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The First Molecule Incorporating $[\eta^5\text{-}NC_4H_4]^-$ and an Organic C−NC_4H_4 Group. Synthesis of $[Co(7\text{-}C_4H_4N(CH_2)_3\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_9)(\eta^5\text{-}NC_4H_4)]$ (R = CH_3, C_6H_5)

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Introduction

While metallacarboranes incorporating $[C_2R_2B_9H_9]^{2-}$ and $[C_5R_5]^-$ have been long known,[1] no work dealing with the electronically and geometrically similar $[NC_4R_2R'_2]^-$ was reported until recently.[2] Pioneering work in the metallacarborane area had been done with small carboranes and substituted pyrrolyl groups. Examples are the double-decker $[(\eta^5\text{-}NC_4Me_2R_2)Co(Et_2C_2B_4H_4)]$, and $[(\eta^5\text{-}NC_4Me_2R_2)Co(Et_2C_2B_3H_5)]$ and the triple-decker $[(\eta^5\text{-}NC_4Me_2R_2)Co(Et_2C_2B_3H_3)Co(Cp)]$, $[(\eta^5\text{-}NC_4Me_2R_2)Co(Et_2C_2B_3H_3)Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)]$, and $[(\eta^5\text{-}NC_4Me_4)_2Co_2(Et_2C_2B_3H_3)]$.[3] Although the number of organometallic compounds incorporating $[\eta^5\text{-}NC_4R_2R'_2]^-$ is meager, since the recent discovery of $[Mn(\eta^5\text{-}NC_4Me_2H_2)(CO)_3]$[4] the number has increased steadily.[5−10] Also, the number of ions complexed has grown, e.g. Li,[11] Na,[12] Mn,[2,4] Fe,[5] Co,[6] Sn,[7] Pb,[8] Ni,[9] Ru.[10] $[NC_4R_2R'_2]^-$ is encountered in these molecules coordinating as M-η^5 and/or M-σ-N motifs, usually protected at the α or α and β positions. Protection was sought to stabilize the complex.[5] On the other hand, conductive pyrrole-based polymers are attracting great interest, and much effort is being dedicated to modulating their properties by doping.[13] Considering the growing number of $[NC_4R_2R'_2]^-$ complexes, the extraordinary stabilizing capacity of $[C_2B_9H_{11}]^{2-}$ derivatives,[14] and that coordinated metal ions can modulate the properties of polypyrrole,[15] the lack of data concerning $[C_2R_2B_9H_9]^{2-}$/$[NC_4R_2R'_2]^-$ mixed metallacarboranes is surprising. Recently we proved that species of the type $[Co(C_2R_2B_9H_9)(\eta^5\text{-}NC_4H_4)]$ may be produced.[2,4,16] Interestingly, there was no need to use protected pyrrolyl ligands, which opened the possibility of performing pyrrole polymerization. Their stability is considerable, as shown by the fact that some of them such as $[Co(7\text{-}(CH_2)_2CH\text{-}8\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_9)(\eta^5\text{-}NC_4H_4)]$ have been generated from $[7\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}8\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_9]^-$ following an electron-transfer and rearrangement process.[16] This strong tendency toward $[\eta^5\text{-}NC_4H_4]^-$ capping seemed to hinder the synthesis of mixed $[C_2R_2B_9H_9]^{2-}$/$[\eta^5\text{-}NC_4H_4]^-$ metallacarboranes, which in addition to these groups, would incorporate pyrrole as an arm substituent. In fact, there is no structural report of any kind of compound whose molecular structure does contain both the $[NC_4R_2R'_2]^-$ moiety and a free organic C−NC_4H_4 group. The existence of a nonprotected second pyrrolyl function, in addition to $[\eta^5\text{-}NC_4H_4]^-$, is of interest for extra polymerization. Here, we present the synthesis and structural determination of $[Co(7\text{-}C_4H_4N(CH_2)_3\text{-}8\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_9)(\eta^5\text{-}NC_4H_4)]$, the first structurally characterized molecule incorporating $[\eta^5\text{-}NC_4H_4]^-$ and an organic C−NC_4H_4 group.

