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C−C Plasticity in Boron Chemistry: Modulation of the $C_c\cdots C_c$ Distance in Mixed Pyrrolyl/Dicarbollide Complexes[†]

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The single, double, and triple bond distances are well defined in conventional organic compounds. Cluster boron chemistry, in particular the *o*-carboranes, provides the possibility to modulate the C−C distance in an almost continuous way within the same family of compounds. As an example, mixed pyrrolyl/dicarbollide sandwich cobalt complexes derived from *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] (**1**) display a continuous range of $C_c\cdots C_c$ distances between 1.640(7) for the parent compound and 1.919(6) for *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$] (**5**). Here, C_c represents the cluster carbon atom. The $C_c\cdots C_c$ modulation was achieved merely by modifying the substituents on the carbon of the cluster compound. The complexes studied were synthesized by reaction of the appropriate *closo* cluster, e.g., 1,2-$(SCH_3)_2$-1,2-$C_2B_{10}H_{10}$ with a suspension of K[NC_4H_4] and anhydrous $CoCl_2$. The new compounds are *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$] (**5**), *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$] (**6**), and *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**7**). Their crystal structures were elucidated by single-crystal X-ray diffraction and are compared with those of the parent compound *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] (**1**) and earlier prepared compounds *closo*-[3-Co(η^5-NC_4H_4)-1-CH_3-2-C_4H_9-1,2-$C_2B_9H_9$] (**2**) and *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-2-C_3H_5-1,2-$C_2B_9H_9$] (**3**). Purely alkyl substituents alter the $C_c\cdots C_c$ distance of the parent compound very little, which implies that steric effects, although relevant, are not the major cause of the lengthening. In contrast, substituents with lone pairs alter the $C_c\cdots C_c$ distance substantially. Computational methods suggest that the cause of the elongation is the transfer of electron density from the available lone pairs on the substituents to the Ψ^* orbitals on C_c, producing a decrease in the $C_c\cdots C_c$ bond order and, thereby, an increase in the $C_c\cdots C_c$ distance.

Introduction

Although the pyrrolyl [pyr]$^-$ and cyclopentadienyl [Cp]$^-$ ligands are formally equivalent, the number of complexes incorporating one or the other is very different. Both ligands are able to coordinate in a η^5-π-bonding fashion, and both are mononegative. However, the pyrrolyl anion easily coordinates to metal by forming a N→M σ-bond. A typical way to facilitate η^5-π-bonding instead has been to insert bulky substituents at the 2,5-carbon atoms of the ring. Thus, the great majority of pyrrolyl complexes reported in the literature are derivatives of 2,5-di-*tert*-butylpyrrolyl or 2,5-dimethylpyrrolyl. Pyrrolyl complexes of metals in almost all groups in the periodic table have been described. Examples are found among main group elements (Pb, Sn),[1] transition metals (Ti, Fe, Co),[2] lanthanides (Nd, Sm, Tm, Yb, Lu),[3] and alkaline-earths (Ca, Sr).[4] Surprisingly, some of the first η^5-π-pyrrolyl complexes reported were a set of semi-sandwich Re(III) complexes[5] in which naked pyrrolyl (nonsubstituted) had been used. Although the number of examples with naked pyrrolyl has grown significantly, the 2,5-disubstituted pyrrolyl derivatives still are much more abundant.

[†] Dedicated to Professor Rafael Usón on the occasion of his 75th birthday in recognition of his notable contributions to organometallic chemistry.

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The 7,8-dicarba-*nido*-undecaborate ion $[7,8\text{-}C_2B_9H_{11}]^{2-}$ is a dianionic cluster with an open face isolobal and isoelectronic to $[Cp]^-$ and $[pyr]^-$. Mixed sandwich complexes of Co(III) containing naked $[pyr]^-$ and $[7,8\text{-}C_2B_9H_{11}]^{2-}$ have been synthesized by our group.[6] The only other reported examples of such sandwich complexes contain Co(III), derivatives of $[C_2B_4H_6]^{2-}$, and C-substituted pyrrolyl ancillary ligands.[7] The capacity to generate a high negative charge of the ligand combination ($[pyr]^-/[7,8\text{-}C_2B_9H_{11}]^{2-}$) facilitates the complexation of metal ions in a higher oxidation state.[8] Thus, at present, the only examples of sandwich trivalent metal ion complexes incorporating pyrrolyl or pyrrolyl derivatives are those also incorporating carboranes.

Certain η^5-π-coordinated $[7,8\text{-}C_2B_9H_{11}]^{2-}$ ligands have been found to display an unusually long $C_c\cdots C_c$ distance. In conventional cluster terminology these species are described as *pseudocloso*, in contrast to the *closo* species where bonding between a pair of neighbor atoms is established. Although examples of such $C_c\cdots C_c$ elongation exist for metal ions in different positions of the periodic table, e.g., with Mo[9] and Ru,[10] most of the examples are complexes with Rh(I).[11] The $C_c\cdots C_c$ elongation has been attributed to steric crowding in the $C_c\cdots C_c$ region,[12] which forces the two carbons to move apart. Although there is evidence for such an interpretation, data for less bulky substituents[13] suggest that an electronic contribution may be relevant as well. As just noted, most of the examples of unusually long $C_c\cdots C_c$ distances have involved Rh(I). However Rh(I) has a strong preference for 16-electron complexes, and it could be that its presence, in itself, facilitated the $C_c\cdots C_c$ elongation, as two fewer electrons were then required to satisfy the electronic demand of the metal. We note, too, that all examples reported so far of metallacarborane clusters with elongated $C_c\cdots C_c$ are with metal ions in low oxidation states such as Mo(I), Rh(I), and Ru(II).[9,10]

In the work here described we chose $[3\text{-}Co(\eta^5\text{-}NC_4H_4)\text{-}1,2\text{-}C_2B_9H_{11}]$ as a probe of the electronic influence of substituents on carbon on the $C_c\cdots C_c$ distance. The naked pyrrolyl group is not sterically demanding, and the cobalt ion is in an unprecedented trivalent state for the $C_c\cdots C_c$ elongation and obeys the 18-electron rule. All these conditions appeared to be necessary to avoid, as far as possible, the complicating effect of steric crowding on the $C_c\cdots C_c$ distance and the possible effect of lower electronic demand of the metal ion. NMR and X-ray crystallographic studies on three derivatives of **1** suggest how the electronic influence of the substituents may affect the $C_c\cdots C_c$ distance.

