer chromatography was also required to purify this large green band, which upon slow rotary evaporation of the solvent yielded 170 mg (22%) of green crystalline I, mp 171°. Anal. Found: C, 38.35; H, 5.04; B, 21.74; Co, 17.55; Ni, 17.34.

(d) $(C_5H_5)_2CoNiCB_7H_8$, IV. One final neutral product was eluted in hexane as a red-orange band. Recrystallization allowed the isolation of 10 mg (1%) of brown crystalline IV, mp 273°. Anal. Found: C, 38.34; H, 5.32; B, 21.78; Co, 16.80; Ni, 17.21.

Polyhedral Expansion of $[C_5H_5CoCB_7H_8]^-$ at 0°. This temperature gave the best combined yield of $(C_5H_5)_2CoNiCB_7H_8$ isomers. The experiment was performed as above, except that the $(CH_3)_4N^+$ salt of $[C_5H_5CoCB_7H_8]^-$ was used (1.176 g, 4 mmol) and to this was added a previously prepared solution of sodium naphthalide (12 mmol in 80 ml of THF). Quantities of other reagents were increased proportionately. Work-up yielded 147 mg of II (11%), 500 mg of I (36%), 5 mg of III (<1%), and 130 mg of IV (10%).

Polyhedral Expansion of $[C_5H_5CoCB_7H_8]^-$ at 25 and 65°. Reduction of $[(CH_3)_4N][C_5H_5CoCB_7H_8]$ with sodium naphthalide at 25° required about 5–7 days and as in all cases seemed complete when the reaction mixture turned black, after having passed through a brown color. Typically, 4 mmol of starting material yielded 80 mg of II (6%), 300 mg of I (22%), 20 mg of III (2%), and 36 mg IV (3%). Compound III was sometimes not observed in appreciable yield at this temperature.

The reduction with sodium naphthalide required about 48 hr when performed at THF reflux. In this case, 4 mmol of $[(CH_3)_4N][C_5H_5CoCB_7H_8]$ yielded 230 mg of II (17%), 110 mg of I (6%), and 10 mg of IV (1%).

$(C_5H_5)_2CoNiCB_7H_7Br$, Ia. Into a 100-ml flask under nitrogen was placed 100 mg of I and 20 ml of CCl_4. To this was added, with stirring, 48 mg of Br_2 in 10 ml of CCl_4, over a period of 30 min. The solution was stirred an additional 30 min, then chromatographed on thick-layer paper, yielding a trace of Ib and black crystals of Ia (100 mg, 81%), mp 173°. Anal. Calcd for $^{12}C_{11}{}^{11}B_7{}^1H_{17}{}^{79}Br^{59}Co^{64}Ni^+$: 427.9777. Found: 427.9778.

$(C_5H_5)_2CoNiCB_7H_6Br_2$, Ib. This compound was synthesized from I by the addition of 2 equiv of Br_2, as above. Thus, when Br_2 was added to a solution of 80 mg of I, a black precipitate was formed. This was filtered and recrystallized from CH_2Cl_2–hexane to yield 72 mg of black crystalline Ib. An additional 14 mg could be obtained by thick-layer chromatography of the filtrates. Total yield = 86 mg (74%), mp 253°. Anal. Calcd for $^{12}C_{11}{}^1H_{16}{}^{11}B_7{}^{81}Br_2{}^{59}Co^{64}Ni^+$: 509.8843. Found: 509.8847.

$(C_5H_5)_2CoNiCB_7H_7Br$, IIa. Synthesized as above from 60 mg of II was 64 mg (87%) of dark green crystals of IIa, isolated by preparative thick-layer chromatography, mp 183°. Anal. Calcd for $^{12}C_{11}{}^1H_{17}{}^{11}B_7{}^{79}Br^{59}Co^{64}Ni^+$: 427.9777. Found: 427.9778.

