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Mixed Cobaltacarboranes Incorporating η^5-Pyrrolyl and Dicarbollide Ligands. Synthetic Routes, Structures, and Mechanistic Implications

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Mixed cobaltacarboranes $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(7\text{-R-8-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)]$ containing η^5-pyrrolyl and dicarbollide ligands have been synthesized. Reaction of $[\text{N(CH}_3)_4][7\text{-R-8-C}_4\text{H}_4\text{N-(CH}_2)_3\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$ (R = CH_3, C_6H_5) with K(*t*-BuO) and $CoCl_2$ in dimethoxyethane leads to two complexes with the formulae $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(7\text{-R-8-C}_4\text{H}_9\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)]$ and $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(7\text{-R-8-C}_3\text{H}_5\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)]$ (R = CH_3, C_6H_5). The 8-C_4H_9 and 8-C_3H_5 groups are produced as a result of the cleavage of the spacer joining the pyrrolyl and carborane moieties in the original ligand. The $[\text{N(CH}_3)_4]^+$ ion is necessary to produce the 8-C_4H_9 substituent. An alternative and more efficient route to $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(7\text{-R-8-C}_3\text{H}_5\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)]$ (R = CH_3, C_6H_5) involves the reaction of $1\text{-Cl(CH}_2)_3\text{-2-R-1,2-C}_2\text{B}_{10}\text{H}_{10}$ (R = CH_3, C_6H_5) with $K(NC_4H_4)$ and $CoCl_2$ in dimethoxyethane. This last route can also be utilized to produce the simple $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(7\text{-R-8-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)]$ compounds starting from *closo*-$1\text{-R-2-R}'\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}$ compounds. The structures of those species have been proven by X-ray structural analyses of $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(7\text{-CH}_3\text{-8-C}_4\text{H}_9\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)]$ and $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(7\text{-C}_6\text{H}_5\text{-8-C}_3\text{H}_5\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)]$.

The pyrrolyl anion has been previously shown to be a powerful σ-bonding ligand via the nitrogen atom.[1] Thus, η^5-pyrrolyl coordination must compete with σ-bonding. However, it seems that although there are few well-characterized mixed complexes incorporating pyrrolyl and carborane, in those complexes, the pyrrolyl derivatives coordinate η^5.[2] These examples are restricted to small carboranes and di- or tetramethyl-substituted pyrrolyl anions. Some examples are the double-decker complexes $[(\eta^5\text{-NC}_4\text{Me}_2\text{R}_2)\text{Co}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]$ and $[(\eta^5\text{-NC}_4\text{Me}_2\text{R}_2)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_5)]$ and the triple-decker complexes $[(\eta^5\text{-NC}_4\text{Me}_2\text{R}_2)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Co(Cp)}]$, $[(\eta^5\text{-NC}_4\text{Me}_2\text{R}_2)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\eta^6\text{-1,4-MeC}_6\text{H}_4\text{-CHMe}_2)]$, and $[(\eta^5\text{-NC}_4\text{Me}_4)_2\text{Co}_2(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)]$.[2a] On the other hand, several examples of mixed metallacarboranes with $(C_5H_5)^-$ and the dicarbollyl ligand $(C_2B_9H_{11})^{2-}$ are known.[3] The pyrrolyl metal−dicarbollyl compounds must be considered structural and electronic analogues of $[(\text{C}_5\text{H}_5)\text{M}(\text{C}_2\text{B}_9\text{H}_{11})]$, formally generated by replacement of $(C_5H_5)^-$ by $(NC_4H_4)^-$.

As outlined before and though a great deal of work in metallacarborane chemistry has been done with $(C_2B_9H_{11})^{2-}$,[4] no examples of mixed pyrrolyl and $(C_2B_9H_{11})^{2-}$ complexes had ever been reported before our recent communication.[5] Conscious of the interest metallacarborane derivatives of $(C_2B_9H_{11})^{2-}$ are generating with respect to their solubility,[6] isolation, separation and characterization of organic bases, radiometal carriers,[7] and electron-acceptor molecules,[8] among other areas, we planned to find easy and high-yield ways to the synthesis of the mixed-$(\eta^5\text{-NC}_4\text{H}_4)^-/(\text{C}_2\text{B}_9\text{H}_{11})^{2-}$ complexes.

In this paper, we describe two general preparative routes to a series of stable cobaltacarborane sandwiches that incorporate the pyrrolyl moiety and $(C_2B_9H_{11})^{2-}$ derivatives, $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(7\text{-R-8-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)]$, their structural characterization, and their electrochemical behavior in a nonaqueous medium.

The $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(7,8\text{-C}_2\text{B}_9\text{H}_{11})]$ compound was earlier synthesized from $K(NC_4H_4)$ and the *nido*-$(7,8\text{-C}_2\text{B}_9\text{H}_{11})^{2-}$ species.[5] Here, we describe its synthesis and that of some derivatives starting from $K(NC_4H_4)$ and

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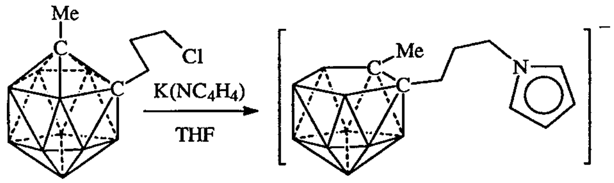
Scheme 1. Synthetic Procedure to the Formation $[7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$



the *closo* *o*-carborane. The reaction is more selective and the yield considerably improved.

In another set of reactions, the starting ligand is a $(7,8\text{-}C_2B_9H_{11})^{2-}$ derivative linked to the pyrrole group through an alkylic backbone. We also report in this paper an initial electrochemical study of $[(\eta^5\text{-}NC_4H_4)\text{-}Co(7\text{-}R\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_9)]$ (R = CH_3 or C_6H_5 and R′ = $(CH_2)_3CH_3$ or $CH(CH_2)_2$), which shows that these complexes exhibit similar properties to $[3,3'\text{-}Co\text{-}1,2\text{-}(C_2B_9H_{11})_2]^-$,[9] and $[(C_5H_5)Co(C_2B_9H_{11})]$.[10]

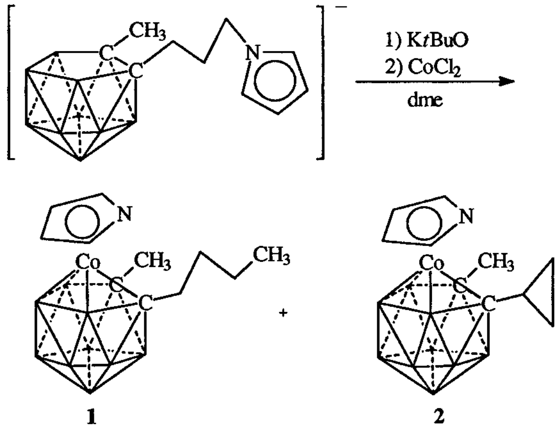
Results and Discussion

As it has been stated in the introduction there have been reported only a few mixed-pyrrolyl/carborane complexes. The pyrrole ligands utilized were substituted at the α or the α and β positions. Their syntheses were based on the reaction of the pyrrolyl anion and the corresponding small *nido* carborane. This reaction is similar to the one reported for the synthesis of $[(\eta^5\text{-}NC_4H_4)Co(7,8\text{-}C_2B_9H_{11})]$.[5]

