

PHENYL-INDUCED 3,1,11-REARRANGEMENT IN THE SYNTHESIS OF MIXED PYRROLYL/DICARBOLLIDE COBALTADICARBORANES

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Professor Jaromir Plesek has excelled in his contribution to boron, carborane and organic chemistry. Although not having worked in his group, our talks and discussions with him have certainly expanded our views of boron chemistry. Thus, we appreciate the honor of being invited to contribute to this issue on the occasion of his 70th birthday.

Mixed pyrrolide cobaltadicarbollides have been prepared from the reaction involving potassium pyrrolide, anhydrous CoCl₂ and the [7,8-(C₆H₅)₂-nido-7,8-C₂B₉H₁₀]⁻ anion in dimethoxyethane. An alternative and higher-yield route consists in the reaction between 1,2-(C₆H₅)₂-*closo*-1,2-C₂B₁₀H₁₀ and potassium pyrrolide in the presence of anhydrous CoCl₂. As confirmed by the X-ray diffraction analysis of [3-(η⁵-NC₄H₄)-1,11-(C₆H₅)₂-*closo*-3,1,11-CoC₂B₉H₉], the phenyl rings were found to enhance the rearrangement of the metallacarborane cluster carbons to produce the 3,1,11-isomer instead of the expected 3,1,2-derivative. As suggested by ¹H and ¹³C NMR spectroscopy, the electron-withdrawing properties and steric requirements of the phenyl rings facilitate the rearrangement.

Key words: Carboranes; Pyrrolide; Cobaltacarboranes.

Although an extensive work in the area of metallacarborane chemistry was reported with the C₂B₉H₁₁²⁻ ligand¹, no examples of the mixed pyrrolide-[C₂B₉H₁₁]²⁻ metalladicarbaborane complexes had been reported prior to our recent communications². Associated with this field of chemistry is the general significance of the [C₂B₉H₁₁]²⁻ metallacarborane derivatives, a great deal of which was generated by Plesek's work in the areas such as solubility of metalladicarbollides³, separation and characterization of organic bases⁴, radioactive-metal carriers⁵, and electron-acceptor molecules⁶. Another aspect of this type of chemistry is the well-established cluster isomerisation of carborane clusters⁷ which has been observed not only in the *closo*-C₂B₁₀H₁₂ series⁸, but also

with many metallocarborane compounds^{9,10}. This isomerisation usually requires high activation energy and elevated temperatures⁷ to effect the space separation of the cage carbon atoms in metallocarborane molecules. As observed in several recent reports, bulkier exo substituents on the cluster generally decrease the activation barrier, thus allowing the rearrangements to be effected at lower temperatures¹¹. Associated with this development is the current and developing interest in pyrrol-metallocarborane chemistry¹². In this specific area we have developed the synthesis of a new compound incorporating the η^5 -pyrrolide and disubstituted carborane $[(C_6H_5)_2C_2B_9H_9]^{2-}$ ligands. As a continuation of this chemistry, we now report two alternative routes to the synthesis of $[3-(\eta^5-NC_4H_4)-1,11-(C_6H_5)_2-closo-3,1,11-CoC_2B_9H_9]^*$ in which $[N(CH_3)_4]^+ [7,8-(C_6H_5)_2-nido-7,8-C_2B_9H_{10}]^-$ (ref.¹³) and $1,2-(C_6H_5)_2-closo-1,2-C_2B_{10}H_{10}$ were used as alternative carborane sources. In both cases, it is observed that a rearrangement of the cluster carbon atoms takes place during the complexation process.

RESULTS AND DISCUSSION

The reaction between $[N(CH_3)_4][7,8-(C_6H_5)_2-nido-7,8-C_2B_9H_{10}]$ and potassium pyrrolide in the presence of anhydrous $CoCl_2$ in refluxing dimethoxyethane (molar ratio 1 : 0.5) for 48 h resulted in the isolation of a yellow, air-stable solid. This was characterized by 1H , ^{13}C , and ^{11}B NMR spectroscopy, mass spectrometry, and microanalysis as a species conforming the expected $[(NC_4H_4)Co(C_6H_5)_2C_2B_9H_9]$ formulation (yield 32%). It is reasonable to suggest that, in this particular case, the potassium pyrrolide acts not only as a base, eliminating the bridging hydrogen atom, but also as an effective η^5 -ligand coordinating the central Co(III) atom.