$(C_5H_5)_2CoNiCB_7H_6Br_2$, IIb. The addition of 1 equiv of Br_2 to 20 mg of IIa in CCl_4 resulted in a clear, deep brown solution. As in the synthesis of all the bromo derivatives, TLC analysis showed the reaction to be essentially spontaneous. Isolated by the thick-layer technique was 10 mg of brown crystalline IIb, mp 249°. Anal. Calcd for $^{12}C_{11}{}^1H_{16}{}^{11}B_7{}^{81}Br_2{}^{59}Co^{64}Ni^+$: 509.8843. Found: 509.8851.

Thermal Rearrangements of Metallocarborane Isomers. (a) Rearrangement of I. Into a 100-ml flask equipped with a nitrogen inlet, condenser, and stirring bar was placed 150 mg of I and 80 ml of *n*-heptane. The solution was refluxed under N_2 for 85 hr, cooled to room temperature and stripped onto silica gel, and chromatographed in hexane. Eluting first was 85 mg (57%) of II, followed by traces of I and IV. Alternately, 80 mg of I was placed in a 50-ml round-bottom flask and attached to the sublimation apparatus described above. After evacuation, the tube was heated to 300°, and the flask heated to about 130°. Scraped off the cold finger was 74 mg of metallocarboranes, separated by thick-layer chromatography yielding 64 mg of II (80%), a trace of I, and 6 mg of IV (7%). At a temperature of 350°, the products were II (55%) and IV (35%).

When sublimed through the hot tube at 300°, 40 mg of Ia yielded, after chromatograhic separation, 25 mg of IIa (63%) and 8 mg of recovered Ia, plus a trace of an orange-brown compound likely to be monobromo-IV, but not characterized. Similarly at 310°, 43 mg of Ib yielded 26 mg of IIb (60%), plus small amounts of recovered Ib and an uncharacterized orange-brown compound.

(b) Rearrangement of II. Sublimation of 140 mg of II through the tube heated to 450° resulted in the following yields of metallocarboranes, after thick-layer chromatographic separation: II (7 mg, 5%), III (7 mg, 5%), and IV (112 mg, 80%). At 400°, 100 mg of II yielded II (25 mg, 25%), III (8 mg, 8%), and IV (57 mg, 57%). The best yield of III was obtained at 380°, where 90 mg of II rearranged to III (13 mg, 15%) and IV (45 mg, 50%), with 24 mg of II recovered.

(c) Rearrangement of III. A temperature of 350° caused 20 mg of III to rearrange to IV (4 mg, 20%) with 14 mg of III recovered, after thick-layer chromatography. At 450°, 20 mg of III yielded 19 mg of IV (95%) and a trace of III.

(d) Pyrolysis of IV. When 140 mg of IV was sublimed through the hot zone heated to 600°, the product (130 mg) was found to be IV, pure by TLC examination, ^1H and ^{11}B NMR spectroscopy.

$(\eta^6\text{-}C_{10}H_8)CoCB_{10}H_{11}$, V. $[(CH_3)_4N][C_5H_5CoCB_{10}H_{11}]$ (1.118 g, 3.4 mmol) was converted to the Na^+ salt in a similar manner as for $[(CH_3)_4N][C_5H_5CoCB_7H_8]$. This was treated with a THF solution of 10.2 mmol of sodium naphthalide under nitrogen. The solution was stirred 7 days at room temperature, yielding a red color. To this was added a solution of NaC_5H_5 (15 mmol in 120 ml of THF) followed by a THF slurry of 6.0 g (15 mmol) of $NiBr_2{\cdot}2C_2H_4(OCH_3)_2$. The mixture was stirred 20 hr, then O_2 was bubbled through for 20 min. After Celite filtration, the solution was added to 20 g of silica gel, and the solvents were removed by rotary evaporation. The solid was placed atop a 5 × 30 cm silica gel chromatography column and eluted with hexane–CH_2Cl_2 mixtures. An orange band eluted in 40% CH_2Cl_2, which upon rotary evaporation of the solvent produced orange needles of V (100 mg, 9.2%), 250–260° dec.