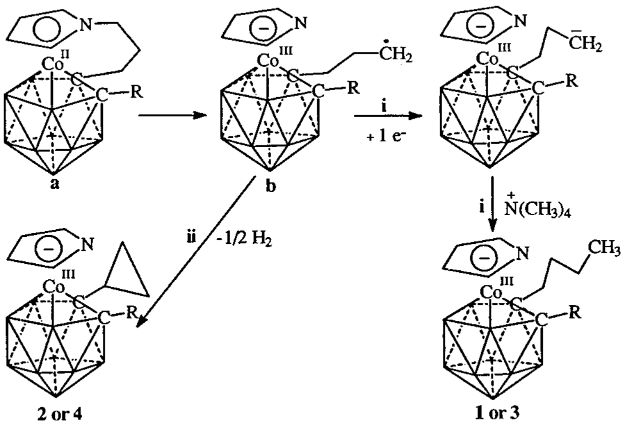
In this paper, we present two new routes to the synthesis of these mixed-$[(\eta^5\text{-}NC_4H_4)Co(7\text{-}R\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_9)]$ complexes. Note, the pyrrolyl ligand is not α protected here, which may indicate that in carborane chemistry, it is not required to protect α positions to facilitate η^5 coordination, as it seems to be necessary in organometallic chemistry.[11] In the first method, named route A, the starting ligand contains both the *nido* dicarbollide moiety and the pyrrole group. These coordinating groups are chemically bonded by a three-carbon-atom backbone. In the second route, named B, the mixed-pyrrolyl/carborane complexes are formed in one step upon reaction of the *closo* carborane ligand and the free pyrrolyl anion. In route B, the ligand does not contain both moieties.

Route A. To follow this route, it was necessary to synthesize the *closo* precursors that would lead to the *nido* carborane ligands having both coordinating moieties in the same molecule. The starting $1\text{-}R\text{-}2\text{-}(CH_2)_3\text{-}Cl\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = CH_3 or C_6H_5) *closo* compound was produced upon reaction of $1\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{11}$ (R = CH_3 or C_6H_5) with BuLi and $Cl(CH_2)_3Br$ at −78 °C. Reaction of $1\text{-}R\text{-}2\text{-}(CH_2)_3Cl\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = CH_3 or C_6H_5) with $K(NC_4H_4)$ produced $[7\text{-}R\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = CH_3 or C_6H_5). The reaction is indicated in Scheme 1 for $[7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$.

Scheme 2. Synthesis of 1 and 2 Following Route A



Scheme 3. Proposed Mechanism in Route A. For 1 and 2, R = CH_3. For 3 and 4, R = C_6H_5



Reaction of $[7\text{-}R\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = CH_3 or C_6H_5) with $CoCl_2$ and K(*t*-BuO) in dimethoxyethane (dme) at reflux for 72 h leads, after working up, to a mixture of chemicals that is partly resolved by TLC. When R = CH_3, complexes **1** and **2** were obtained as the first and second band in the TLC [(CH_2Cl_2/C_6H_{14}, 8/2); R_f (prep) = 0.56, 0.5], respectively. When R = C_6H_5, the reaction leads to **3** and **4** and their separation procedures are similar. The numbers given correspond to $[(\eta^5\text{-}NC_4H_4)Co(7\text{-}CH_3\text{-}8\text{-}C_4H_9\text{-}7,8\text{-}C_2B_9H_9)]$ (**1**), $[(\eta^5\text{-}NC_4H_4)Co(7\text{-}CH_3\text{-}8\text{-}C_3H_5\text{-}7,8\text{-}C_2B_9H_9)]$ (**2**). $[(\eta^5\text{-}NC_4H_4)\text{-}Co(7\text{-}C_6H_5\text{-}8\text{-}C_4H_9\text{-}7,8\text{-}C_2B_9H_9)]$ (**3**), and $[(\eta^5\text{-}NC_4H_4)Co\text{-}(7\text{-}C_6H_5\text{-}8\text{-}C_3H_5\text{-}7,8\text{-}C_2B_9H_9)]$ (**4**). The reaction leading to these complexes is indicated in Scheme 2. A mechanism explaining their formation is discussed later in Scheme 3.

The $^1H\{^{11}B\}$-NMR spectrum of **1** displays a resonance at δ = 2.54 corresponding to the carborane's $C_c{-}CH_3$ signal and a series of other signals attributed to the alkyl backbone (C_c represents the carbon atom of the carborane cluster). Another set of signals was observed at 1.00 ppm, which integrated as the carborane's $C_c{-}CH_3$. Besides, the $(NC_4H_4)^-$ set of $^1H\{^{11}B\}$-NMR aromatic signals had shifted downfield from those displayed by the free ligand (6.66 and 5.98 ppm in $[7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ vs 7.06 and 6.48 ppm in **1**). The $^{13}C\{^1H\}$-NMR signals of the β-pyrrolyl carbon atoms in compound **1** are at higher field (δ = 91.0, 90.7) than those of the *nido* ligand (δ = 118.1, 107.1). The $^{11}B\{^1H\}$-NMR spectrum of **1** displays eight resonances with the pattern 1:1:1:1:2:1:1:1 in the range between 5.32 and −13.56 ppm. This chemical shift range suggests a *closo* cluster, indicating that the *nido* carborane moiety should be η^5 bonded to the Co atom. The second

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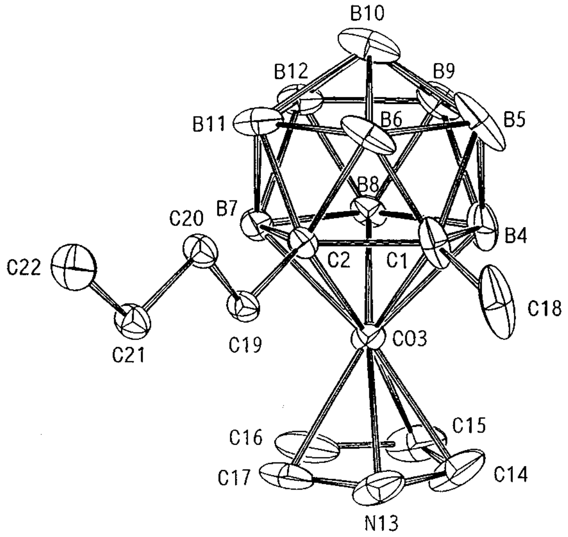


Figure 1. ORTEP plot of **1**, showing 20% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

band in the TLC showed an even more unexpected spectrum. The ^{1}H{^{11}B}-NMR spectrum is similar to that of **1** in the (NC$_4$H$_4$)$^-$ region, however, it differs considerably in the alkyl backbone region where two sets of signals are found at 0.87 and 1.25 ppm with intensity areas of 4:1. This is also seen when comparing the ^{13}C{^{1}H}-NMR of **1** and **2**. In addition to the Cc−CH$_3$ resonance, four signals are found for **1** in the alkyl area between 41.3 and 13.1 ppm, while **2** shows only two resonances. The ^{11}B{^{1}H}-NMR spectrum of **2** does not differ greatly with that of **1**.