In the previous communications from our group, the strongly nucleophilic potassium pyrrolide was shown to be capable of acting as an effective cage degradation agent^{2b,2c}. In this respect, treatment of $1,2-(C_6H_5)_2-closo-1,2-C_2B_{10}H_{10}$ with the pyrrolide anion was expected to result both in remarkable improvement of the yield due to a lower number of reaction steps involved and also in the same type of rearrangement as in the previous case^{2b,2c}. In accord with this presumption, this one-pot reaction, not requiring the synthesis of the *nido* ligand, was found to proceed very smoothly and to lead to an improved yield (65%) of the same $[(NC_4H_4)Co(C_6H_5)_2C_2B_9H_9]$ complex, as assessed by NMR spectroscopy. Moreover, the *in situ* generation of the *nido* species evidently prevents the product from further degradation processes.

* Correct numbering for compound $[(\eta^5-NC_4H_4)-1,11-(C_6H_5)_2-3,1,11-CoC_2B_9H_9]$ is $2-\eta^5-NC_4H_4-1,10-(C_6H_5)_2-2,1,10-CoC_2B_9H_9$. A different numbering was used to relate this compound to the basic 3,1,2-isomer and according to a previous report¹¹.

The relatively high number of the ^{11}B and ^1H resonances found for the $[(\text{NC}_4\text{H}_4)\text{Co}(\text{C}_6\text{H}_5)_2\text{C}_2\text{B}_9\text{H}_9]$ complex suggests asymmetrical constitution which is in agreement with a considerable rearrangement of the cage carbons. This asymmetry would not be present if the two carbon cluster atoms remained on the open face of the carborane ligand. In accord with this assumption, the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of the complex displays four resonances at the pyrrolyl region. The resonances at 5.99 and 6.13 ppm correspond to the β -protons, while those at 6.19 and 6.37 ppm are assigned to the α -protons. Another set of signals corresponding to the phenyl protons appears in the range of 7.28 and 7.76 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR signals of the β -pyrrolide carbons also appear at a higher field than the α ones (93.3, 93.9 vs 112.9, 113.9 ppm). The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum exhibits 1 : 1 : 2 : 1 : 1 : 2 : 1 patterns (reading upfield) in the narrow range between 2.72 and -13.90 ppm, which is typical for other complexes of the metal-dicarbollide constitution.

The asymmetric disposition of the cage carbons was determined by an X-ray diffraction study that resulted in the molecular structure shown in Figs 1–3. The selected distances and angles are shown in Table I. The analysis confirmed unambiguously that the molecule is $[3-(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,11\text{-(C}_6\text{H}_5)_2\text{-}closo\text{-}3,1,11\text{-CoC}_2\text{B}_9\text{H}_9]$ isomer (for comparison purposes, the numbering is identical with that for the 3,1,2-isomer) and that a rearrangement process had taken place in the carborane ligand during the complexation reaction. The asymmetric unit of the crystal structure consists of two similar, but not identical $[3-(\eta^5\text{-NC}_4\text{H}_4)\text{-}1,11\text{-(C}_6\text{H}_5)_2\text{-}closo\text{-}3,1,11\text{-CoC}_2\text{B}_9\text{H}_9]$ molecules (see Table I and Figs 1 and 2). In both molecules the metal is sandwiched by the pentagonal faces of the dicarbollide and pyrrolyl ligands. The disorder of the pyrrolyl ligands in both

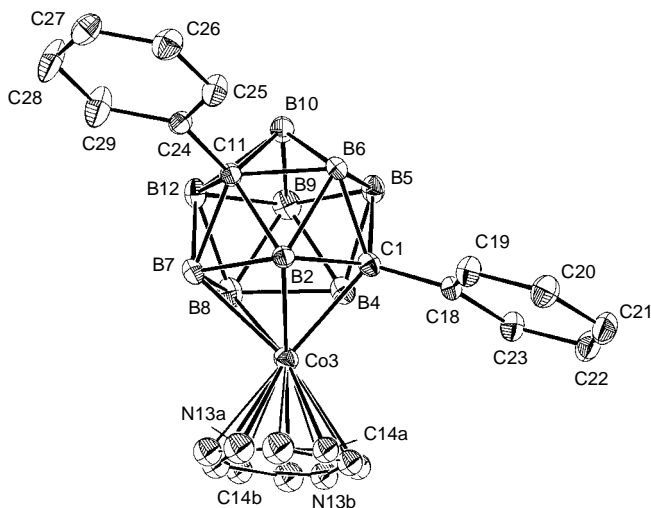


FIG. 1

Perspective drawing of molecule **1**. Displacement ellipsoids are drawn at the 20% probability level