Results and Discussion

The crystal structure of *closo*-$[3\text{-}Co(\eta^5\text{-}NC_4H_4)\text{-}1,2\text{-}C_2B_9H_{11}]$ (**1**) revealed an extraordinary resemblance between the $C_c\cdots C_c$ distance in this molecule, 1.640(7) Å,[6a] and the $C_c\cdots C_c$ distance in the *o*-carborane, 1,2-$C_2B_{10}H_{12}$, which is given as 1.629(6) Å.[14] This did not seem a coincidence considering that *closo*-$[3\text{-}Co(\eta^5\text{-}NC_4H_4)\text{-}1\text{-}CH_3\text{-}2\text{-}C_4H_9\text{-}1,2\text{-}C_2B_9H_9]$ (**2**) exhibits a value of 1.671(7) Å, which is comparable to the 1.684(6) Å found for *closo* 1,2-μ-$(CH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2)$-1,2-$C_2B_{10}H_{10}$.[15] This last compound, despite its complexity, has similar substituents. Further similarity is evident for *closo*-1,2-$(C_6H_5)_2$-1,2-$C_2B_{10}H_{10}$,[16] with a distance of 1.733(4) Å, and *closo*-$[3\text{-}Co(\eta^5\text{-}NC_4H_4)\text{-}1\text{-}C_6H_5\text{-}2\text{-}C_3H_5\text{-}1,2\text{-}C_2B_9H_9]$ (**3**), with a distance of 1.737(4) Å. The similarity of these pairs of values prompted us to seek further examples of such parallelism. One controversial point in 1,2-$C_2B_{10}H_{12}$ chemistry, studied by us and others,[17] is the long $C_c\cdots C_c$ distance, over 1.8 Å, when the carbon atoms are substituted by thioethers. A lengthening also occurs when phosphorus atoms are bonded to the cluster carbon atoms. For example, in *closo*-1-$P(C_6H_5)_2$-2-CH_3-1,2-$C_2B_{10}H_{10}$ the $C_c\cdots C_c$ distance is 1.702(6) Å,[18] and in *closo*-1,2-$(P(C_6H_5)_2)_2$-1,2-$C_2B_{10}H_{10}$, it is 1.722(4) Å.[19] Although we did not rule out steric crowding as the reason for this elongation, we proposed an additional explanation in terms of partial overlap of the tangentially oriented p atomic orbitals of the cluster with appropriate-symmetry atomic orbitals (AOs) of the exocluster atom connected to the cluster carbon.[18] For purposes of the present work, therefore, we designed a set of reactions that would allow us to decide if the parallelism was of significance and to corroborate the AOs explanation given earlier. For this purpose we synthesized *closo*-$[3\text{-}Co(\eta^5\text{-}NC_4H_4)\text{-}1,2\text{-}C_2B_9H_{11}]$ derivatives (compounds **5** and **6**) where the cluster carbon atoms were substituted with thioethers that could be expected to be clearly different in their effect. In other words, one was clearly more electron donating than the other. In addition, a phenyl-substituted $[7,8\text{-}C_2B_9H_{12}]^-$ derivative (**7**) was necessary to compare with **3**, which has an additional cyclopropyl group.

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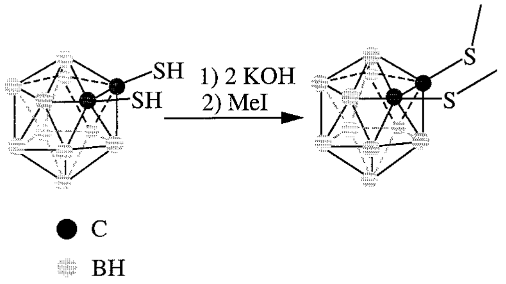
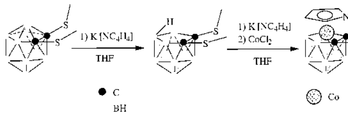
Scheme 1. Alkylation of *closo*-1,2- $(SH)_2$-1,2-$C_2B_{10}H_{12}$



Preparation of these complexes required the prior synthesis of 1,2-$(SC_6H_5)_2$-1,2-$C_2B_{10}H_{10}$[25b] and 1,2-$(SCH_3)_2$-1,2-$C_2B_{10}H_{10}$ (**4**). The two syntheses are very different since the first compound contains an aryl substituent on sulfur and the second an alkyl. The synthesis reaction for compound **4** is presented in Scheme 1. Both *closo* species were characterized by NMR techniques, and chemical analyses and are in agreement with the proposed formulas.

Syntheses and NMR Characterization of Mixed Pyrrolyl/Dicarbollide Complexes. The thioether and phenyl derivatives of *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$][6a] were synthesized in the same manner as the parent compound. That is, K[NC_4H_4] in large excess was reacted with 1,2-$(SCH_3)_2$-1,2-$C_2B_{10}H_{10}$, 1,2-$(SC_6H_5)_2$-1,2-$C_2B_{10}H_{10}$, or 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ in THF. After 4 h refluxing, which was required to partially degrade the cluster and remove the open face proton, anhydrous $CoCl_2$ was added. The ratio of the reagents was 12:1:5, in the order reported. The reaction that is illustrated in Scheme 2 was terminated after 48 h refluxing. Following workup, *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$] (**5**), *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$] (**6**), and *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**7**) were obtained.

