Journal of Organometallic Chemistry, 113 (1976) 29—43
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SUBSTITUENT NMR EFFECTS IN TRIPLE-DECKED SANDWICH METALLOCARBORANES

RICHARD WEISS and RUSSELL N. GRIMES *
Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901 (U.S.A.)

(Received December 22nd, 1975)

Summary

The electronic structure of the triple-decked metallocarborane complexes 1,7,2,3- and 1,7,2,4-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ has been examined via ^{11}B and ^1H pulse Fourier transform nuclear magnetic resonance spectroscopy of a series of derivatives containing substituents on the central ($C_2B_3H_5{}^{4-}$) or end ($C_5H_5{}^-$) rings. The results suggest that the 1,7,2,4 complex contains a highly electron-delocalized, metallocene-like central ring, while the 1,7,2,3 system is dominated by strong local π-interactions between the metals and an ethylenic C—C bond in the central ring. In both isomers, the substitution of CH_3, C_6H_5, or $Si(CH_3)_3$ at a carboranyl ring carbon atom, or of Br or I at B(5), produces moderate to large changes in chemical shift (relative to the parent molecule) at all boron positions and at all hydrogens in each ring. End-ring substitution by CH_3, C_2H_5, or $Si(CH_3)_3$ in each isomer generates strong chemical shift effects in the central ring, and the $Si(CH_3)_3$ species also show a small effect in the unsubstituted C_5H_5 ring. A direct *trans*-polyhedral electronic interaction between the metal atoms is proposed to account for the observed antipodal effects.

Since the discovery of ferrocene a quarter-century ago the study of bis(η^5-cyclopentadienyl) transition metal complexes or "sandwich compounds" has developed into a major area of organometallic research. Despite the proliferation of metallocene types and derivatives, not until very recently has the sandwich concept been extended to isolable, characterizable species containing three planar parallel ring ligands and two metal ions. The existence of triple-decked sandwich ions has been postulated in the mass spectra of nickelocene and ferrocene [1], but the first such species to be actually isolated was the tris(η^5-cyclopentadienyl)dinickel cation, $(\eta^5\text{-}C_5H_5)_3Ni_2{}^+$, prepared by Werner and Salzer [2] in 1972. In 1973 the first electrically neutral triple-decked sandwiches, two isomers of $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, were prepared in this laboratory and reported together with a crystallographic characterization of a methyl derivative of one

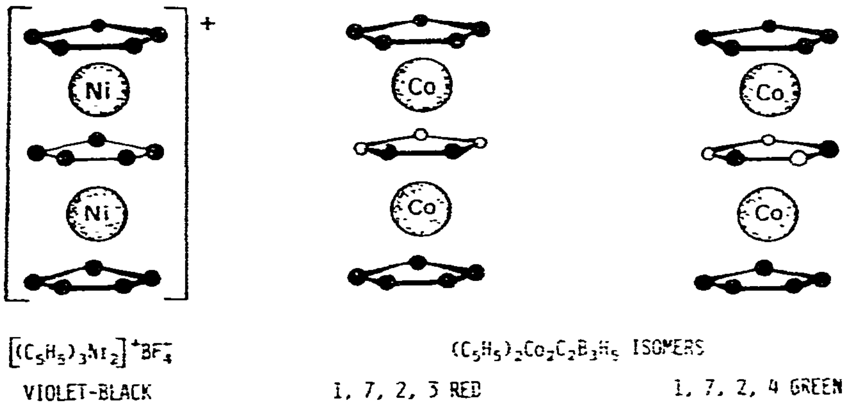

Fig. 1. Structures of the known triple-decked sandwich systems, depicted schematically. Orientations of the end C_5H_5 rings, which undergo rapid rotation in solution, are shown arbitrarily.

of these [3]. More recently, crystal structures of the dinickel cation [4] and a second isomer of the dicobalt system [5] have been published. At this writing, therefore, three true triple-decked systems are known and the molecular structures of all three have been definitively established (Fig. 1).

The novelty of these triple-decked sandwich complexes and their inherent interest from an electronic and bonding viewpoint led us to conduct a detailed study of the two dicobalt isomers. In the work described here, pulse Fourier transform nuclear magnetic resonance spectroscopy was employed to probe the electronic nature of these systems by measuring the effects of placing substituent groups at varying points on the molecules. The FTNMR technique allowed substantially improved precision and signal-to-noise ratio in comparison with the continuous-wave NMR spectra produced in the earlier studies [3,6]; in addition, the use of ^1H- and ^{11}B-decoupling further enhanced the quality of the spectra obtained in this work.

Properties and bonding descriptions

The parent compounds, 1,7,2,3-, and 1,7,2,4-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, are air-stable crystalline solids [3,6] which exhibit the thermal and chemical stability characteristic of metallocarboranes, and indeed are lower homologs of a family of dicobalt polyhedral metallocarboranes [7] having the general formula $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_nH_{n+2}$ of which examples are known for n = 3—10 inclusive [3,6—20]. The red 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ undergoes quantitative thermal rearrangement [10] at 400°C to the green 1,7,2,4 isomer in which the central ring carbon atoms are non-adjacent; in the course of this isomerization two additional isomers of $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ are formed as isolable intermediates, but these are not triple-decked structures and will not be further considered here.