Results and Discussion

The reaction of $[N(CH_3)_4][7\text{-}C_4H_4N(CH_2)_3\text{-}8\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_{10}]$ with anhydrous $CoCl_2$, and K^tBuO in a 1:5:5 ratio had led to a mixture of compounds including $[Co(7\text{-}CH_3(CH_2)_3\text{-}8\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_9)(\eta^5\text{-}NC_4H_4)]$ and $[Co(7\text{-}(CH_2)_2CH\text{-}8\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_9)(\eta^5\text{-}NC_4H_4)]$. Although several bands obtained in preparative TLC remain to be studied (see later), the fact that none of the isolated compounds contained the $[7\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}8\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ moiety suggested that an alternative route had to be investigated. Former results of our research group suggested that $K[NC_4H_4]$ on $1\text{-}Cl(CH_2)_3\text{-}2\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{10}$ could function in several roles: (i) as a nucleophile producing the C−NC_4H_4 bond; (ii) as a nucleophile to remove B(3) in the initial *closo*-$1\text{-}Cl(CH_2)_3\text{-}2\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{10}$ compound; (iii) as a base to remove the bridging hydrogen atom on the open C_2B_3 face; and (iv) as an η^5-coordinating ligand. Thus, the reaction of *closo*-$1\text{-}Cl(CH_2)_3\text{-}2\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{10}$, (R = CH_3, C_6H_5) with a suspension of $K[NC_4H_4]$ in dimethoxyethane and anhydrous $CoCl_2$ led to the $[Co(7\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_9)(\eta^5\text{-}NC_4H_4)]$

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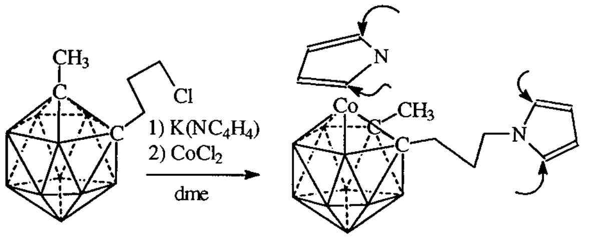

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Figure 1. Schematic synthesis of [Co(7-$C_4H_4N(CH_2)_3$-8-CH_3-7,8-$C_2B_9H_9$)(η^5-NC_4H_4)]. The curved arrows on **1** point toward sites susceptible to polymerization.

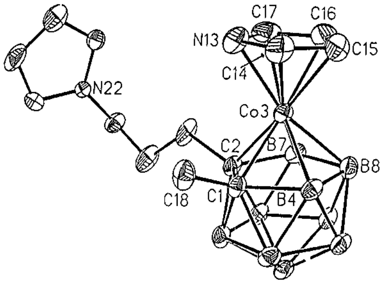

Figure 2. ORTEP diagram of **1**.

Table 1. Selected Atomic Coordinates and Equivalent Displacement Parameters for **1**

	x/a	*y/b*	*z/c*	U_{eq}, Å^2
C(1)	0.7939(3)	0.7627(5)	0.4623(3)	0.050(2)
C(2)	0.6985(4)	0.8537(5)	0.4933(3)	0.052(2)
Co(3)	0.71940(5)	0.91776(7)	0.38295(4)	0.0496(2)
B(4)	0.7471(4)	0.6984(6)	0.3630(3)	0.052(2)
B(7)	0.5861(5)	0.8561(7)	0.4161(4)	0.058(2)
B(8)	0.6119(4)	0.7542(6)	0.3320(3)	0.056(2)
N(13)	0.8161(5)	1.1034(5)	0.3992(3)	0.087(2)
C(14)	0.8287(6)	1.0200(7)	0.3341(4)	0.083(3)
C(15)	0.7335(7)	1.0062(7)	0.2744(4)	0.089(3)
C(16)	0.6594(6)	1.0856(8)	0.3017(4)	0.093(3)
C(17)	0.7129(8)	1.1439(6)	0.3770(5)	0.093(3)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