Scheme 2. Synthesis of *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$]



The $^{11}B\{^1H\}$ NMR spectra of complexes **5** and **6** displayed six resonances with a pattern 1:1:2:2:2:1. The $^{13}C\{^1H\}$ NMR spectra showed two different resonances in the pyrrolyl region, corresponding to two different pairs of pyrrolyl carbon atoms and suggesting, as with compound **1**, the existence of either a symmetry plane or a free rotation of the pyrrolyl group resulting in an average spectrum. The $^{11}B\{^1H\}$ NMR spectrum of compound **7** displayed five resonances with pattern 1:1:4:1:2. The resonance of intensity four is the result of the fortuitous overlapping of at least two different signals, as revealed by the ^{11}B NMR spectrum. The $^{13}C\{^1H\}$ and ^1H NMR spectra of **7** showed four different signals, one for each of the carbon and hydrogen atoms in the pyrrolyl unit. This is consistent with the asymmetry caused by the monosubstitution on the carborane cluster.

X-ray Diffraction Studies. X-ray data were crucial to studying the $C_c\cdots C_c$ elongation as a function of the substituents on carbon. Good quality crystals for X-ray diffraction studies were grown by slow evaporation of CH_2Cl_2/C_6H_{14} solutions of compounds **5**, **6**, and **7** (Table 1).

Table 1. Crystallographic Data and Structural Refinement Details for *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$] (5), *closo*-[3-Co(η^5-NC_4H_4)(1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$] (6), and *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (7)

	5	6	7
empirical formula	$C_8H_{19}B_9CoNS_2$	$C_{18}H_{23}B_9CoNS_2$	$C_{12}H_{19}B_9CoN$
fw	349.58	473.71	333.50
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*Pnma* (No. 62)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a (Å)	9.3805(15)	11.780(2)	10.889(5)
b (Å)	12.897(2)	8.835(2)	11.444(3)
c (Å)	13.438(2)	21.581(2)	13.026(7)
β (deg)	90	96.400(11)	90
V (Å^3)	1625.7(4)	2232.1(7)	1623.2(12)
Z	4	4	4
T (°C)	21	21	21
λ (Å)	0.71069	0.71069	0.71069
ρ (g cm^{-3})	1.428	1.410	1.365
μ (cm^{-1})	12.93	9.63	10.45
goodness-of-fit	1.035	1.028	1.142
R^a [$I > 2\sigma(I)$]	0.0344	0.0412	0.0495
$R_w{}^b$ [$I > 2\sigma(I)$]	0.0758	0.0908	0.1232

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}.^{1/2}$

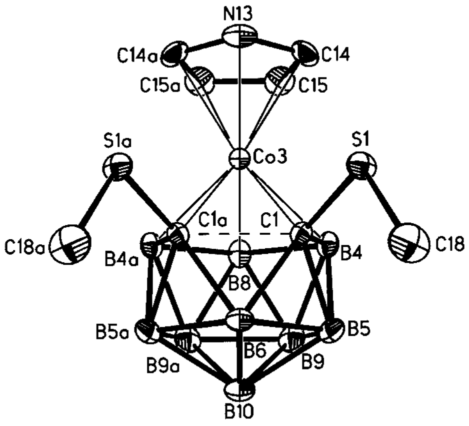


Figure 1. ORTEP drawing of *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$] (**5**). The letter a refers to equivalent position *x*, $-y+1/2$, *z*.

Compound **5** (Figure 1, Table 1) assumes crystallographic σ symmetry with the mirror plane passing through the atoms Co3, B6, B8, B10, and N13, and thus the pyrrolyl nitrogen is bisecting the $C_c-Co3-C_c$ angle. This preferential orientation of $[C_2B_9H_{11}]^{2-}$ ligands in semisandwich complexes had been seen with carbonyl,[20] indenyl,[21] and amide[22] ligands. In the structure of **7** (Figure 2, Table 1) the nitrogen atom is shifted slightly (7.5°) from the bisecting position. The N position in the

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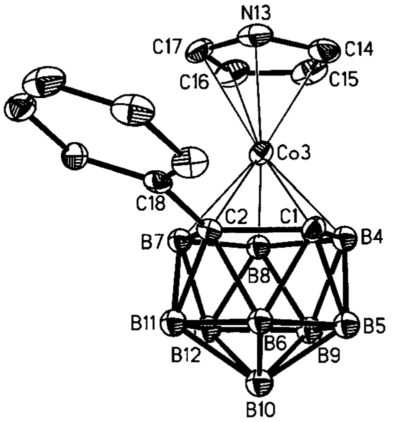

Figure 2. ORTEP drawing of *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**7**).