Two equivalent, but distinct, qualitative views of the bonding in these systems are schematically depicted in Fig. 2. The first approach recognizes that the 7-vertex pentagonal bipyramidal $Co_2C_2B_3$ cage is isoelectronic and isostructural with a wide variety of species including the $B_7H_7^{2-}$ ion, the carborane $C_2B_5H_7$,

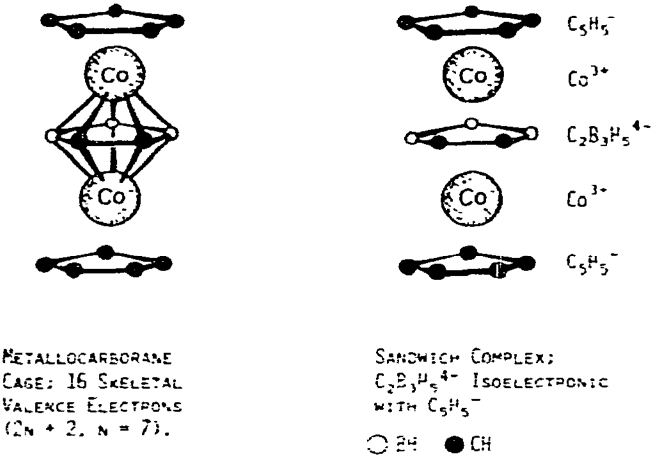

Fig. 2. Two equivalent qualitative representations of the 1,7,2,3-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$ system.

the metallocarboranes (η^5-C_5H_5)$CoC_2B_4H_6$, $(CO)_3FeC_2B_4H_6$, $CH_3GaC_2B_4H_6$, the organometallic cluster $(C_6H_5)_4C_4Fe_3(CO)_9$, and numerous others. All of these structures contain 16 valence electrons in the central polyhedral framework and are consistent with the general rule [21] that predicts closed polyhedral geometry for n-atom clusters having $2n + 2$ skeletal valence electrons *.

An alternative view [3,6,7] is based on a formal separation of the molecule into three planar ring systems and two Co^{3+} ions, the central ligand being a $C_2B_3H_5^{4-}$ ring isoelectronic with $C_5H_5^-$. This description facilitates direct comparison with the (η^5-C_5H_5)$_3Ni_2^+$ complex and other metallocenes and is the one that we shall utilize in the following discussion.

Comparison of 1,7,2,3 and 1,7,2,4-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$

Prior to the inception of this work there were several indications of significant differences in the electronic structures of the two triple-decked dicobalt isomers. The 1,7,2,3 species is red and exhibits a major band at 776 μm in its UV-visible spectrum in CH_3CN [10], while the 1,7,2,4 isomer is green and lacks any significant maxima beyond 555 μm, other than a shoulder at 670 μm [8]. Secondly, major differences in the ^{11}B and ^1H FTNMR spectra [6] (Table 1) are apparent. The range of chemical shifts in the ^{11}B spectrum is about 48 ppm in the 1,7,2,3 isomer compared to 9 ppm in the 1,7,2,4; in the proton spectra the ranges of H—B resonances are respectively 2.66 and 0.85 ppm. These data suggest that the electron density in the central ring is more evenly distributed in the 1,7,2,4 than in the 1,7,2,3 isomer, a point to which we shall return in later dis-

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[*] The (η^5-C_5H_5)$_3Ni_2^+$ complex has four more electrons than (η^5-C_5H_5)$_2Co_2C_2B_3H_5$ and is formally a $2n$+6-electron system: while it is not a typical *nido* (open cage) framework, the long Ni—Ni distance of 3.58 Å indicates a significant departure from "normal" 7-vertex polyhedral geometry as represented by the dicobalt species (the Co—Co distance in both isomers is 3.14 Å). The concept that polyhedral systems having more than $2n$+2 skeletal electrons may in some circumstances experience structural distortions (bond-stretching) as an alternative to the usual cage-opening (bond-breaking) has been discussed elsewhere (see [22]).

TABLE 3

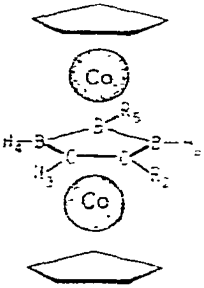
32.1-MHz ^{11}B FTNMR DATA ON $(\eta^5\text{-}C_5H_5)_2Co_2B_3H_5$ DERIVATIVES[a]