These data suggest that in both **1** and **2**, the (NC$_4$H$_4$)$^-$ and *nido* carborane moieties bond to Co in a similar way. The two molecular structures differ on the alkyl chain. To prove that this reaction was not an isolated case, it was reproduced with the phenyl-substituted equivalent [7-C$_6$H$_5$-8-C$_4$H$_4$N-(CH$_2$)$_3$-7,8-C$_2$B$_9$H$_{10}$]$^-$. The reaction was carried out following the same experimental conditions reported in the synthesis of **1** and **2**, and compounds **3** and **4** were obtained, which had similar appearance. The NMR data of **3** and **4** are also very comparable to those of **1** and **2**, if we consider the C$_6$H$_5$ influence on the NMR chemical shifts. As a consequence, equal structural information could be drawn in both cases.

To adequately interpret the structures of these complexes, it was necessary to grow adequate crystals of both families, the **1,3** and the **2,4**. Good crystals for X-ray diffraction analysis were obtained for compounds **1** and **4**.

The molecular structures are shown in Figure 1 for **1** and Figure 2 for **4**. Relevant distances and angles are shown in Table 1 for **1** and Table 2 for **4**. The crystallographic data for **1** and **4** are listed in Table 3.

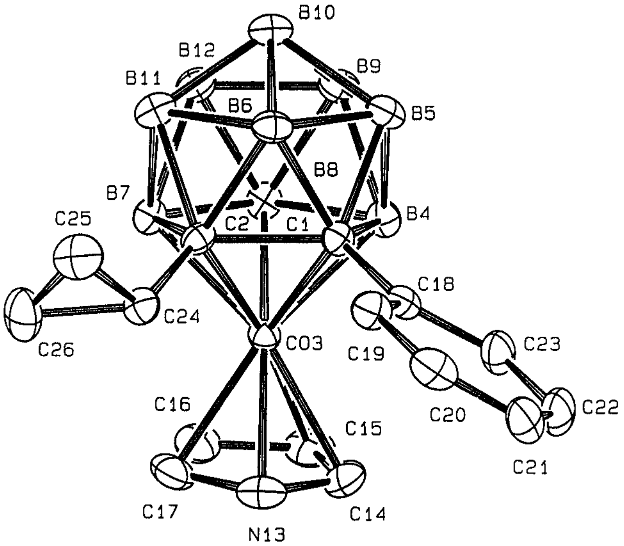


Figure 2. ORTEP plot of **4**, showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [(η^5-NC$_4$H$_4$)Co(7-CH$_3$-8-C$_4$H$_9$-7,8-C$_2$B$_9$H$_9$)]

C(1)−C(2)	1.671(7)	Co(3)−N(13)	2.078(6)
C(1)−C(18)	1.52(1)	Co(3)−C(14)	2.030(7)
C(2)−C(19)	1.538(7)	Co(3)−C(15)	2.034(7)
Co(3)−C(1)	2.009(6)	Co(3)−C(16)	2.049(8)
Co(3)−C(2)	2.013(5)	Co(3)−C(17)	2.046(8)
Co(3)−B(4)	2.054(7)	N(13)−C(14)	1.36(1)
Co(3)−B(7)	2.028(6)	N(13)−C(17)	1.36(1)
Co(3)−B(8)	2.066(6)		

C(2)−C(1)−C(18)	119.9(5)	C(1)−Co(3)−C(16)	174.0(3)
Co(3)−C(1)−C(18)	112.8(4)	C(2)−Co(3)−N(13)	109.1(2)
B(4)−C(1)−C(18)	122.5(5)	C(2)−Co(3)−C(15)	172.5(3)
C(1)−C(2)−C(19)	120.6(4)	B(4)−Co(3)−C(17)	163.8(3)
Co(3)−C(2)−C(19)	110.7(3)	B(7)−Co(3)−C(14)	165.4(3)
B(7)−C(2)−C(19)	122.5(4)	B(8)−Co(3)−N(13)	163.2(2)
C(1)−Co(3)−N(13)	106.4(2)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [(η^5-NC$_4$H$_4$)Co(7-C$_6$H$_5$-8-C$_3$H$_5$-C$_2$B$_9$H$_9$)]

C(1)−C(2)	1.737(4)	Co(3)−C(14)	2.048(3)
C(1)−C(18)	1.529(4)	Co(3)−C(15)	2.063(3)
C(2)−C(24)	1.497(4)	Co(3)−C(16)	2.056(3)
Co(3)−C(1)	2.036(3)	Co(3)−C(17)	2.038(3)
Co(3)−C(2)	2.029(3)	N(13)−C(14)	1.362(4)
Co(3)−B(4)	2.077(4)	N(13)−C(17)	1.363(4)
Co(3)−B(7)	2.067(4)	C(24)−C(25)	1.493(4)
Co(3)−B(8)	2.085(3)	C(24)−C(26)	1.491(4)
Co(3)−N(13)	2.078(3)	C(25)−C(26)	1.489(5)

C(2)−C(1)−C(18)	121.1(2)	C(1)−Co(3)−N(13)	108.4(1)
Co(3)−C(1)−C(18)	113.0(2)	C(1)−Co(3)−C(16)	175.1(1)
B(4)−C(1)−C(18)	121.9(3)	C(2)−Co(3)−N(13)	107.4(1)
C(1)−C(2)−C(24)	119.4(2)	C(2)−Co(3)−C(15)	170.8(1)
Co(3)−C(2)−C(24)	110.0(2)	B(4)−Co(3)−C(17)	166.0(1)
B(7)−C(2)−C(24)	123.4(2)		

The common components of both structures are very similar. The metal is sandwiched by the pentagonal faces of the pyrrolyl ion and the dicarbollide ligand. The conformation of the faces is staggered, with the pyrrolyl nitrogen being placed between the two cluster carbons. The faces are not parallel but tilted 6.2(3)° and 6.3(1)° for compounds **1** and **4**, respectively. As a result, the intramolecular distances between N(13) and cluster carbons are about 0.2 Å longer that the B(8)···C(15) and B(8)···C(16) distances. Although some significant differences exist between the corresponding X···M bond lengths, the difference in these bond lengths are less than 0.04 Å. The most remarkable difference between the compounds is the C(1)−C(2) distances, 1.671(8) and 1.737(4) Å in **1** and **4**, respectively. This may be due to the steric repulsions between the phenyl and cyclopropyl Cc substituents.