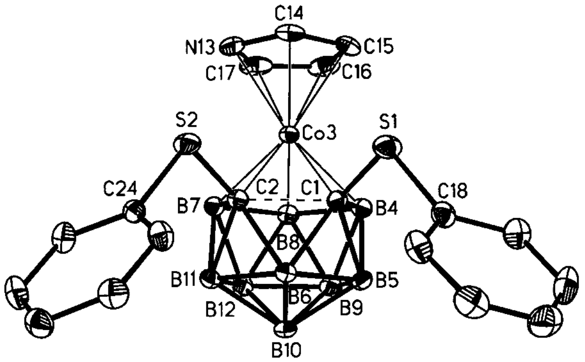

Figure 3. ORTEP drawing of *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$] (**6**).

pyrrolyl ligand in the solid state, almost bisecting the C_c−C_c distance, is the same as in other reported structures of *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] derivatives.[6] However, a surprising result was obtained for compound **6** (Figure 3, Table 1). Whereas the $^{13}C\{^1H\}$ and ^1H NMR spectra indicated pseudo-symmetry, the X-ray results revealed that the nitrogen atom was not located between the cluster carbons but was displaced 71.15° from the central position. This is the first example of a mixed η^5-pyrrolyl/dicarbollide cobaltacarborane in which the nitrogen atom is not found in solid state to lie between the cluster carbon atoms. The pseudo-symmetry observed in solution and the asymmetry in the solid state would seem to indicate that the pyrrolyl moiety rotates in a manner similar to ferrocene. Although preliminary low-temperature NMR experiments and theoretical studies support this hypothesis, the phenomenon is in need of further study. In addition to the structural parameters of **5**, **6**, and **7**, Table 2 shows the most significant distances and angles obtained from structural studies of compounds **1**−**3**. As can be seen, the Co−C_c and C_c−B6 distances are almost invariable, while the $C_c\cdots C_c$ distance and C_c−B6−C_c and C_c−Co3−C_c angles are strongly affected by the changes in substituents.

Compounds **5**, **6**, and **7** are an addition to the mixed pyrrolyl/dicarbollide compounds prepared earlier by our group:[6] *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] (**1**), *closo*-[3-Co(η^5-NC_4H_4)-1-CH_3-2-C_4H_9-1,2-$C_2B_9H_9$] (**2**), and *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-2-C_3H_5-1,2-$C_2B_9H_9$] (**3**). According to X-ray data, one common structural feature of **1**, **2**, and **3** is that, in all of them, the nitrogen atom is almost bisecting the C_c−Co−C_c angle. Thus N was fixed between the dicarbollide carbon atoms C(1) and C(2). The crystal data for **5** and **7** likewise show N to be located between the two carbon atoms. However, as noted above, this was not the case for compound **6**. Compound **6** is unique among our compounds in that the nitrogen is not bisecting the $C_c\cdots C_c$ connection, and this suggests that some rotation about the pyrrolyl centroid/Co/dicarbollide centroid is taking place. We intend to examine this possibility in a future publication. A second point of interest is the modulation of the $C_c\cdots C_c$ distance, as demonstrated by comparative X-ray analysis of these compounds.

Two techniques have been utilized in the attempt to describe the effect of the carbon substituents on the $C_c\cdots C_c$ distance. The first involved monitoring the ($\langle^{11}B\{^1H\}\rangle$) position and the second the X-ray analysis for the C(1)−C(2) distance.

As has recently been shown by Welch et al.,[23] a close correspondence appears to exist between the average $^{11}B\{^1H\}$ NMR position ($\langle^{11}B\{^1H\}\rangle$) of sandwich rhodium complexes that incorporate one Cp* and one dicarbollide unit and the *pseudocloso* character of these compounds. Greater *pseudocloso* character of the complex (which means a longer C(1)−C(2) distance) implies a more positive value of this averaged $^{11}B\{^1H\}$ NMR position. Thus, by monitoring the $\langle^{11}B\{^1H\}\rangle$ position, we thought it might be possible to establish a correspondence between the C(1)−C(2) distance and the bulkiness of the C(1) and C(2) substituents and/or their electronic properties. The second way to describe the effect of the carbon substituents on the $C_c\cdots C_c$ distance, X-ray measurement of the C(1)−C(2) distance, offered a more reliable approach. We first examine the X-ray measurements.

In our analysis, the elongation caused by the substituents on carbon will be referenced to the C(1)−C(2) distance in the parent compound **1**. Leaving aside the packing forces, we consider that three factors may influence the C(1)−C(2) distance: (i) steric effects due to substituting one or both of the contiguous carbon atoms with bulky groups, (ii) an electronic effect due to the electronegativity differences between hydrogen atoms and substituting groups, and (iii) a π-electronic back-donation from the substituting groups into Ψ^* orbitals of the cluster, mostly sited on the C(1)−C(2) bond. Steric crowding would produce repulsive forces that would tend to move the contiguous carbon atoms apart, an enhanced electronegativity of the substituent would deplete electron density between C(1) and C(2) and would lengthen the distance, and π-electronic back-donation to the LUMO (Ψ^*) orbital, mostly sited on the two carbon atoms, would weaken the $C_c\cdots C_c$ bond order.

The complexes that were studied are listed in Table 2. If we compare the $C_c\cdots C_c$ distances found in compounds **2** and **3**, 1.671(7) and 1.737(4) Å, respectively, with the same distance for **5**, 1.919(6) Å, we find that, while Δd(**2**−**1**) and Δd(**3**−**1**) are 0.031 and 0.097 Å, respectively, Δd(**5**−**1**) is increased to 0.279. It seems clear, then, that although influential, the steric crowding is not sufficient to explain the $C_c\cdots C_c$ lengthening in **5**. As a consequence, electronic factors should be

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 1−3 and 5−7[a]

	5	**6**	**7**	**1**[6a]	**2**[6b]	**3**[6b]
C1−Co3	2.021(3)	2.019(3)	2.036(6)	2.007(5)	2.009(6)	2.036(3)
C2−Co3	2.021(3)	2.014(3)	2.041(6)	2.017(5)	2.013(5)	2.029(3)
C1−B6	1.726(5)	1.724(5)	1.754(10)	1.728(8)	1.72(1)	1.715(4)
C2−B6	1.726(5)	1.720(5)	1.712(10)	1.727(8)	1.713(9)	1.746(4)
C1−C2	1.919(6)	1.864(5)	1.682(9)	1.640(7)	1.671(7)	1.737(4)
C1−Co3−C2	56.68(16)	55.04(13)	48.7(3)	48.1(2)	49.1(2)	50.6(1)
C1−B6−C2	67.5(3)	65.5(2)	57.7(4)	56.7(3)	58.2(4)	60.2(2)

[a] For compound **5** C2 refers to C1 at equivalent position x, $-y+1/2$, z.