Position of substitution	Substituent	δ[b] (ppm)		
		B(4)	B(5)	B(6)
1,7,2,3 isomer				
(Parent)		−5.66	−53.26	−5.66
C(2)	CH_3	−7.48	−54.72	−7.48
C(2)	C_6H_5	−7.12	−55.75	−7.12
C(2)	$(CH_3)_3Si$	−3.12	−51.43	−10.78
B(5)	Br	−3.28	−58.92	−3.28
B(5)	I	−7.40	−42.20	−7.40
Cp ring	CH_3	−5.67	−52.34	−5.67
Cp ring	C_2H_5	−5.63	−51.62	−5.63
Cp ring	$(CH_3)_3Si$	−5.86	−53.49	−5.86
		B(3)	B(5)	B(6)
1,7,2,4 isomer				
(Parent)		−11.95	−21.17	−21.17
C(2)	CH_3	−13.50	−22.27	−22.27
C(2)	C_6H_5	−12.37	−22.12	−22.12
C(2)	$(CH_3)_3Si$	−15.41	−21.07	−26.42
Cp ring	CH_3	−11.79	−20.93	−20.93
Cp ring	C_2H_5	−11.87	−20.83	−20.83
Cp ring	$(CH_3)_3Si$	−12.38	−21.38	−21.38

[a] All spectra run in $CDCl_3$ solution and proton-decoupled. [b] Chemical shifts relative to BF_3 $O(C_2H_5)_2$. The estimated standard deviation for these data is 0.10 ppm.

TABLE 4

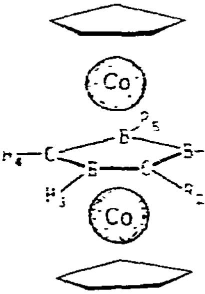
100-MHz ^1H FTNMR MIDDLE RING SUBSTITUENT EFFECTS



1,7,2,3 Isomer

Δδ[a] (Hz)

R_2	R_5	H_2	H_3	H_4	H_5	H_6	C_5H_5
H	H		0	0	0	0	0
CH_3	H		21.4	−1.9	4.4	−11.7	5.8
C_6H_5	H		−21.0	−14.4	−15.6	−47.2	5.6
$(CH_3)_3Si$	H		−38.0	6.9	0.2	−32.2	6.8
H	Br	20.5	20.5	−9.5		−9.5	−6.9
H	I	31.9	31.9	−15.6		−15.6	−5.6



1,7,2,4 Isomer

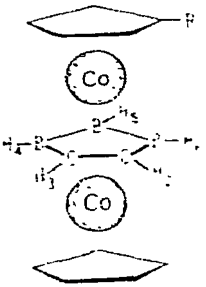
Δδ[a] (Hz)

R_2	R_5	H_2	H_3	H_4	H_5	H_6	C_5H_5
CH_3	H		11.8	−0.3	11.7	11.7	3.0
C_6H_5	H		−23.1	−26.2	−7.4	−31.2	3.8
$(CH_3)_3Si$	H		−16.9	53.2	−13.6	−13.6	3.2

[a] $\Delta\delta = \delta_R - \delta_H$. Negative sign denotes shift to lower yield.

TABLE 5

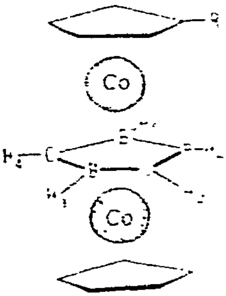
100-MHz ^1H FTNMR END RING SUBSTITUENT EFFECTS



1,7,2,3 Isomer

$\Delta\delta$ [a] (Hz)

R	$H_{2,3}$	$H_{4,6}$	H_5	C_5H_5 [b]
H	0	0	0	0
CH_3	8.2	7.6	−1.7	0.4
C_2H_5	7.6	6.4	16.6	0.6
$(CH_3)_3Si$	4.3	−0.5	1.9	1.6



1,7,2,4 Isomer

$\Delta\delta$ [a] (Hz)

R	$H_{2,4}$	$H_{5,6}$	H_3	C_5H_5 [b]
CH_3	6.9	10.0	5.2	0.1
C_2H_5	6.1	8.6	8.1	0.5
$(CH_3)_3Si$	3.6	0.7	−1.1	1.7

[a] $\Delta\delta = \delta_R - \delta_H$. [b] Unsubstituted ring.

this system is aromatic in character with the effects of electron withdrawing groups occurring primarily at the α positions (adjacent to the substituted atom) and the response to electron-donating substituents being felt mainly at the β positions (nonadjacent to the substituted atom). Since resonance effects are normally exhibited at the β ring locations while electron transfer by an inductive mechanism is reflected at the α positions, it has been argued [23a] that electron withdrawal from ferrocene is primarily inductive, while electron donation occurs by a combination of inductive and resonance mechanisms. In the case of cobalticinium ion similar results [24] have been recorded for electron-donating substituents, but electron-withdrawing groups produce shielding at the β positions, in contrast to ferrocene; it has been suggested [23a] that electron withdrawal is relatively unimportant in any substituted cobalticinium species because of the high metal oxidation state.

With these metallocene studies in mind, we turn to the data on proton substituent effects in the $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ systems in Table 4. For the methyl-, phenyl-, and trimethylsilyl-C-substituted 1,7,2,3 species the largest absolute $\Delta\delta$ values are found at the α(3,6) positions, and the shifts at the β(4,5) atoms are relatively small. This trend may be contrasted with the corresponding 1,7,2,4 derivatives, in which the effects produced at the β positions are generally comparable to those at the α locations, and in one instance (H_4 in the trimethylsilyl species) a very large β effect is observed. A distinct difference between the isomers is also evident in the shifts of the C_5H_5 resonances, which in all cases are very sharp singlets ($\omega_{1/2} \approx 0.5$ Hz) due to rapid ring rotation in solution. The C_5H_5 $\Delta\delta$ values for the 1,7,2,3 derivatives are consistently greater than the 1,7,2,4 shifts by nearly a factor of two, indicating a more effective transmission of electronic effects in the former case.