The major differences between complexes **1** and **4** are found on the Cc substituents. Compound **1** has a butyl chain, while compound **4** has reconverted the original −(CH$_2$)$_3$− spacer in [7-C$_6$H$_5$-8-C$_4$H$_4$N-(CH$_2$)$_3$-7,8-C$_2$B$_9$H$_{10}$]$^-$ to a cyclopropyl group. The +3 charge of

Table 3. Crystallographic Data for $[(\eta^5\text{-}NC_4H_4)Co(C_7H_{21}B_9)]$ and $[(\eta^5\text{-}NC_4H_4)Co(C_{11}H_{19}B_9)]$

	1	4
chem formula	$C_{11}H_{25}B_9CoN$	$C_{15}H_{23}B_9CoN$
fw	327.55	373.58
a (Å)	9.061(6)	13.184(2)
b (Å)	15.524(9)	9.333(1)
c (Å)	12.116(6)	15.185(1)
β (deg)	90.94(5)	98.809(7)
V (Å^3)	1704(2)	1846.4(4)
Z	4	4
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
T (°C)	21	21
λ (Å)	0.71069	0.71069
ρ_{calcd} (g cm^{-3})	1.277	1.344
μ (cm^{-1})	9.9	9.2
transmissn coeff	0.89−1.00	0.90−1.00
$R(F_o)$	0.051	0.034
$wR(F_o)$	0.052	0.031

Table 4. Electrochemical Data

compound	E_{p_c} (V)^a	E_{p_a} (V)^a	ΔE_p (mV)	*C* (mol·dm^{-3})
1	−0.543	−0.430	113	1.02×10^{-2}
2	−0.550	−0.435	115	2.24×10^{-3}
3	−0.428	−0.305	123	1.28×10^{-3}
4	−0.453	−0.335	118	4.01×10^{-2}

[a] Reported vs SCE, $v = 100$ mV/s.

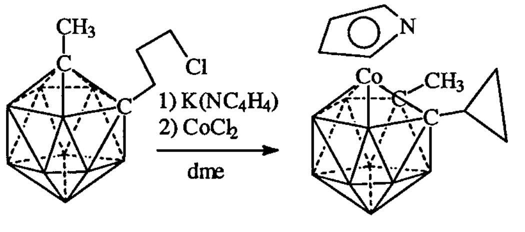
cobalt is compensated by the pyrrolyl (1−) and the dicarbollide (2−) moieties.

The present structures are very similar to that of $[(\eta^5\text{-}NC_4H_4)Co(C_2B_9H_{11})]$ reported earlier.[5] The formation of compounds **1,3** and **2,4** can be represented by the mechanism indicated in Scheme 3. The deprotonation of the *nido* ligand $[7\text{-}R\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ ($R = CH_3$, C_6H_5) by K(*t*-BuO) leads to the corresponding dianion. This reacts with Co(II) to yield compound **a**. Co(II) simply transfers one e$^-$ to the $-N-CH_2-$ fragment producing the neutral radical **b**. This last step may proceed in two ways: (i) it can be reduced either by Co(II) or another process to give the corresponding anion, which in turn is methylated to produce compounds **1** ($R = CH_3$) and **3** ($R = C_6H_5$) or (ii) it may follow an intramolecular rearrangement with the loss of $^1/_2$ H_2 to produce complexes **2** ($R = CH_3$) and **4** ($R = C_6H_5$). The source of $(CH_3)^+$ for **1** and **3** is the $[N(CH_3)_4]^+$ salt. This was proven by carrying out the same reaction leading to **1** and **2** but starting from $K^+[7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ instead of the $[N(CH_3)_4]^+$ salt. In this case, compound **2** was found but not compound **1**.

In CH_3CN, complexes **1**−**4** are reduced in a quasi-reversible one-electron step. E_{p_c} and E_{p_a} vs SCE are reported in Table 4. The electrochemical behavior of **1**−**4** resembles that of the mixed cobalt−dicarbollide sandwich complex $(C_5H_5)Co(C_2B_9H_{11})$,[9] confirming the analogy between the two complexes.

Route B. It may seem that route A, starting with a prearranged *nido* ligand, should lead to a more concerted reaction, however, it is not so. As we have indicated, several bands do separate in the TLC which should give rise to a rich variety of structures, up to now not fully investigated. This procedure is, in addition, difficult because it requires the synthesis of the precursor ligand, e.g., $[7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$. This is not a straightforward reaction and does not produce easily separable solids. The $[N(CH_3)_4]^+$ salt is oily and difficult to purify. To overcome these problems, route B was investigated, which did not make use of the ligand with the two components in the molecule. The reaction is schematically indicated in Scheme 4.

Scheme 4. Synthesis of 2 Following Route B



The reaction proceeds very well, it is a simple one-pot reaction, it does not require the synthesis of the *nido* ligand, avoiding separation problems and progressively decreasing yields, and it provides the same mixture as with *nido* $[7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ ligand. The only band missing in the TLC is that corresponding to compound **1**. This is logical since no source of $(CH_3)^+$ is present in the reaction vessel. We have extended this reaction to the simple pyrrolyl/dicarbollide sandwich complex reported recently in a yield of 68%.[5] The reaction of *o*-carborane with $K(NC_4H_4)$ and $CoCl_2$ in the ratio 1:12:5 in dme produced, after working up, $[(\eta^5\text{-}NC_4H_4)Co(C_2B_9H_{11})]$ in 76% yield. In the purification process, a TLC band was separated which was partly contaminated with the major complex. However, some NMR studies have been performed which seem to indicate that a species equal or similar to $[B(NC_4H_4)_3]_2$·dme is formed in the process.[12] This new procedure from the *closo* species does not require the synthesis of the *nido* species, is less time consuming, requires less working up, produces a relatively higher yield, and is one-pot reaction.

Conclusion

Different strategies have been presented that permit the synthesis of cobaltacarborane mixed sandwiches incorporating pyrrolyl and dicarbollide derivatives. The starting carborane compound can be either *nido* or *closo*. Furthermore, the *nido* species incorporates the pyrrolyl fragment in the molecule. In this case, a rich variety of different sandwich species can be formed due to the breaking of the spacer connecting the carborane and pyrrole moieties. The *closo* procedure seems more straightforward and easier, since it is more selective, produces good yields, and it is performed as a one-pot reaction. These mixed-sandwich complexes have been studied by cyclic voltammetry. They show a behavior comparable to that of the analogous $[(C_5H_5)Co(C_2B_9H_{11})]$ complex.