Table 3. Chemical Shift Average $\langle {}^{11}B\{{}^1H\}\rangle$ Position (in ppm) and C_c-C_c Distances (in Å) for Semisandwich Cobalt Complexes Which Incorporate a Pyrrolyl Unit

	C_c substituents					
	H/H (**1**)	C_6H_5/H (**7**)	C_4H_9/CH_3 (**2**)	C_3H_5/C_6H_5 (**3**)	SCH_3/SCH_3 (**5**)	SC_6H_5/SC_6H_5 (**6**)
$\langle {}^{11}B\{{}^1H\}\rangle$	−5.82	−4.67	−4.57	−3.90	−2.95	−2.76
$d_{C_c\cdots C_c}$	1.640(7)	1.685(8)	1.671(7)	1.737(4)	1.919(6)	1.864(5)

considered, as we pointed out earlier[24] when we proposed that the $C_c\cdots C_c$ distances could be estimated with the empirical equation $d = d_0 + \sum a_i + \sum S_i$. Here d is the $C_c\cdots C_c$ distance in the carborane derivative, d_0 the $C_c\cdots C_c$ distance in the *o*-carborane, a_i the summed electronic contributions, and S_i the summed steric contributions.

The $S-CH_3$ and $S-C_6H_5$ substituents were selected as suitable probes to determine the major factors influencing the $C_c\cdots C_c$ lengthening. In fact, since $S-C_6H_5$ is larger than $S-CH_3$, it should facilitate $C_c\cdots C_c$ elongation for reasons of steric crowding. $S-C_6H_5$ is also more electron-withdrawing than $S-CH_3$, and its stronger capability for electron polarization and the greater electron-depletion it effects in the $C_c\cdots C_c$ bond should promote $C_c\cdots C_c$ elongation.

Electron Withdrawing or LUMO Implication? Table 3 shows experimental $\langle {}^{11}B\{{}^1H\}\rangle$ positions and the corresponding C_c-C_c distances measured for compounds **1**−**3** and **5**−**7**, arranged in order of increasing $\langle {}^{11}B\{{}^1H\}\rangle$.

Although only a near linear correlation exists between $\langle {}^{11}B\{{}^1H\}\rangle$ and the $C_c\cdots C_c$ distances, the trend is reasonably good, permitting, within a reasonable degree of error, prediction of the $C_c\cdots C_c$ distance from the $\langle {}^{11}B\{{}^1H\}\rangle$ position. This correlation also allows us to state that the conversion from *closo* to *pseudocloso* is gradual. No pure *closo* or pure *pseudocloso* clusters exist, but most probably only clusters with more or less character of one or the other.

If we restrict our discussion to the structural data obtained by X-ray diffraction, we observe that the two thioether species **5** and **6** (see Table 2) have a long $C_c\cdots C_c$ distance, almost 25% longer than that of a single C−C bond. This raises some doubts about whether a significant degree of bonding exists at all. However, as seen in Table 2, a continuous range of $C_c\cdots C_c$ distances is observed, ranging from 1.640 to 1.919 Å, indicating that a smooth elongation and not an abrupt break takes place. This implies that the $C_c\cdots C_c$ is a bond of gradually decreasing strength. As noted above, our interpretation is that steric crowding, although partly responsible for the elongation, is not the major factor responsible for the weakening of the bond. Electronic effects are the major factor. We go on, now, to discuss electronic effects of the H/H (**1**), SCH_3/SCH_3 (**5**), and SC_6H_5/SC_6H_5 (**6**) substituents on the $C_c\cdots C_c$ distance. The Pauling electronegativity of sulfur (2.5) is identical with that of carbon. However, the inductive character can be modulated by substituents on S. The methyl group will make the sulfur atom less electron-withdrawing than the phenyl group. If electronegativity, or electron polarization toward sulfur, was the reason for the $C_c\cdots C_c$ elongation, the SC_6H_5/SC_6H_5 substituents should produce the longer $C_c\cdots C_c$ distance, due to electron density depletion. This conclusion is in contradiction with the experimental evidence, however, since the longer distance is found with SCH_3/SCH_3 (**5**). In earlier work, the $C_c\cdots C_c$ elongation produced by phosphorus in 1-P$(C_6H_5)_2$-2-CH_3-1,2-$C_2B_{10}H_{10}$ was interpreted in terms of overlap of the tangential p orbitals in the cluster with p or d orbitals on the phosphorus.[18] At that time, we did not pursue this explanation. Our interpretation of the $C_c\cdots C_c$ distance in the present series of *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] derivatives is that π-back-donation from an occupied orbital on sulfur, the lone pair, is partially transferred to the LUMO (Ψ^*) on the cluster with important orbital contributions for the carbon atoms. Thus the LUMO antibonding orbital on the carbon atoms is partially filled, decreasing the $C_c\cdots C_c$ bond order.

This hypothesis is supported by theoretical calculations made on compounds **1** and **5**. Single-point calculations were performed at the ZINDO/1 level using crystallographic atomic coordinates. The same results were obtained at the HF/TZV level of theory. Figure 4 shows the LUMO calculated at the ZINDO/1 level for **1** from different perspectives. As can be seen, this molecular orbital exhibits antibonding character between C(1) and C(2). When a hydrogen atom is replaced by a S−R group, formally, the HOMO which is occupied by the lone pair combines with the former LUMO of compound **1** to form two new molecular orbitals (see Figure 5). One of them will have an important contribution from the former LUMO present in the parent species **1**. This transfer of electronic density into the Ψ^* orbitals on C(1) and C(2) is the cause of bond lengthening when hydrogen atoms are replaced by π-donor groups.