The overall pattern suggests that resonance interactions between the substituent and the central ring are more important in the 1,7,2,4 system as compared to the 1,7,2,3 and that an inductive mechanism is primarily operative in the latter system. This is interpreted in terms of greater delocalization of electrons in the 1,7,2,4 ring which appears a more typically metallocene-like system: the 1,7,2,3 isomer in contrast, reflects a high local concentration of electron density in the region of the C—C bond. These conclusions are of course relative, and do not take into account paramagnetic contributions to the shielding tensors which may be important [25], masking some effects. Nevertheless, this qualitative distinction between the two isomers is supported by the remainder of the data as well as the previously mentioned X-ray evidence for a short C—C bond in the 1,7,2,3 isomer.

Interpretation of the ^{11}B substituent effects (Table 3) is complicated by the strong dependence [26] of the shielding tensor on the paramagnetic component σ_p, which is proportional to electron density but also includes contributions from the average excitation energy and p-orbital occupation anisotropy, neither of which is well defined. The problem is illustrated by the 5-bromo and 5-iodo 1,7,2,3 derivatives. In the bromo compound the B(5) resonance is shifted downfield and the B(4,6) signal moves upfield, while the effects in the iodo derivative are reversed (Table 3). From the known Hammett σ values one might expect shifts in the same direction, since both I and Br are electron-withdrawing by induction and electron-donating by a resonance mechanism. However, the shifts in bromo and iodo derivatives of $B_{10}H_{14}$ are identical in direction to those described here, and have been shown [27] to be consistent only with changes in the paramagnetic shielding tensor. In light of the present unpredictability of the paramagnetic contribution, we restrict our discussion of the ^{11}B NMR data to the relatively large antipodal effects described below.

Substitution on the end rings

The proton $\Delta\delta$ values for the derivatives substituted on a C_5H_5 ligand (Table 5) are sizeable for the middle ring hydrogens and indicate substantial electronic interaction between the rings, comparable in magnitude to the metallocenes (e.g., methyl substitution produces a 12 Hz shift in the resonance of the unsubstituted ring in cobalticinium ion, and 6 Hz in ferrocene). In the case of the trimethylsilyl derivatives there is even an end ring—end ring effect, despite the very large direct distance, in excess of 6 Å; although small, the effect is reproducible and real (the slight apparent end ring shifts of the methyl and ethyl species are close to the experimental uncertainty (~0.2 Hz) and may not be real). Again there is a clear contrast between the 1,7,2,3 and 1,7,2,4 systems. In the 1,7,2,4 complex the effects are felt fairly equally at different locations on the central ring, while a greater variance occurs in the 1,7,2,3. Thus, the average deviation from the mean (Hz) for the shifts of the five central ring protons is 1.76, 1.12, and 1.68 for the CH_3-, C_2H_5-, and $(CH_3)_3Si$-1,7,2,4 derivatives, respectively; in the 1,7,2,3 species the corresponding values are 3.07, 2.81, and 2.00. The ^{11}B shifts follow essentially the same pattern, with the 1,7,2,4 derivatives exhibiting less variation than their 1,7,2,3 counterparts. The C_5H_5-bonded trimethylsilyl group has only a small effect in both systems, but methyl- and ethyl-substitution produces large shifts at the B(5) position in the 1,7,2,3; no such effect is observed in the 1,7,2,4, all of the $\Delta\delta$'s being less than 0.5 ppm.

Conclusions

A significant difference in the electronic structure of the two triple-decked complexes is evident from these data. The model which in our view most satisfactorily accounts for these findings and at the same time is consistent with X-ray diffraction results, assumes a central ring C—C interaction close to double-bond character in the 1,7,2,3 system, which engages in π-ethylene type overlap with cobalt orbitals. This concept offers a qualitative explanation for the central ring homoannular substituent effects as well as central ring—end ring and end ring—central ring interannular phenomena. Further support for this view is derived from related carborane and metallocarborane systems. The X-ray structural investigation [28] of $C_2B_4H_8$ (a pentagonal pyramid with a BH group occupying the apex position) and its *C,C'*-dimethyl derivative, disclosed cage C—C bond lengths of 1.419(6) and 1.431(6) Å, respectively, which were interpreted as evidence of C—C multiple bonding. This impression was strengthened by the presence of $H_3C—C—B$ bond angles near 120° and was later given even more support by an ab initio SCF MO treatment of 2,3-$C_2B_4H_8$ [29] which indicated that the C—C link forms an ethylenic system which is π-bonded to the apex boron atom, utilizing almost pure *p* orbitals on the carbons. The same calculation predicted the strongest B—B interaction to be that between the apex and the unique basal boron, B(5). The latter conclusion was later supported by a recent ^{11}B NMR study [30] of the same molecule, which demonstrated via line narrowing that the apex is more strongly coupled to B(5) than to any other boron.