Experimental Section

All experimental manipulations were carried out using standard high-vacuum or inert atmosphere techniques.

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(12) The identification of the removed BH unit has been done for the case of *o*-carborane as a ligand. It seems that $[NC_4H_4]^-$ acts first as a nucleophile leading to the formal elimination of a B^+ fragment in the starting complex $C_2B_{10}H_{12}$, then as a base removing the bridging hydrogen atom on the C_2B_3 open face, and finally as an η^5-coordinating ligand. Although it is not conclusive, the NMR spectra support that $[B(NC_4H_4)_3]_2$·dme is formed in the process. $^1H\{^{11}B\}$-NMR: $\delta = 6.50$ (s, 6H, $-N-CH=$), 5.90 (s, 6H, $-CH=$), 3.36 (m, 2H, $-O-CH_2-$), 3.28 (m, 3H, CH_3-O-). $^{13}C\{^1H\}$-NMR: δ 128.70 ($-N-CH=$), 116.75 ($-CH=$), 72.44 ($-O-CH_2-$), 61.08 (CH_3-O-). ^{11}B-NMR: δ 1.37 (s).

Materials. Before use, commercially available 1-CH_3-1,2-$C_2B_{10}H_{11}$ was purified by sublimation at 0.01 mmHg, 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ was synthesized according to the literature procedure.[13] A solution of *n*-butyllithium in hexane (1.6 M) and $Br(CH_2)_3Cl$ were used as received. Degassed 1,2-dimethoxyethane (dme) was stored over sodium−benzophenone before use. Dichloromethane was dried over $CaCl_2$, transferred onto activated 4-Å molecular sieves, and stored under vacuum before use. Hexane was dried over $CaCl_2$ and distilled. Tetrabutylammonium perchlorate and tetrabutylammonium chloride (TBAP, TBACl) (>99%) were used as received.

Physical Measurements. ^{11}B-NMR spectra (96.29 MHz), $^{13}C\{^1H\}$-NMR spectra (75.47 MHz), and $^1H\{^{11}B\}$-NMR spectra (300.13 MHz) were recorded on a Bruker ARX-300 spectrometer equipped with the appropriate decoupling accesories. All of the NMR spectroscopic data were in acetone-d_6 at 22 °C. Chemical shift values for the ^{11}B-NMR spectra were referenced to external $BF_3\cdot O(C_2H_5)_2$. Chemical shift values for $^1H\{^{11}B\}$ and $^{13}C\{^1H\}$-NMR spectra were referenced to $Si(CH_3)_4$. Electrochemical measurements were made on a PAR 273 potentiostat. The potential is reported vs SCE. The concentrations for **1**, **2**, **3**, and **4** are 1.02×10^{-2} M, 2.24×10^{-3} M, 1.28×10^{-3} M, and 4.01×10^{-2} M, respectively, in CH_3CN, in the presence of tetrabutylammonium perchlorate, 0.1 M, $v = 100$ mV s^{-1}.

The electrochemical studies were performed in a three-electrode, one-compartment cell. The working electrode was a disk of platinum ($\phi = 2.2$ mm). A Pt wire was used as the counter electrode. Ag/AgCl/Cl$^-$ (1 M TBACl in acetonitrile) was used as the reference electrode. The solution was degassed by bubbling (10−15 min) with dry oxygen-free dinitrogen. Analytical thin-layer chromatography was performed on 0.25 mm (20 × 20) silica gel F-254 plates (Tracer).

Synthesis of 1-$\mathbf{CH_3}$-2-$\mathbf{(CH_2)_3}$-Cl-1,2-$\mathbf{C_2B_{10}H_{10}}$. Under dinitrogen, to a two-necked flask containing 1-CH_3-1,2-$C_2B_{10}H_{11}$ (1 g, 6.28 mmol) in dry THF (70 mL) was added 1-bromo-3-chloropropane (1.3 g, 8.25 mmol). The solution was cooled to −78 °C for 1 h, and an equimolar solution of butyllithium in hexane was added dropwise. After the addition, the mixture was left at room temperature for 24 h. The solvent was evaporated, and the disubstituted *o*-carborane was extracted with diethyl ether. The recrystallization in hexane gave the pure solid product in a yield of 95%. $^1H\{^{11}B\}$-NMR: δ 3.67 (t, ^1J(H,H) = 8.1 Hz, 2H, $-C\mathbf{H}_2Cl$), 2.53 (m, 2H, $-C\mathbf{H}_2-CH_2Cl$), 2.14 (s, 3H, $-C\mathbf{H}_3$), 2.08 (m, 2H, $B-C-C\mathbf{H}_2$). $^{13}C\{^1H\}$-NMR: δ 78.04 and 75.67 (**C**c), 43.80 ($\mathbf{C}H_2-Cl$), 32.37 ($-\mathbf{C}H_2-CH_2$-Cl), 32.50 ($-C-\mathbf{C}H_3$), 32.13 ($B-C-\mathbf{C}H_2$). ^{11}B-NMR: δ −4.60 (d, ^1J(B,H) = 170.77 Hz, 1B), −6.17 (d, ^1J(B,H) = 170.77 Hz, 1B), −9.20 (d, ^1J(B,H) = 113.0 Hz, 2B), −9.96 (d, ^1J(B,H) = 142.52 Hz, 2B), −10.96 (d, ^1J(B,H) = 142.52 Hz, 4B). Anal. Calcd for $C_6H_{19}B_{10}Cl$: C, 30.70; H, 8.16. Found: C, 30.64; H, 8.45. FTIR (KBr): ν_{max} (B−H) 2594, 2580 cm^{-1}; ν_{max} (C−Cl) 731 cm^{-1}.

Synthesis of 1-$\mathbf{C_6H_5}$-2-$\mathbf{(CH_2)_3Cl}$-1,2-$\mathbf{C_2B_{10}H_{10}}$. The procedure was similar to that described to 1-CH_3-2-$(CH_2)_3Cl$-1,2-$C_2B_{10}H_{10}$, but using 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ (1 g, 4.54 mmol) as the starting material. Yield: 93%. $^1H\{^{11}B\}$-NMR: δ 7.53−7.76 (m, 5H, $-C_6\mathbf{H}_5$), 3.46 (t, ^1J(H,H) = 6.0 Hz, 2H, $-C\mathbf{H}_2Cl$), 2.10 (m, 2H, $-C\mathbf{H}_2-CH_2Cl$), 1.88 (m, 2H, $B-C-C\mathbf{H}_2-$). $^{13}C\{^1H\}$-NMR: δ 129.18−131.09 ($-\mathbf{C}_6H_5$), 81.83 and 84.51 (**C**c), 43.21 ($-\mathbf{C}H_2-Cl$), 32.18 ($-\mathbf{C}H_2-CH_2Cl$), 32.16 ($B-C-\mathbf{C}H_2$). ^{11}B-NMR: δ 3.57 (d, ^1J(B,H) = 144.45 Hz, 2B), −9.28 (d, ^1J(B,H) = 96.3 Hz, 2B), −10.28 (d, ^1J(B,H) = 144.45 Hz, 6B). Anal. Calcd for $C_{11}H_{21}B_{10}Cl$: C, 44.51; H, 7.13. Found: C, 44.47; H, 7.13. FTIR (KBr): ν_{max} (B−H) 2602, 2575, 2566, 2546 cm^{-1}; ν_{max} (C−Cl) 727 cm^{-1}.