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(8) We are grateful to Professor C. E. Strouse and Mr. Gordon Hardy for this information received prior to publication.

(9) This is in accord with previous observations[10] that a low-coordinate boron atom adjacent to one metal will occur at low field (ca. −40 to −80 ppm) in the ^{11}B spectrum. It is also apparent from the few examples available[10a,11] that a low-coordinate boron adjacent to two metals will occur between ca. −85 and −145 ppm (the above arguments seem to hold for 8-vertex and larger polyhedra).

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(17) We have not considered possibilities containing a low-coordinate cobalt vertex, as this has not yet been observed in closo-metallocarboranes having eight or more vertices.

(18) R. N. Leyden and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 310, (1975).

(19) This, as well as subsequent statements concerning rearrangement, can be verified with the use of models.

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(21) Low field carborane C–H resonances seem to correlate only with low-coordinate carbon atoms, usually adjacent to one or more metals. We have previously mentioned this observation,[22] as have other workers.[23]

(22) C. G. Salentine, R. R. Rietz, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 3025 (1974).

(23) V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 3090 (1974).

(24) It is possible, and has been experimentally observed,[25] that halogenated carboranes do not rearrange by the same mechanism as their unhalogenated counterparts. However, recent studies[26] on halogenated icosahedral carboranes suggest that the major rearrangement products do follow the same mechanism as the parent carborane, $C_2B_{10}H_{12}$. We can only assume an analogous result here, as no studies of this kind have been performed on 10-vertex polyhedra.

(25) See, for example, H. D. Kaesz, R. Bau, H. A. Veall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **89**, 4218 (1967).

(26) H. V. Hart and W. N. Lipscomb, *Inorg. Chem.*, **12**, 2644 (1973).

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(28) For example, 1,2-$C_2B_{10}H_{12}$ thermally rearranges to the more stable 1,7 isomer. However, two-electron reduction of 1,7-$C_2B_{10}H_{12}$ followed by oxidation produces a high yield of 1,2-$C_2B_{10}H_{12}$ (see G. B. Dunks, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 3174 (1973), and references therein).

(29) It has been observed[30] in cobaltacarboranes of the formula $(C_5H_5Co)_2C_2B_nH_{n+2}$ (n = 6,7,8) that positions of bands in the visible spectrum, and hence the color of the complex, can be correlated with the presence or absence of metal–metal bonds. A similar situation may exist here, noting that I and II are green while III is red and IV is orange.

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Preparation of *B*-σ-Carboranyl Iridium Complexes by Oxidative Addition of Terminal Boron–Hydrogen Bonds to Iridium(I) Species

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Abstract: A number of *B*-σ-carboranyl iridium complexes have been prepared by both intra- and intermolecular oxidative addition of terminal boron–hydrogen bonds to iridium(I) species. The products from reactions between 1,2-, 1,7-, or 1,12-$C_2B_{10}H_{12}$ and L_2IrCl (L = PPh_3 or $AsPh_3$) are trigonal bipyramidal complexes of iridium(III) with axial hydride and chloride ligands, two equatorial L ligands, and an equatorial carboranyl ligand σ-bonded to the metal through one of the boron atoms closest to the carbon atoms. The preparation, characterization, and structures of these complexes are discussed, as well as their significance as model intermediates for transition metal catalyzed deuterium exchange at terminal boron–hydrogen bonds.

The class of metallocarboranes and metalloboranes in which the metal atoms are π-bonded to the carborane or borane ligand has been widely studied in the last decade.[2] Complexes of boranes and carboranes in which the metal is bonded to boron or carbon by two-center, two-electron σ-bonds are less well known. A number of *C*-σ-carboranyl metal complexes have been prepared by reactions between transition metal halide complexes and *C*-lithiocarbor-