C(1)−Co(3)	2.010(4)	C(1)−C(18)	1.522(7)
C(2)−Co(3)	2.034(5)	N(13)−C(14)	1.376(9)
Co(3)−B(4)	2.053(5)	N(13)−C(17)	1.37(1)
Co(3)−B(7)	2.052(7)	C(14)−C(15)	1.403(9)
Co(3)−B(8)	2.074(6)	C(15)−C(16)	1.38(1)
Co(3)−N(13)	2.079(5)	C(16)−C(17)	1.39(1)
Co(3)−C(14)	2.053(8)	N(22)−C(23)	1.358(6)
Co(3)−C(15)	2.049(7)	N(22)−C(26)	1.354(6)
Co(3)−C(16	2.059(7)	C(23)−C(24)	1.36(1)
Co(3)−C(1)	2.040(5)	C(24)−C(25)	1.37(1)
C(2)−C(19)	1.551(7)	C(25)−C(26)	1.340(9)
C(1)−Co(3)−C(2)	49.5(2)	B(8)−Co(3)−C(15)	96.5(2)
C(1)−Co(3)−N(13)	106.9(2)	B(8)−Co(3)−C(16)	97.9(2)
C(1)−Co(3)−C(14)	107.7(2)	C(14)−N(13)−C(17)	104.0(5)
C(2)−Co(3)−N(13)	109.2(2)	C(23)−N(22)−C(26)	107.9(4)
C(2)−Co(3)−C(17)	108.3(3)		

Table 3. Crystallographic Data for **1**

chem formula	$C_{14}H_{26}B_9CoN_2$	β, deg	104.69(1)
fw	378.58	V, Å^3	1939.7(5)
T, °C	21	Z	4
λ, Å	0.710 69	d_{calcd}, g cm^{-3}	1.296
cryst syst	monoclinic	μ, cm^{-1}	8.8
space group	$P2_1/c$ (No. 14)	transm coeff	0.889−1.000
a, Å	13.192(3)	F(000)	784
b, Å	9.006(1)	R^a	0.050
c, Å	16.878(2)	$R_w{}^b$	0.047

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

complexes **1**, R = CH_3, and **2**, R = C_6H_5 (yields 48% and 46%, respectively). See Figure 1 for R = CH_3. Both compounds display similar NMR characteristics. The $^{11}B\{^1H\}$-NMR of **1** produces eight resonances with relative intensities 1:1:1:2:1:1:1:1 in the range −14 to +5 ppm, very similar to the $^{11}B\{^1H\}$-NMR of [Co($C_2B_9H_{11}$)(η^5-NC_4H_4)].[2] The ^1H-NMR of **1** is very informative regarding the aromatic region. It shows five sets of resonances at 6.07 (2H), 6.40 (2H), 6.61 (1H), 6.81 (2H), and 6.94 (1H) ppm. Upon comparison with the ^1H-NMR of [Co($C_2B_9H_{11}$)(η^5-NC_4H_4)], which displays[2] only two sets at 6.85 (2H) and 7.01 (2H) ppm, and that of [7-C_4H_4N-$(CH_2)_3$-8-CH_3-7,8-$C_2B_9H_{10}$]$^-$, which displays[16] resonances at 6.66 (2H) and 5.98 (2H) ppm, it is concluded that compound **1** contains two types of pyrrolyl fragments in the molecule, one as a η^5 ligand (resonances at 6.40 (2H) and 6.81 (2H) ppm) and the second one as an N-substituted pyrrolyl fragment (resonances at 6.07 (2H), 6.61 (1H), and 6.94 (1H) ppm). The NMR of compound **2** can be interpreted in the same way.

A brown prismatic crystal of **1**, suitable for X-ray analysis, was grown from a mixture of CH_3CN/C_6H_{14}. Its analysis confirms the two types of pyrrolyl fragments indicated previously; see Figure 2. The metal ion is sandwiched between the [NC_4H_4]$^-$ ion and the carborane's C_2B_3 open face, leaving the carborane [7-C_4H_4N-$(CH_2)_3$-8-CH_3-7,8-$C_2B_9H_9$]$^-$ ligand as such with its pyrrolyl group uncoordinated. The [$C_2B_9H_{11}$]$^{2-}$/[NC_4H_4]$^-$/Co^{3+} metallacarborane fragment closely resembles those already published for [Co($C_2B_9H_{11}$)(η^5-NC_4H_4)], [Co(7-$(CH_2)_2$CH-8-CH_3-7,8-$C_2B_9H_9$)(η^5-NC_4H_4)], and [Co(7-CH_3-$(CH_2)_3$-8-CH_3-7,8-$C_2B_9H_9$)(η^5-NC_4H_4)].[2,4,16] In all of these structures, the nitrogen atom of the [η^5-NC_4H_4]$^-$ ligand adopts a position bisecting the two carborane cluster carbon atoms, suggesting that this is the most stable conformation of all possible rotamers. Atomic coordinates and equivalent displacement parameters are given in Table 1, selected bond lengths and angles are shown in Table 2, and crystallographic data are presented in Table 3.