Synthesis of $\mathbf{[N(CH_3)_4][7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]}$. In a two-necked flask, 1-CH_3-2-$(CH_2)_3Cl$-1,2-$C_2B_{10}H_{10}$ (1 g, 4.26 mmol) was dissolved in a suspension of $K(NC_4H_4)$ (2.24 g, 21.3 mmol) in dry THF (70 mL) under dinitrogen. The reaction mixture was refluxed for 48 h. After the mixture was cooled at room temperature and filtered, the solvent was evaporated in vacuo and the yellow solid was treated by a saturated $[N(CH_3)_4]Cl$ aqueous solution. The precipitate was filtered off and washed with water and hexane to obtain the product. Yield: 65%. The purification was done by preparative TLC, using CH_2Cl_2/CH_3CN (10/3) as the mobile phase, R_f (prep) = 0.64. $^1H\{^{11}B\}$-NMR: δ 6.66 (m, 2H, $-N-C\mathbf{H}=$), 5.98 (m, 2H, $-C\mathbf{H}=$), 3.67 (m, 2H, $-C\mathbf{H}_2-N$), 3.41 (s, 12H, $N(C\mathbf{H}_3)_4$), 1.88 (m, 2H, $-CH_2-C\mathbf{H}_2-CH_2-$), 1.30 (m, 2H, $-C-C\mathbf{H}_2-$), 1.22 (s, 3H, $-C\mathbf{H}_3$). $^{13}C\{^1H\}$-NMR: δ 123.87 and 121.2 ($-N-\mathbf{C}H=$), 118.1 and 107.1 ($-\mathbf{C}H=$), 81.0 and 91.0 (**C**c), 56.0 ($N(\mathbf{C}H_3)_4$), 50.0 ($-N-\mathbf{C}H_2-$), 33.4 ($-N-CH_2-\mathbf{C}H_2-$), 21.8 ($-\mathbf{C}H_3$), 33.1 ($-C-\mathbf{C}H_2-$). ^{11}B-NMR: δ −8.9 (d, ^1J(B,H) = 115.56 Hz, 1B), −10.59 (d, ^1J(B,H) = 115.56 Hz, 2B), −17.92 (d, ^1J(B,H) = 134.82 Hz, 4B), −34.21 (d, ^1J(B,H) = 144.45 Hz, 1B), −36.67 (d, ^1J(B,H) = 134.82 Hz, 1B). Anal. Calcd for $C_{14}H_{35}N_2B_9\cdot{}^1/_4CH_3CN$: C, 49.55; H, 10.32; N, 8.26. Found: C, 49.20; H, 10.02; N, 7.85. FTIR (KBr): ν_{max} (B−H) 2516 cm^{-1}; ν_{max} (pyrrole ring) 1428 cm^{-1}; ν_{max} (C−N) 1435, 948 cm^{-1}.

Synthesis of $\mathbf{[N(CH_3)_4][7\text{-}C_6H_5\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]}$. In a two-necked flask, 1-C_6H_5-2-$(CH_2)_3Cl$-1,2-$C_2B_{10}H_{10}$ (1 g, 3.37 mmol) was dissolved in a suspension of $K(NC_4H_4)$ (1.77 g, 16.84 mmol) in dry THF (70 mL) under dinitrogen. The reaction conditions and work up were as before. Yield: 62%. Its purification was done by preparative TLC, using CH_2Cl_2/CH_3CN (10/4) as the mobile phase, R_f (prep) = 0.77. $^1H\{^{11}B\}$-NMR: δ 7.35−7.10 (m, 5H, $-C_6\mathbf{H}_5$), 6.40 (m, 2H, $-N-C\mathbf{H}=$), 5.89 (m, 2H, $-C\mathbf{H}=$), 3.38 (m, 2H, $-C\mathbf{H}_2-N$), 3.40 (s, 12H, $N(C\mathbf{H}_3)_4$), 1.68 (m, 2H, $-CH_2-C\mathbf{H}_2-CH_2-$), 1.30 (m, 2H, $-C-C\mathbf{H}_2$). $^{13}C\{^1H\}$-NMR: δ 126.9−132.0 ($-\mathbf{C}_6H_5$), 123.1 and 125.5 ($-N-\mathbf{C}H=$), 119.8 and 107.1 ($-\mathbf{C}H=$), 55.2 ($N(\mathbf{C}H_3)_4$), 49.2 ($-N-\mathbf{C}H_2-$), 33.2 ($-N-CH_2-\mathbf{C}H_2-$), 32.2 ($-C-\mathbf{C}H_2-$). ^{11}B-NMR: δ −7.99 (d, ^1J(B,H) = 168.52 Hz, 1B), −10.19 (d, ^1J(B,H) = 208.97 Hz, 1B), −12.21 (d, ^1J(B,H) = 160.82 Hz, 1B), −17.22 (d, ^1J(B,H) = 112.67 Hz, 2B), −18.71 (d, ^1J(B,H) = 152.15 Hz, 2B), −33.69 (d, ^1J(B,H) = 128.08 Hz, 1B), −36.20 (d, ^1J(B,H) = 144.45 Hz, 1B). Anal. Calcd for $C_{19}H_{37}N_2B_9\cdot{}^1/_3CH_3CN$: C, 56.37; H, 9.15; N, 6.92. Found: C, 56.00; H, 8.90; N, 6.70. FTIR (KBr): ν_{max} (B−H) 2523 cm^{-1}; ν_{max} (pyrrole ring) 1419 cm^{-1}; ν_{max} (C−N) 1482, 941 cm^{-1}.