Similar quantitative treatments of ring-apex interactions in metallocarboranes are not yet available, but X-ray diffraction studies of the pentagonal pyramidal or pentagonal bipyramidal molecules 1-CH_3-1-$GaC_2B_4H_5$ [31], 2,3-$(CH_3)_2$-1,2,3-$(\eta^5$-$C_5H_5)CoC_2B_4H_4$ [32], and 1-$(CO)_3FeC_2B_3H_7$ [33] revealed central ring C—C distances of 1.47, 1.46, and 1.41 Å; these values are comparable to the 1.44 Å distance in 2-CH_3-1,7,2,3-$(\eta^5$-$C_5H_5)_2Co_2C_2B_3H_4$ [3], and are within the normal range of ethylenic interactions. It also appears significant that the chemical shift of the central ring C—H protons in the 1,7,2,3 complex (τ 4.38) is typical of ethylenic systems, and that it differs considerably from the corresponsing 1,7,2,4 shift (τ 7.62).

This model also suggests a rationale for the anomalously low ^{11}B NMR chemical shift of B(5) in the 1,7,2,3 system. It is a well-established [9,12] empirical rule in metalloboron cage chemistry that 4-coordinate BH groups adjacent to transition metal atoms, especially Co and Fe, exhibit low field chemical shifts, i.e., below ~—40 ppm relative to $BF_3 \cdot O(C_2H_5)_2$. All of the BH units in the 1,7,2,3 and 1,7,2,4 triple-decked isomers occupy 4-coordinate vertices, yet only B(5) has the expected low-field shift. This is now accounted for in terms of a relatively strong direct interaction between B(5) and the metal atoms, analogous to the B(5)-apex bonding in $C_2B_4H_8$ as discussed above; the other boron—metal interactions in both systems are comparatively weak and hence the influence of the metal on the chemical shifts of these borons is diminished.

In summary, the results suggest that in the 1,7,2,4 isomer the metals interact with highly delocalized metallocene-like orbitals on the carboranyl rings, and in the 1,7,2,3 system there is more localized metal—C=C and metal—B(5) bonding.

Finally, the triple-decked complexes afford some interesting comparisons with other systems in terms of antipodal or trans effects [34], in which substitution on a polyhedral cage exerts a large influence on the NMR chemical shift of a nucleus directly opposite the point of substitution. In a pentagonal bipyramid the only antipodal vertices are the 1,7 apices, and the effects of replacement of one apical BH group in 2,3-$C_2B_5H_7$ and 2,4-$C_2B_5H_7$ or their *C*-methyl derivatives with a (η^5-C_5H_5)Co group are seen in the ^{11}B chemical shifts listed in Table 6. In each case, a pronounced deshielding of the remaining apex boron occurs, while the equatorial boron resonances are affected to a much lesser extent. These trends are evident despite the ambiguity in assigning some of the signals in the cobaltacarborane spectra. This large antipodal deshielding may be due to direct interaction of a suitable metal orbital with a symmetry-related orbital on the opposite apex atom. Such a mechanism bypasses the central ring and hence should be essentially independent of it. In the triple-decked complexes it is difficult to directly identify antipodal effects since both apices are occupied by (η^5-C_5H_5)Co groups, but it is noteworthy that silyl substitution on an end ring induces a measurable effect on the proton shifts at the other end ring (Table 5) and that the magnitude is identical in the two isomers. Moreover, the metal—metal distance of 3.14 Å in these systems is not incompatible with a direct interaction.

Future investigations will hopefully elucidate more precisely some of the aspects of the electronic structures of these molecules which we have discussed. Studies of the dicobalt triple-decked complexes and closely related species such

TABLE 6

^{11}B NMR CHEMICAL SHIFTS OF PENTAGONAL BIPYRAMIDAL CARBORANES AND MONOCOBALTACARBORANES [a]

Compound	Apex B(H)	Equatorial B(H) (Rel. Area)	Ref.
Adjacent-carbon Systems			
2,3-$C_2B_5H_7$ [b]	+25	−15, +2	39
1,2,3-$(C_5H_5)CoC_2B_4H_6$	−13.1 or −6.8	−2(2); −13.1(1) or −6.8(1)	6
2,3-$(CH_3)_2C_2B_5H_5$	+12.1	−10.6(2), −5.2(1)	39
1,2,3-$(C_5H_5)Co(CH_3)_2C_2B_4H_4$	−10.8 or −5.5	−5.5(1) or −10.8(1)	6
1,2,3-$(C_5H_5)Co(CH_3)C_2B_4H_5$	−13.1 or −8.0	−2.3(2), −8.0(1) or −13.1(1)	6
Nonadjacent-carbon Systems			
2,4-$C_2B_5H_7$	+22.0	−3.5(2), −6.6(1)	39
1,2,4-$(C_5H_5)CoC_2B_4H_6$	−6.7 or −1.4	−6.7(2), −1.4(1)	9
2,4-$(CH_3)C_2B_5H_6$	+18.8	−5.4(2), −8.2(1)	40
1,2,4-$(C_5H_5)Co(CH_3)C_2B_5H_5$	−6.1 or −2.9	−6.1(2), −2.9(1)	10
2,4-$(CH_3)_2C_2B_5H_5$	+17.3	−5.9(2), −8.5(1)	39