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(23) Garrioch, R. M.; Rosair, G. M.; Welch, A. J. *J. Organomet. Chem.* **2000**, *614*−*615*, 153.

(24) Kivekäs, R.; Sillanpää, R.; Teixidor, F.; Viñas, C.; Nuñez, R.; Abad, M. *Acta Crystallogr.* **1995**, *C51*, 1864.

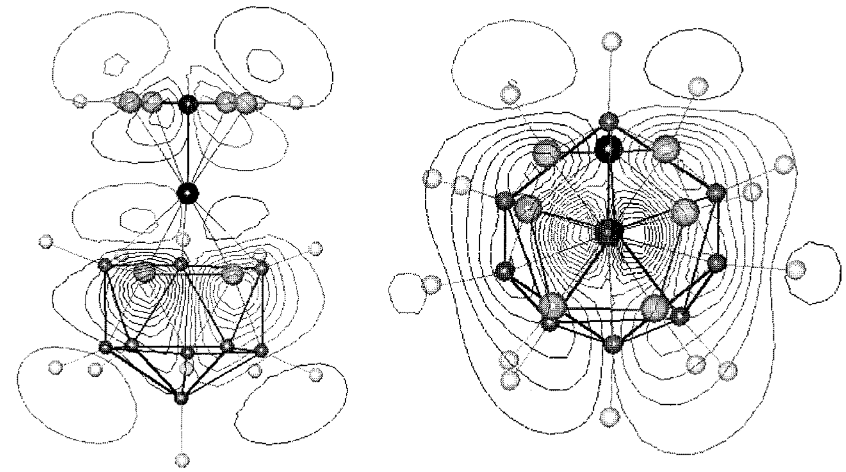

Figure 4. LUMO of compound **1** calculated at the ZINDO/1 level using crystallographic coordinates.

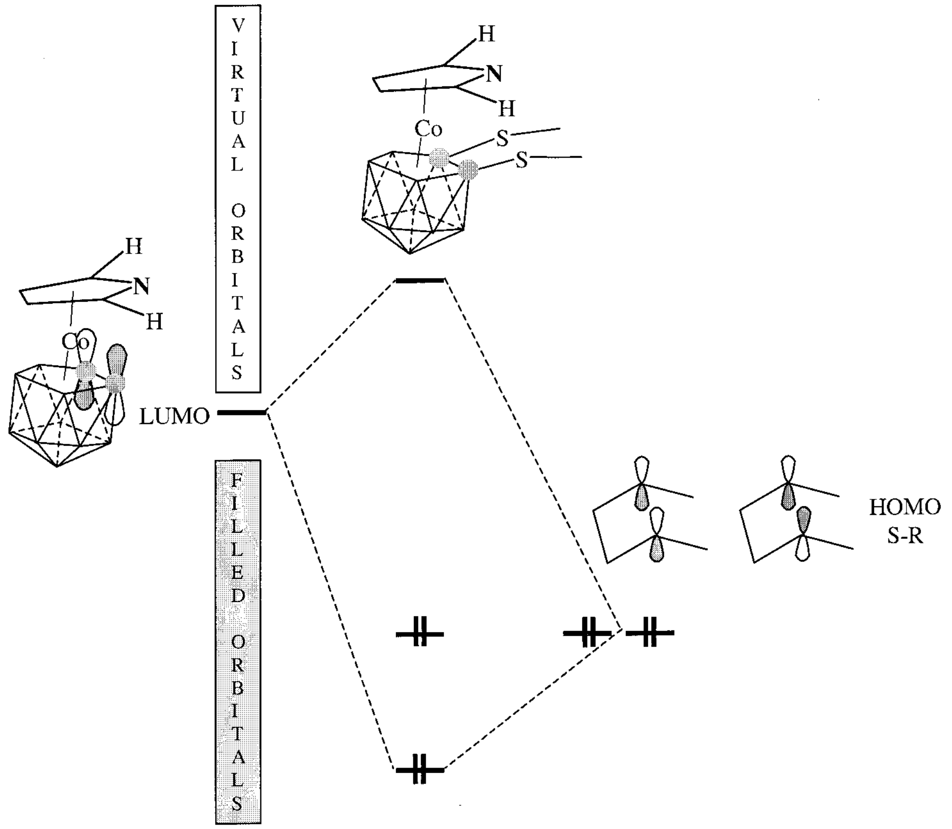

Figure 5. Schematic energy level diagram for combination of the LUMO of compound **1** and the HOMO of S−R groups.

Conclusions

The $C_c \cdots C_c$ distance in *o*-carborane is much more plastic than that in conventional organic compounds. A similar situation occurs in η^5-metallacarboranes. This distance can be modified by substituents on the carbons. Purely alkyl substituents do not substantially alter the $C_c \cdots C_c$ distance of the parent compound, implying that steric effects, although relevant, are not the major cause of the lengthening. In contrast, substituents with lone pairs alter the $C_c \cdots C_c$ distance substantially. This cannot be explained by the effect of electron-polarizing groups. The more plausible explanation has to do with the transfer of electron density from the available lone pairs on the carbon substituents to the Ψ^* orbitals, producing a decrease in the $C_c \cdots C_c$ bond order and, thereby, an increase in the $C_c \cdots C_c$ distance.