A reinvestigation of the reaction of [7-C_4H_4N-$(CH_2)_3$-8-CH_3-7,8-$C_2B_9H_{10}$]$^-$ with anhydrous $CoCl_2$ described at the beginning of the paper showed that, under the same TLC conditions, one band at R_f(prep) 0.35 was found. This suggested that **1** was also formed under these conditions, a fact that was confirmed by the NMR data. In this case, the yield was lower (21%)[17] but still reasonable. In the reaction vessel there was no additional free [NC_4H_4]$^-$, which means that the latter was generated by a Co(II) electron transfer to [7-$C_4H_4N(CH_2)_3$-8-CH_3-7,8-$C_2B_9H_{10}$]$^-$, breaking the C−NC_4H_4 bond. This again supports the high stability of these [Co($C_2RR'B_9H_9$)(η^5-NC_4H_4)] metallacarboranes, resembling that of [M($C_2RR'B_9H_9$)(η^5-C_5H_5)].[14] The synthesis of compounds **1** and **2**, containing [η^5-NC_4H_4]$^-$ and C−NC_4H_4, both unprotected moieties, opens the possibilities of electrosynthesized polypyrrole films of intricate structure and of [η^5-NC_4H_4]$^-$ polymerization. The stabilizing capacity of [$C_2B_9H_{11}$]$^{2-}$ derivatives may afford the right conditions to achieve these possibilities. In Figure 1, the sites susceptible to polymerization are indicated with curved arrows. Ensuing research is being performed in our group to synthesize similar species with longer metallacarborane−pyrrole spacers, $(CH_2)_5$ or $(CH_2)_6$, that can facilitate the electropolymerization.

Experimental Section

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

Materials. The preparation of 1-Cl$(CH_2)_3$-2-R-1,2-$C_2B_{10}H_{10}$, (R = CH_3, C_6H_5) was described in a preceding paper.[16] Degassed 1,2-

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(17) To make both yields comparable those have been referred to the starting 1-Cl$(CH_2)_3$-2−CH_3-1,2-$C_2B_{10}H_{10}$.

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. All organic and inorganic salts were of analytical reagent grade and were used as received.

Physical Measurements. ^{11}B-NMR (96.29 MHz), ^{13}C{^{1}H}-NMR (75.47 MHz), and ^{1}H{^{11}B}-NMR spectra (300.13 MHz) were recorded on a Bruker ARX-300 spectrometer equipped with the appropriate decoupling accessories. All NMR spectroscopic data were acquired in acetone-d_6 at 22 °C. Chemical shift values for ^{11}B-NMR spectra were referenced to external $BF_3{\cdot}O(C_2H_5)_2$, and those for ^{1}H{^{11}B}- and ^{13}C{^{1}H}-NMR spectra were referenced to $Si(CH_3)_4$. MS data were recorded on a Hewlet-Packard 5989X mass spectrometer, elemental analyses were carried out on a Perkin-Elmer 240B analyzer, and analytical thin-layer chromatography was performed on 0.25 mm (20 × 20 cm^2) silica gel F-254 plates (Tracer).

Synthesis of 1 and 2. In a two-necked flask, *closo*-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] in 70 mL of dimethoxyethane and anhydrous $CoCl_2$ (molar ratio 1:12:5). After being stirred and refluxed for 48 h, the mixture was cooled and the solvent was evaporated in vacuum. A yellow solid was extracted with hexane, and its purification by preparative TLC, using $CH_2Cl_2-C_6H_{14}$ (8:2) as the mobile phase [R_f(prep) 0.35 (**1**), 0.27 (**2**)] led to the isolation of complex **1**, R = CH_3, or **2**, R = C_6H_5 (yield 48% (0.77 g, 2.03 mmol) or 46% (0.87 g, 1.95 mmol), respectively).