[a] Chemical shifts relative to $BF_3 \cdot O(C_2H_5)_2$: H—^{11}B coupling constants (~120 to 180 Hz) are omitted.
[b] Incompletely characterized compound.

as $(CO)_3Fe[(CH_3)_2C_2B_3H_3]Co(\eta^5\text{-}C_5H_5)$ [35] should be experimentally attractive in view of their high chemical and thermal stability and electrical neutrality.

Experimental section

Materials

Solutions of 2,3-dicarba-*nido*-hexaborate(1—) ($NaC_2B_3H_7$) in tetrahydrofuran (THF) were prepared from $C_2B_4H_8$ and sodium hydride as described elsewhere [36]. Anhydrous cobalt(II) chloride was obtained from $CoCl_2 \cdot 6H_2O$ (Baker) by dehydration in vacuo at 160°C. All solvents were reagent grade and tetrahydrofuran was dried over lithium aluminum hydride before use. Solutions of sodium cyclopentadienide (NaC_5H_5) in THF were prepared from cyclopentadiene and sodium hydride. Cyclopentadiene was distilled from dicyclopentadiene (Aldrich).

Spectra

Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were obtained on a JEOL PS-100P pulse Fourier transform spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Unit resolution mass spectra were obtained on a Hitachi Perkin—Elmer RMU-6E mass spectrometer. Infrared spectra were obtained on a Beckman IR-8 instrument.

Preparation of triple-decked complexes

The syntheses of 1,7,2,3- and 1,7,2,4-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ and their 2-methyl derivatives were conducted as described elsewhere [6,10]. The remaining 2-substituted derivatives of the 1,7,2,3 system employed in this study were prepared by conversion of the corresponding 2-R-$C_2B_4H_7$ species (obtained from B_5H_9 and the appropriate alkyne) to the $Na^+RC_2B_4H_6^-$ salt, followed by reaction with NaC_5H_5 and $CoCl_2$ in a procedure analogous to the preparation of parent 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ from $C_2B_4H_8$ [6]. As in the latter reaction, side products were obtained, usually including the C-substituted derivatives of 1,2,3-$(\eta^5\text{-}C_5H_5)$-$CoC_2B_4H_6$ and the open-cage system 1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$.

The cyclopentadienyl 1,7,2,3 ring-substituted derivatives were obtained by reaction of the appropriate $Na^+RC_5H_4^-$ salt, prepared as described below, with $Na^+[1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_3H_6]^-$ and $CoCl_2$ in THF [6]. The derivatives of the 1,7,2,4 system were in all cases prepared by thermal isomerization of the corresponding 1,7,2,3 complex.

Separation and purification of all of the desired triple-decked species were achieved by preparative layer or column chromatography on silica, and the products were identified from their mass spectra, ^{11}B NMR, and ^1H NMR spectra. In all cases the mass spectra contained intense parent ion peaks, with relative intensities in the parent region consistent with the calculated isotopic compositions.

Assignment of spectra

The correlation of individual ^1H and ^{11}B resonances with specific atoms was in many cases clear and unambiguous by comparison of the derivative spectra with that of the parent compound. All ^{11}B spectra were proton-decoupled, and all ^1H spectra were ^{11}B-decoupled, the latter technique allowing clear observation of previously unobserved or ambiguous H—B resonances. Where ambiguity existed (i.e., in cage C—R substituted derivatives), the assignments were facilitated by (*1*) fine splitting of proton resonances due to H—C—B—H coupling (observed earlier in undecoupled spectra) [3,6—9]; (*2*) assuming that $\Delta\delta$ values of α and β protons differ from each other to a greater extent than do β—β and α—α protons; (*3*) the general observation that the largest $\Delta\delta$ values tend to correspond to the resonances closest to the point of substitution; and (*4*) comparison of ^{1}H and ^{11}B data for the same derivative. In each instance, independent application of each of these considerations led to the same assignment (H—C—B—H fine structure was resolvable in some, but not all, of the proton spectra examined).

2-$(CH_3)_3$Si-1,7,2,3-(η^5-$C_5H_5)_2Co_2C_2B_3H_4$. The carborane 2-$(CH_3)_3$Si-2,3-$C_2B_4H_7$ was prepared by the method of Thompson and Grimes [37] and identified from its IR spectrum. A filtered solution of $Na^+(CH_3)_3SiC_2B_4H_6^-$ prepared [37] from 1.13 mmol of 2-$(CH_3)_3$Si-2,3-$C_2B_4H_7$ and 6.4 mmol of NaH in THF was added to a filtered solution of NaC_5H_5 obtained from 5.0 mmol of C_5H_6 and 32.5 mmol of NaH in THF, and the combined solution was added dropwise over a 10 min period to a stirred solution of 6.5 mmol of anhydrous $CoCl_2$ in THF. After stirring for 2 h at 25°C, the solvent was distilled off under reduced pressure and the residue suspended in 20 ml of 0.01 *M* HCl, exposed to the atmosphere, and stirred for 30 min. After filtration, the residue was extracted with methylene chloride and purified by column chromatography, yielding 2-$(CH_3)_3$Si-1,2,3-(η^5-C_5H_5)$CoC_2B_4H_5$ and 2-$(CH_3)_3$Si-1,7,2,3-(η^5-$C_5H_5)_2Co_2C_2B_3H_4$.