Experimental Section

Instrumentation. Elemental analyses were performed using a Carlo Erba EA 1108 microanalyzer. IR spectra were recorded with KBr pellets on a FTIR-8300 Shimadzu spectrophotometer. ^1H and $^1H\{^{11}B\}$ NMR (300.13 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz), and ^{11}B and $^{11}B\{^1H\}$ NMR (96.29 MHz) spectra were recorded in $CDCl_3$ with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories at room temperature. Chemical shift values for ^1H, $^1H\{^{11}B\}$, and $^{13}C\{^1H\}$ NMR spectra were referenced to $Si(CH_3)_4$ and those for ^{11}B and $^{11}B\{^1H\}$ NMR spectra to external $BF_3 \rightarrow O(CH_2CH_3)_2$. Chemical shifts are reported in units of parts per million downfield from $Si(CH_3)_4$, and coupling constants are given in hertz.

Materials. Experiments were carried out under dry, oxygen-free dinitrogen atmosphere, using standard Schlenk techniques, with some subsequent manipulation in the open air. THF was freshly distilled from sodium benzophenone. Other solvents were of reagent grade quality and were used without further purification. Pyrrole (Aldrich) was freshly distilled before use. Hexahydrated cobalt(II) chloride (Aldrich) was heated under vacuum overnight to obtain the anhydrous form. Potassium was refluxed in THF before use. Phenyl disulfide (Aldrich) was used as received. 1-C_6H_5-1,2-$C_2B_{10}H_{11}$, 1,2-$(SC_6H_5)_2$-1,2-$C_2B_{10}H_{10}$, and 1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$ were prepared according to literature methods.[25] *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] (**1**), *closo*-[3-Co(η^5-NC_4H_4)-1-CH_3-2-C_4H_9-1,2-$C_2B_9H_9$] (**2**), and *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-2-C_3H_5-1,2-$C_2B_9H_9$] (**3**) were prepared according to literature methods.[6]

Synthesis of 1,2-$(SCH_3)_2$-1,2-$C_2B_{10}H_{10}$ (4). 1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$ (0.50 g, 2.4 mmol) was added to a solution of KOH (0.33 g, 5.0 mmol) in 50 mL of methanol. After 30 min of stirring at 0 °C, CH_3I (0.3 mL, 4.8 mmol) was added to the reaction mixture. Stirring was continued for an additional 30 min at 0 °C and for 30 min at room temperature. The solution was vacuum-dried, and the resulting white solid was treated with 100 mL of diethyl ether/water (1:1). The organic phase was dried over $MgSO_4$ and then vacuum-dried. Recrystallization from petroleum ether at 40−60 °C gave white microcrystals. Yield: 0.46 g (80%). Anal. Calcd for $C_4B_{10}S_2H_{16}$: C, 20.32; H, 6.82; S, 27.13. Found: C, 20.40; H, 6.91; S, 27.24. IR: ν [cm^{-1}] 2921 (C−H), 2633, 2602, 2554, 2581 (B−H). ^1H NMR: δ 2.4 (s, CH_3, 6H), 3.5−1.5 (br, B−H). $^{13}C\{^1H\}$ NMR: δ 92.5 (s, C_c), 19.9 (s, $-CH_3$). ^{11}B NMR: δ −3.3 (d, $^1J(B,H)$ = 149, 2B), −8.6 (4B), −9.7 (2B), −11.2 (2B).

Synthesis of *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$] (5). 1,2-$(SCH_3)_2$-1,2-$C_2B_{10}H_{10}$ (0.50 g, 2.12 mmol) was dissolved in a suspension of K(NC_4H_4) (2.67 g, 25.44 mmol) in 100 mL of THF. After 4 h of stirring under reflux, anhydrous $CoCl_2$ (1.37 g, 10.6 mmol) was added. The reaction mixture was refluxed for 48 h. After cooling, the solvent was evaporated in vacuo, and the resulting dark solid was treated with 80 mL of CH_2Cl_2. The suspension was filtered, and the orange solution was concentrated to 1 mL. Chromatography of the crude orange solution using CH_2Cl_2/C_6H_{14} (8:2) as the mobile phase provided a pure orange complex (R_f(prep) = 0.50). Yield: 0.35 g, (47%). Anal. Calcd for $C_8B_9S_2H_{19}CoN$: C, 27.48; H, 5.48; S, 18.34; N, 4.01. Found: C, 27.31; H, 5.29; S, 18.32; N, 4.12. IR: ν [cm^{-1}] 3099 (C−H), 2553, 2536 (B−H). ^1H NMR: δ 6.8 (s, $N-C_{pyr}-H$, 2H), 6.2 (s, $C_{pyr}-C_{pyr}-H$, 2H), 3.5−2.0 (br, B−H), 2.4 (s, $-CH_3$, 6H). $^1H\{^{11}B\}$ NMR: δ 6.8 (s, $N-C_{pyr}-H$, 2H), 6.2 (s, $C_{pyr}-C_{pyr}-H$, 2H), 3.3 (br s, B−H, 5H), 2.2 (br s, B−H, 4H), 2.4 (s, $-CH_3$, 6H). $^{13}C\{^1H\}$ NMR: δ 116.3 (s, $N-C_{pyr}$), 105.0 (s, C_c), 92.3 (s, $C_{pyr}-C_{pyr}$), 21.5 (s, $-CH_3$). ^{11}B NMR: δ 11.6 (d, $^1J(B,H)$ = 141, 1B), 5.9 (d, $^1J(B,H)$ = 148, 1B), 0.5 (d, $^1J(B,H)$ = 158, 2B), −3.4 (d, $^1J(B,H)$ = 145, 2B), −9.5 (d, $^1J(B,H)$ = 163, 2B), −19.2 (d, $^1J(B,H)$ = 167, 1B).