Synthesis of Mixed Complexes. Route A. Synthesis of 1, 2, 3, and 4. In a two-necked flask under dinitrogen, the *nido* ligand $[N(CH_3)_4][7\text{-}R\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]$ (3.00 mmol), R = CH_3 or C_6H_5, was dissolved in 70 mL of dme. Then, $CoCl_2$ (1.97 g, 15.17 mmol) and K(*t*-BuO) (1.79 g, 16.00 mmol) were added. After the mixture was stirred and refluxed under dinitrogen for 72 h, it was cooled to room temperature and the solvent was evaporated in vacuo. The residue was poured into 500 mL of water and extracted several times with 100 mL of CH_2Cl_2. The solvent present in the organic phase was eliminated under vacuum. Chromatography of the crude red solid using CH_2Cl_2/C_6H_{14} as the mobile phase (8/2 for R = CH_3 and 7/3 for R = C_6H_5) provided the pure yellow complexes **1** (R_f (prep) = 0.56), **2** (R_f (prep) = 0.5), **3** (R_f (prep) = 0.45), and **4** (R_f (prep) = 0.39) in a yield of 13%, 11%, 16%, and 12%, respectively, and other boron compounds that are not yet characterized.

Route B. Synthesis of 2 and 4. In a two-necked flask, 1-$Cl(CH_2)_3$-2-R-1,2-$C_2B_{10}H_{10}$ (4.26 mmol), R = CH_3 or C_6H_5, was dissolved in a suspension of $K(NC_4H_4)$. Then, $CoCl_2$ was added in a ratio of 1:12:5 in dme (70 mL) under dinitrogen. The reaction mixture was refluxed for 48 h. After the mixture was cooled and filtered, the solvent was evaporated in vacuo. The yellow solid was extracted with hexane to obtain the corresponding complexes **2** (R = CH_3) and **4** (R = C_6H_5) and other cobaltacarborane complexes that are not yet characterized. Yield: 26% (**2**), 21% (**4**). Purification was performed as indicated in route A.

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[13] Fein, M. M.; Grafstein, D.; Paustian, J. E.; Bobinski, J.; Lichstein, B. M.; Mayes, N.; Schwartz, N. N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1115.

Characterization of 1, 2, 3, and 4. $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(7\text{-}\mathrm{CH_3}\text{-}8\text{-}\mathrm{C_4H_9}\text{-}7,8\text{-}\mathrm{C_2B_9H_9})]$, 1. ^{1}H{^{11}B}-NMR: δ 7.06 (s, 2H, −N−C**H**=), 6.48 (s, 2H, −C**H**=), 3.10 (m, 1H, B−C−C**H**$_2$−), 2.65 (m, 1H, B−C−C**H**$_2$−), 2.54 (s, 3H, B−C−C**H**$_3$), 1.85 (m, 1H, −CH$_2$−C**H**$_2$−CH$_2$−), 1.60 (m, 1H, −CH$_2$−C**H**$_2$−CH$_2$−), 1.42 (m, 2H, CH$_3$−C**H**$_2$−CH$_2$−), 1 (t, ^1J(H,H) = 8.57 Hz, 3H, C**H**$_3$−CH$_2$−). ^{13}C{^{1}H}-NMR: δ 115.8 and 114.4 (−N−**C**H=), 91.0 and 90.7 (−**C**H=), 85.5 and 80.0 (**C**c), 41.3 (B−Cc−**C**H$_2$−), 32.3 (−CH$_2$−**C**H$_2$−CH$_2$−), 29.5 (CH$_3$−**C**H$_2$−), 22.4 (**C**H$_3$−C−B), 13.1 (**C**H$_3$−CH$_2$−). ^{11}B-NMR: δ 5.32 (d, ^1J(B,H) = 144.45 Hz, 1B), 3.77 (d, ^1J(B,H) = 144.45 Hz, 1B), −0.67 (d, ^1J(B,H) = 60.18 Hz, 1B), −1.30 (d, ^1J(B,H) = 60.18 Hz, 1B), −5.37 (d, ^1J(B,H) = 144.45 Hz, 2B), −11.53 (d, ^1J(B,H) = 84.26 Hz, 1B), −12.45 (d, ^1J(B,H) = 168.52 Hz, 1B), −13.56 (d, ^1J(B,H) = 168.52 Hz, 1B). Anal. Calcd for $\mathrm{C_{11}H_{25}NB_9Co\cdot{}^1/_{12}C_6H_{14}}$: C, 41.28; H, 7.82; N, 4.18. Found: C, 41.29; H, 7.50; N, 4.11. FTIR (KBr): $\nu_{\max}$ (B−H) 2544 cm^{-1}; $\nu_{\max}$ (pyrrole ring) 1454, 1426 cm^{-1}.

$[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(7\text{-}\mathrm{CH_3}\text{-}8\text{-}\mathrm{C_3H_5}\text{-}7,8\text{-}\mathrm{C_2B_9H_9})]$, 2. ^{1}H{^{11}B}-NMR: δ 7.11 (s, 1H, −N−C**H**=), 7.00 (s, 1H,−N−C**H**=), 6.47 (s, 2H, −C**H**=), 2.57 (s, 3H, B−C−C**H**$_3$), 1.25 (m, 1H, −C**H**(CH$_2$)$_2$), 0.75−1 (m, 4H, −CH(C**H**$_2$)$_2$). ^{13}C{^{1}H}-NMR: δ 116.3 (−N−**C**H=), 115.5 (−N−**C**H=), 90.5 and 90.3 (−**C**H=), 86.5 and 80.5 (**C**c), 21.8 (B−C−**C**H$_3$), 10.8 (−CH(**C**H$_2$)$_2$), 8.8 (−**C**H(CH$_2$)$_2$). ^{11}B-NMR: δ 4.8 (d, ^1J(B,H) = 124.23 Hz, 1B), 3.2 (d, ^1J(B,H) = 124.23 Hz, 1B), −0.7 (d, ^1J(B,H) = 141.53 Hz, 2B), −5.5 (d, ^1J(B,H) = 124.23 Hz, 1B), −6.9 (d, ^1J(B,H) = 124.23 Hz, 1B), −12.3 (d, ^1J(B,H) = 147.34 Hz, 2B), −16.6 (d, ^1J(B,H) = 141.56 Hz, 1B). Anal. Calcd for $\mathrm{C_{10}H_{21}NB_9Co}$: C, 38.56; H, 6.79; N, 4.50. Found: C, 38.92; H, 6.42; N, 4.38. FTIR (KBr): $\nu_{\max}$ (B−H) 2551 cm^{-1}; $\nu_{\max}$ (pyrrole ring) 1447, 1419 cm^{-1}.