Data for Compound 1. Anal. Calcd for $C_{14}B_9H_{26}N_2Co$: C, 44.41; H, 6.92; N, 7.40. Found: C, 44.34; H, 6.82; N, 7.26. FTIR (KBr): υ (cm^{-1}) = 3135, 3107, 2959, 2931, 2860 (C−H), 2607, 2558 (B−H), 1447 (ring system). ^{11}B{^{1}H}-NMR: δ = −13.55, −12.49, −11.32, −5.54, −1.75, −0.70, 3.82, 5.67 with relative intensities 1:1:1:2:1:1:1:1. ^{1}H{^{11}B}-NMR: δ = 2.15 (1H, Cc−C$\mathbf{H_2}$−), 2.16 (1H, Cc−C$\mathbf{H_2}$−), 2.44 (3H, Cc−C$\mathbf{H_3}$), 2.61 (1H, Cc−CH_2−C$\mathbf{H_2}$−), 3.05 (1H, Cc−CH_2−C$\mathbf{H_2}$−), 4.00 (2H, −C$\mathbf{H_2}$−N−), 6.07 (2H, (−C**H**=)*), 6.40 (2H, −C**H**=), 6.61 (1H, (−N−C**H**=)*), 6.81 (2H, −N−C**H**=), 6.94 (1H, (−N−C**H**=)*). [Here and elsewhere the asterisk indicates an aliphatic chain pyrrolyl and Cc indicates one of the cluster carbon atoms.] ^{13}C{^{1}H}-NMR: δ = 28.56 (Cc−**C**H_3), 32.45 (Cc−**C**H_2−), 38.72 (Cc−CH_2−**C**H_2−), 48.53 (−**C**H_2−N−), 79.89 (**C**c), 83.95 (**C**c), 90.97 (−**C**H=), 91.23 (−**C**H=), 108.09 ((−**C**H=)*), 114.73 (−N−**C**H=), 115.58 (−N−**C**H=), 120.53 ((−N−**C**H=)*. MS: $(m/z)_{max}$ 377.20 (21%, M$^+$).

Data for Compound 2. Anal. Calcd for $C_{19}B_9H_{28}N_2Co$: C, 51.79; H, 6.40; N, 6.36. Found: C, 52.22; H, 6.13; N, 6.09. FTIR (KBr): υ (cm^{-1}) = 3133, 3113 (arC−H), 2956, 2925 (C−H), 2566, 2534 (B−H), 1495, 1442 (ring system). ^{11}B{^{1}H}-NMR: δ = −15.48, −13.19, −9.69, −5.23, −3.39, −1.05, 5.33, 8.53 with relative intensities 1:1:1:1:2:1:1:1. ^{1}H{^{11}B}-NMR: δ = 2.18 (1H, Cc−C$\mathbf{H_2}$−), 2.50 (1H, Cc−C$\mathbf{H_2}$−), 3.00 (1H, Cc−CH_2−C$\mathbf{H_2}$−), 3.16 (1H, Cc−CH_2−C$\mathbf{H_2}$−), 4.10 (2H, −C$\mathbf{H_2}$−N−), 5.85 (1H, (−C**H**=)*), 6.06 (2H, −C**H**=), 6.41 (1H, (−C**H**=)*), 6.49 (1H, (−N−C**H**=)*), 6.72 (1H, (−N-C**H**=)*), 6.82 (2H, −N−CH=), 7.39−7.70 (5H, −$C_6$$\mathbf{H_5}$). ^{13}C{^{1}H}-NMR: δ = 32.73 (Cc−**C**H_2−), 40.87 (Cc−CH_2−**C**H_2−), 48.43 (−**C**H_2−N−), 93.27 (−**C**H=), 94.13 (−**C**H=), 107.87 ((−**C**H=)*), 112.17 (−N−**C**H=), 117.82 (−N−**C**H=), 120.63 ((−N−**C**H=)*), 127.83−142.34 (−**C**$_6H_5$). MS: $(m/z)_{max}$ 439.30 (21%, M$^+$).

X-ray study of 1. The data were corrected for Lorentz and polarization effects, dispersion, extinction, and absorption (ψ scans, transmission coefficient 0.889−1.000). The structure was solved by direct methods using MITRIL[18] and refined to $R(F) = 0.050$ [$R_w(F) = 0.045$] and GOF = 1.261 for 2572 independent reflections [$|F| > 4\sigma(F)$] using the XTAL3.2 program system.[19] Heavy atoms were refined with anisotropic and hydrogen atoms with fixed isotropic displacement parameters (1.2 times that of the host atom).

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal displacement parameters, bond distances and angles, and least-squares planes (11 pages). Ordering information is given on any current masthead page.

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