Synthesis of *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$] (6). The procedure was similar to that used for **5** but with 1,2-$(SC_6H_5)_2$-1,2-$C_2B_{10}H_{10}$ (0.76 g, 2.12 mmol) as starting material. Yield: 0.51 g (51%) (R_f(prep) = 0.58). Anal. Calcd for $C_{18}B_9S_2H_{23}CoN$: C, 45.63; H, 4.89; S, 13.54; N, 2.96. Found: C, 45.50; H, 4.75; S, 13.61; N, 2.98. IR: ν [cm^{-1}] = 2608, 2600, 2565, 2534 (B−H). ^1H NMR: δ 7.7−7.4 (m, $-C_6H_5$, 10H), 6.9 (s, $N-C_{pyr}-H$, 2H), 6.3 (s, $C_{pyr}-C_{pyr}-H$, 2H), 2.3−1.0 (br, B−H). $^1H\{^{11}B\}$ NMR: δ 7.7−7.4 (m, $-C_6H_5$, 10H), 6.9 (s, $N-C_{pyr}-H$, 2H), 6.3 (s, $C_{pyr}-C_{pyr}-H$, 2H), 3.4 (br s, B−H, 2H), 2.9 (br s, B−H, 2H), 2.1 (br s, B−H, 2H), 1.8 (br s, B−H, 1H), 1.1 (br s, B−H, 2H). $^{13}C\{^1H\}$ NMR: δ 137.2, 133.3, 130.6, 128.9 (s, $-C_6H_5$), 116.6 (s, $N-C_{pyr}$), 101.0 (s, C_c), 92.6 (s, $C_{pyr}-C_{pyr}$). ^{11}B NMR: δ 11.6 (d, $^1J(B,H)$ = 146, 1B), 6.0 (d, $^1J(B,H)$ = 144, 1B), 0.2 (d, $^1J(B,H)$ = 153, 2B), −3.4 (d, $^1J(B,H)$ = 141, 2B), −9.1 (d, $^1J(B,H)$ = 145, 2B), −17.9 (d, $^1J(B,H)$ = 160, 1B).

Synthesis of *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (7). The procedure was similar to that used for **5** but with 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ (0.47 g, 2.12 mmol) as starting material. Yield: 0.55 g (77%) (R_f(prep) = 0.54). Anal. Calcd for $C_{12}B_9H_{19}CoN$: C, 43.21; H, 5.74; N, 4.20. Found: C, 43.35; H, 5.81; N, 4.11. IR: ν [cm^{-1}] 3110, 3085 (C−H), 2607, 2570, 2547, 2530 (B−H). ^1H NMR: δ 7.6−7.2 (m, $-C_6H_5$, 5H), 6.7 (s, $N-C_{pyr}-H$, 1H), 6.2 (s, $C_{pyr}-C_{pyr}-H$, 1H), 6.1 (s, $C_{pyr}-C_{pyr}-H$, 1H), 5.3 (s, C_c-H, 1H), 5.2 (s, $N-C_{pyr}-H$, 1H), 4.0−1.8 (br, B−H). $^1H\{^{11}B\}$ NMR: δ 7.6−7.2 (m, $-C_6H_5$, 5H), 6.7 (s, $N-C_{pyr}-H$, 1H), 6.2 (s, $C_{pyr}-C_{pyr}-H$, 1H), 6.1 (s, $C_{pyr}-C_{pyr}-H$, 1H), 5.3 (s, C_c-H, 1H), 5.2 (s, $N-C_{pyr}-H$, 1H), 3.9 (br s, B−H, 1H), 3.4 (br s, B−H, 2H), 2.1 (br s, B−H, 4H), 1.9 (br s, B−H, 2H). $^{13}C\{^1H\}$ NMR: δ 143.4, 128.5, 128.2, 125.3 (s, $-C_6H_5$), 117.0 (s, $N-C_{pyr}$), 111.1 (s, $N-C_{pyr}$), 92.6 (s, $C_{pyr}-C_{pyr}$), 90.9 (s, $C_{pyr}-C_{pyr}$), 54.6 (s, C_c), 53.4 (s, C_c). ^{11}B NMR: δ 8.3 (d, $^1J(B,H)$ = 148, 1B), 6.7 (d, $^1J(B,H)$ = 150, 1B), 3.9 (4B), −10.6 (d, $^1J(B,H)$ = 161, 1B), −15.5 (d, $^1J(B,H)$ = 155, 2B).

X-ray Structure Determinations of 5, 6, and 7. Single-crystal data collections were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite-monochromatized Mo Kα radiation. A total of 1495, 3946, and 1651 unique reflections were collected by $\omega/2\theta$ scan mode ($2\theta_{max}$ = 50°) for **5**, **6**, and **7**, respectively. Compound **7** crystallizes in a noncentrosymmetric space group. The absolute configuration was determined by refinement of Flack *x* parameter.

The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[26] Non-hydrogen atoms were refined with anisotropic displacement parameters, except for B atoms of **7**, which were refined with isotropic displacement parameters. Hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. N and C atoms of the pyrrolyl ligands could be reliably distinguished in all structures and also the cage carbons of **7**. Crystallographic data and structural refinement details for compounds **5**, **6**, and **7** are listed in Table 1.

Computational Details

All calculations were performed with the Gamess 98[27] package. A triple-ζ valence basis set was used for all calculations, with no additional polarization functions. That means (5s)/[3s] for hydrogen; (10s, 6p)/[5s, 3p] for carbon, boron, and nitrogen; (14s, 11p, 6d)/[10s, 8p, 3d] for cobalt; and (12s, 9p)/[6s, 5p] for sulfur. A total of 194 uncontracted basis functions were used for calculations with compound **1**, and 244 were used for calculations with compound **5**. Single-point calculations were made at the HF level of theory, using crystallographic data as atom coordinates. HOMO and LUMO energies and spatial distribution were also calculated with the Hyperchem 5.0 package (Version 5.0, Hypercube Inc.) installed on a PC-Pentium III 700 MHz computer, at ZINDO/1 level of theory.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$] (**5**), *closo*-[3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$] (**6**), and *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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