$[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(7\text{-}\mathrm{C_6H_5}\text{-}8\text{-}\mathrm{C_4H_9}\text{-}7,8\text{-}\mathrm{C_2B_9H_9})]$, 3. ^{1}H{^{11}B}-NMR: δ 7.42−7.81 (m, 5H, −C$_6$**H**$_5$), 6.92 (s, 1H, −N−C**H**=), 6.52 (s, 1H, −N−C**H**=), 6.48 (s, 1H, −C**H**=), 5.88 (s, 1H, −C**H**=), 3.18 (m, 1H, B−C−C**H**$_2$−), 3.04 (m, 1H, B−C−C**H**$_2$−), 2.01 (m, 1H, −CH$_2$−C**H**$_2$−CH$_3$), 1.74 (m, 1H, −CH$_2$−C**H**$_2$−CH$_3$), 1.45 (m, 2H, −C**H**$_2$−CH$_3$), 1.08 (t, ^1J(H,H) = 8 Hz, 3H, −CH$_2$−C**H**$_3$). ^{13}C{^{1}H}-NMR: δ 127.9−142.5 (−**C**$_6$H$_5$), 118.8 and 112.1 (−N−**C**H=), 93.1 and 90.7 (−**C**H=), 43.1 (B−**C**−CH$_2$−), 32.7 (−CH$_2$−**C**H$_2$−CH$_3$), 23.6 (−**C**H$_2$−CH$_3$), 13.13 (−CH$_2$−**C**H$_3$). ^{11}B-NMR: δ 8.25 (d, ^1J(B,H) = 147.66 Hz, 1B), 5.47 (d, ^1J(B,H) = 147.66 Hz, 1B), 0.76 (d, ^1J(B,H) = 154.08 Hz, 1B), −3.24 (d, ^1J(B,H) = 173.34 Hz, 2B), −5.27 (d, ^1J(B,H) = 173.34 Hz, 1B), −9.72 (d, ^1J(B,H) = 160.5 Hz, 1B), −13.16 (d, ^1J(B,H) = 179.76 Hz, 1B), −15.50 (d, ^1J(B,H) = 179.76 Hz, 1B). Anal. Calcd for $\mathrm{C_{16}H_{27}NB_9Co}$: C, 49.32; H, 6.98; N, 3.59. Found: C, 49.43; H, 6.71; N, 3.43. FTIR (KBr): $\nu_{\max}$ (B−H) 2555, 2496 cm^{-1}; $\nu_{\max}$ (pyrrole ring) 1459, 1443 cm^{-1}.

$[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(7\text{-}\mathrm{C_6H_5}\text{-}8\text{-}\mathrm{C_3H_5}\text{-}7,8\text{-}\mathrm{C_2B_9H_9})]$, 4. ^{1}H{^{11}B}-NMR: δ 7.42−8.04 (m, 5H, −C$_6$**H**$_5$), 6.78 (s, 1H, −N−C**H**=), 6.54 (s, 1H, −N−C**H**=), 6.48 (s, 1H, −C**H**=), 6.41 (s, 1H, −C**H**=), 1.30 (m, 1H, −C**H**(CH$_2$)$_2$), 0.92−1.12 (m, 4H, −CH(C**H**$_2$)$_2$). ^{13}C{^{1}H}-NMR: δ 127.8−137.6 (−**C**$_6$H$_5$), 118.7 (−N−**C**H=), 115.7 (−N−**C**H=), 91.6 (−**C**H=), 24.6 (−CH(**C**H$_2$)$_2$), 11.3 (−**C**H(CH$_2$)$_2$). ^{11}B-NMR: δ 6.35 (d, ^1J(B,H) = 166.92 Hz, 1B), 4.42 (d, ^1J(B,H) = 166.92 Hz, 1B), −0.35 (d, ^1J(B,H) = 154.08 Hz, 2B), −3.71 (d, ^1J(B,H) = 166.92 Hz, 1B), −5.99 (d, ^1J(B,H) = 166.92 Hz, 1B), −10.82 (d, ^1J(B,H) = 154.08 Hz, 1B), −14.55 (d, ^1J(B,H) = 173.34 Hz, 1B), −17.24 (d, ^1J(B,H) = 154.08 Hz, 1B). Anal. Calcd for $\mathrm{C_{15}H_{23}NB_9Co\cdot{}^1/_5CH_3CN}$: C, 48.45; H, 6.23; N, 4.40. Found: C, 48.58; H, 5.93; N, 4.38. FTIR (KBr): $\nu_{\max}$ (B−H) 2604, 2574, 2566, 2541, 2514, 2503 cm^{-1}; $\nu_{\max}$ (pyrrole ring) 1493, 1418 cm^{-1}. Resonances attributed to hexane and acetonitrile are omitted.

Synthesis of $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_2B_9H_{11}})]$. This compound had already been synthesized in our recent publication, but starting from the *nido* ligand. Conducting the reaction following route B, the yield has been improved from 68% (calculated from the *nido* ligand) to 76%, with the advantage of avoiding the synthesis of the *nido*-carborane precursor. Spectroscopic data and elemental analysis are reported in our previous publication.[5]

X-ray Data Collections for $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_7H_{21}B_9})]$ and $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_{11}H_{19}B_9})]$. Single-crystal data collections were performed at ambient temperature with a Rigaku AFC5S diffractometer using monochromatized Mo Kα radiation (λ = 0.710 69 Å) and the $\omega-2\theta$ scan mode. The unit cell parameters were determined by least-squares refinements of 25 carefully centered reflections. The data were corrected for Lorentz and polarization effects and for absorption (ψ scans). For $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_{11}H_{19}B_9})]$, a linear correction for decay (−3.6%) was also applied. A total of 3000 and 3477 unique reflections were collected ($2\theta_{\max}$ = 50°) for $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_7H_{21}B_9})]$ and $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_{11}H_{19}B_9})]$, respectively, and of those, 1877 and 2441 were considered as observed.

Structure Determinations of $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_7H_{21}B_9})]$ and $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_{11}H_{19}B_9})]$. The structures were solved by direct methods using SHELXS86.[14] Least-squares refinements and all subsequent calculations were performed using the XTAL[15] (for $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_7H_{21}B_9})]$) and TEXSAN[16] (for $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_{11}H_{19}B_9})]$) crystallographic software packages, which minimized the function $\sum w(\Delta F)^2$, where $1/w = \sigma^2(F_o)$. For both structures, the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_7H_{21}B_9})]$ were placed at their calculated positions (B−H = 1.10 and C−H = 0.95 Å, $U(\mathrm{H}) = 1.2 \times U_{\mathrm{eq}}$ (host atom)). For $[\eta^5\text{-}(\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_{11}H_{19}B_9})]$, the H(B) hydrogen atoms were refined with fixed isotropic displacement parameters and the rest of hydrogen atoms were placed at their calculated positions.

Selected bond parameters are listed in Tables 1 and 2 for $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_7H_{21}B_9})]$ and $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_{11}H_{19}B_9})]$, respectively. Crystallographic data for both compounds are presented in Table 3.

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Supporting Information Available: Listings of experimental details of X-ray structure determinations, atomic positional and isotropic displacement parameters, atomic anisotropic displacement parameters, interatomic distances and angles, and least-squares planes for $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_7H_{21}B_9})]$ and $[(\eta^5\text{-}\mathrm{NC_4H_4})\mathrm{Co}(\mathrm{C_{11}H_{19}B_9})]$ (23 pages). Ordering information is given on any current masthead page.

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