2-C_6H_5-1,7,2,3-(η^5-$C_5H_5)_2Co_2C_2B_3H_4$. The $C_2B_4H_8$ derivative 2-C_6H_5-2,3-$C_2B_4H_7$ was prepared by the method of Onak [38] and identified from its mass spectrum. A filtered solution of $Na^+C_6H_5C_2B_4H_6^-$, obtained from 1.08 mmol of 2-C_6H_5-2,3-$C_2B_4H_7$ and 1.73 mmol of NaH in THF, was added to a filtered solution of NaC_5H_5 prepared from 5.05 mmol of C_5H_6 and 8.45 mmol of NaH in THF, and the combined solution was added dropwise over a 10 min period to a stirred solution of 6.05 mmol anhydrous $CoCl_2$ in THF. After stirring for 2 h at 25°C, the solvent was distilled off under reduced pressure and the residue was suspended in 20 ml of 1 *M* HCl, exposed to the atmosphere, and stirred for 30 min. After filtration and extraction with CH_2Cl_2 the reaction products were separated via column chromatography on silica, yielding 2-C_6H_5-1,2,3-(η^5-C_5H_5)-$CoC_2B_3H_6$ (119 mg, 0.452 mmol, 41.8% yield), and 2-C_6H_5-1,7,2,3-(η^5-$C_5H_5)_2$-$Co_2C_2B_3H_4$ (15.8 mg, 0.041 mmol, 3.8% yield) as the major products.

1,7,2,3-(η^5-$CH_3C_5H_4$)(η^5-C_5H_5)$Co_2C_2B_3H_5$. A filtered solution of $Na^+C_5H_5^-$, prepared from 1.21 mmol of C_5H_6 and 4.90 mmol of NaH in THF, was allowed to react with 1.24 mmol of CH_3I with stirring for 30 min. The mixture was filtered onto the NaH remaining from the preparation of $Na^+C_5H_5^-$, allowed to react for 45 min, filtered and added to a filtered solution of $Na^+(C_5H_5)CoC_2B_3H_6^-$ prepared from 0.336 mmol of (η^5-C_5H_5)$CoC_2B_3H_7$ and 0.788 mmol of NaH in THF. The combined solutions were then added dropwise over a 10-min period to a stirred solution of anhydrous $CoCl_2$ in THF. After stirring for 20 h, the solvent was distilled off under reduced pressure and the residue exposed to the atmosphere, suspended in 20 ml of H_2O and stirred for 1 h. After filtration, the residue was extracted with CH_2Cl_2 and separated via TLC yielding, in addition to starting material, 1,7,2,3-(η^5-$C_5H_5)_2Co_2C_2B_3H_5$ and a mixture of the mono- and di-methyl derivatives. As no solvent system could be found which would separate the mixture, the method of separation employed was to place the mixture on a long thin chromatographic column with a rather slow eluent flow, resulting in a broad band which was collected in three fractions. The second fraction was about 90% pure 1,7,2,3-(η^5-$CH_3C_5H_4$)(η^5-C_5H_5)$Co_2C_2B_3H_5$, as determined by the mass spectrum, and this sample was employed in the NMR measurements.

1,7,2,3-(η^5-$C_2H_5C_5H_4$)(η^5-C_5H_5)$Co_2C_2B_3H_5$. A filtered solution of $Na^+C_5H_5^-$, prepared from 5.0 mmol of C_5H_6 and 16.7 mmol of NaH, was allowed to react with 5.65 mmol of C_2H_5Br for 30 min with stirring. This solution was then filtered onto the NaH remaining from the preparation of $Na^+C_5H_5^-$ and allowed to react until gas evolution had ceased (~40 min). After pumping off the non-condensables, the solution was filtered and added to a filtered solution of $Na^+C_2B_4H_7^-$ prepared from 1.35 mmol of $C_2B_4H_8$ and 1.94 mmol of NaH in THF. The combined solutions were then added dropwise over a 10-min period to a stirred solution of 6.16 mmol of anhydrous $CoCl_2$ in THF. After 2.5 h, the solvent was distilled off under reduced pressure and the residue exposed to air, suspended in 36 ml of 1 *M* HCl and stirred for 1 h. After filtration the residue was extracted with CH_2Cl_2 and separated via TLC. The major product was 1,2,3-(η^5-$C_2H_5C_5H_4$)-$CoC_2B_4H_6$, accompanied by a smaller quantity of 1,7,2,3-(η^5-$C_2H_5C_5H_4$)-(η^5-C_5H_5)$Co_2C_2B_3H_5$.

1,7,2,3-[η^5-$(CH_3)_3SiC_5H_4$](η^5-C_5H_5)$Co_2C_2B_3H_5$. A filtered solution of $Na^+C_5H_5^-$ (prepared from 1.21 mmol of C_5H_6 and 5.02 mmol of NaH) and 1.25 mmol of $(CH_3)_3SiCl$ were allowed to react with stirring for 30 min. This solution was then filtered onto the NaH remaining from the preparation of $Na^+C_5H_5^-$ and allowed to react until no further gas evolution was observed (~40 min). After removal of noncondensables the solution was filtered and added to a filtered solution of $Na^+(C_5H_5)CoC_2B_3H_6^-$, prepared from 0.355 mmol of $(C_5H_5)CoC_2B_3H_7$ [6] and 0.805 mmol of NaH in THF. The combined solutions were then added dropwise over a 10-min period to a stirred solution of 1.56 mmol of anhydrous $CoCl_2$ in THF. After 18 h the solvent was distilled off under reduced pressure and the residue was exposed to air, suspended in 20 ml of H_2O, and stirred for 1 h. After filtration the residue was extracted with methylene chloride and separated via TLC and column chromatography yielding 1,7,2,3-[η^5-$(CH_3)_3SiC_5H_4$](η^5-C_5H_5)-$Co_2C_2B_3H_5$ in addition to the starting material, $(C_5H_5)CoC_2B_3H_7$.

2-$(CH_3)_3$Si-1,7,2,4-(η^5-C_5H_5)$_2Co_2C_2B_3H_4$. In a typical reaction, ~10 mg of 2-$(CH_3)_3$Si-1,7,2,3-(η^5-C_5H_5)$_2Co_2C_2B_3H_4$ was placed in a 1-l bulb, evacuated, sealed, and placed in an oven at 325°C. After 16 h the flask was removed from the oven, opened, and the product extracted with CH_2Cl_2 and purified via TLC.

Other substituted derivatives of 1,7,2,4-(η^5-C_5H_5)$_2Co_2C_2B_3H_5$. All other 1,7,2,4 species used in this study were prepared by thermolysis of the corresponding 1,7,2,3 derivative at 325°C for 16 h, and isolated in a procedure identical to that followed for the preceding compound.

5-Br-1,7,2,3-(η^5-C_5H_5)$_2Co_2C_2B_3H_4$. A solution of 0.129 mmol of 1,7,2,3-(η^5-C_5H_5)$_2Co_2C_2B_3H_5$ and excess CH_3Li in THF was allowed to react with stirring for 30 min. At this point excess C_2H_5Br was added to the solution and the mixture stirred for another 30 min. The volatile materials were distilled off under reduced pressure and the remaining solid separated via column chromatography, yielding the starting carborane plus a red crystalline material which was identified as $Br(C_5H_5)_2Co_2C_2B_3H_4$ from its mass spectroscopic parent peak at *m/e* 390 and its pattern of relative intensities, which was in agreement with the indicated composition based on natural isotopic distributions. The presence of a fragment having a cutoff at *m/e* 189, corresponding to $(C_5H_5)_2Co^+$, suggested that the bromine substitution had taken place on the central (carboranyl) ring, and the ^{11}B and ^1H NMR spectra established the position of substitution as B(5).

5-I-1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_4$. The compound was obtained fortuitously in an attempted preparation of 1,7,2,3-$(\eta^5\text{-}CH_3C_5H_4)(\eta^5\text{-}C_5H_5)Co_2C_2B_3H_5$ as described above, in the course of which CH_3I was employed. A filtered solution of $Na^+C_5H_5^-$, prepared from 1.21 mmol of C_5H_6 and 2.1 mmol of NaH in THF, was allowed to react with 1.92 mmol of CH_3I for 30 min with stirring. After adding 2.5 mmol of CH_3I, the mixture stood for 30 min. The volatile products were then fractionated through a —95°C trap, and the —95°C contents were vacuum-distilled onto 2.08 mmol of NaH, allowed to react for 45 min, filtered, and added to a filtered solution of $Na^+(C_5H_5)CoC_2B_3H_6^-$ prepared from 0.357 mmol of 1,2,3-$(C_5H_5)CoC_2B_3H_7$ and 0.520 mmol of NaH in THF. The combined solutions were added to a stirred solution of 1.52 mmol of anhydrous $CoCl_2$ in THF. After stirring for 16 h, the residue was suspended in 20 ml H_2O, stirred for 1 h, and extracted with CH_2Cl_2. TLC separation yielded 1,2,3-$(C_5H_5)CoC_2B_3H_7$ and 5-I-1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_4$, the identity of which was confirmed by a high-resolution mass spectrometric analysis. (Found 433.9155. $^{127}I^{59}Co_2{}^{12}C_{10}{}^{11}B^{10}B_2\text{-}{}^1H_{14}^+$ calcd.: 433.9155.)

Acknowledgments

This work was supported in part by the Office of Naval Research. The pulse Fourier transform NMR equipment was obtained in part via a departmental instrument grant from the National Science Foundation.

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