TABLE I
Selected bond lengths (Å), angles (°), and torsion angles (°) with estimated standard deviations in parentheses

Lengths			Angles		
	1	2		1	2
C1–B2	1.71(1)	1.72(1)	Co3–C1–C18	114.7(3)	114.1(3)
C1–B4	1.741(1)	1.744(7)	C1–Co3–N13a	135.5(2)	103.9(3)
Co3–C1	2.056(5)	2.050(5)	C1–Co3–N13b	121.0(5)	171.5(4)
Co3–B2	2.019(5)	2.009(5)	Torsion angles		
Co3–B4	2.067(6)	2.054(6)	Co3–C1–C18–C19	–100.3(4)	89.6(5)
Co3–B7	2.062(8)	2.049(7)	Co3–C1–C18–C23	80.6(5)	–90.5(5)
Co3–B8	2.091(6)	2.090(6)	B2–C11–C24–C25	52.7(6)	–114.3(7)
Co3–N13b	2.094(6)	2.055(8)	B2–C11–C24–C29	–126.5(5)	61.2(7)
Co3–N13b	2.06(1)	2.082(9)			
Co3–C(pyrrole)	2.059(7)– 2.094(8)	2.05(1)– 2.09(1)			
C1–C18	1.512(9)	1.509(8)			
C11–C24	1.513(8)	1.520(9)			

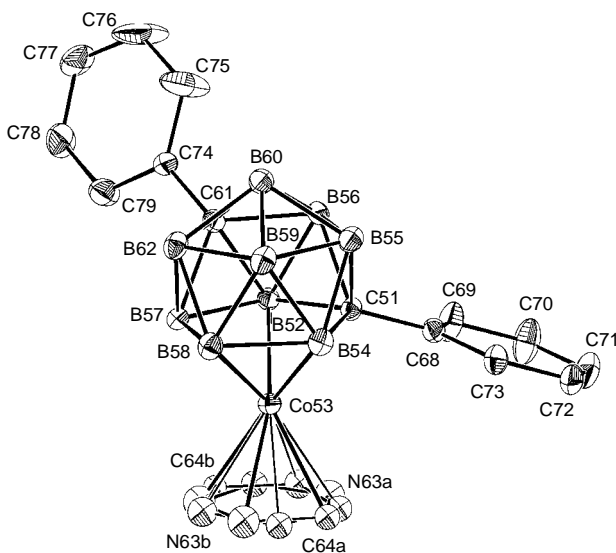


FIG. 2
Perspective drawing of molecule 2. Displacement ellipsoids are drawn at the 20% probability level

molecules makes identification of the nitrogen atom of each rotamer difficult, and the rotamers presented are those most probable according to the calculations. The pentagonal faces of the pyrrolyl ligands may adopt staggered and eclipsed orientations with respect to the dicarbollide ring and both these orientations are present in the title compound. Molecule **1** (Fig. 3a) shows the situation clearly. In a staggered conformation (72%) N(13a) is located between B(2) and B(7), while in the eclipsed conformation (28%) N(13b) is found below the B(4) centre. In molecule **2** (Fig. 3b) N(63a) is not exactly below C(51) and this eclipsed conformation (53%) deviates 14° from the ideal. In a staggered conformation (47%) N(63b) is between B(57) and B(58), but also this is 10° away from the ideal conformation. Thus, in each molecule the two N positions of different rotamers are found on opposite sites. In addition to the differences in the site occupation parameters and mutual orientation of the pyrrolyl rings, another prominent difference between the two molecules is in the orientation of the phenyl groups, as suggested by the torsion angles listed in Table I.

The notable difference between the title compound and the 1,2-disubstituted Co-pyrrolyl-dicarbollides reported earlier is in the orientation of the pyrrolyl group. In the latter complexes the nitrogen atom is situated between the two carbon atoms of the dicarbollide ligand, and therefore only one rotamer has been found in those complexes. The reason for the formation of several rotamers in the title compound seems to be the presence of only one carbon atom in the dicarbollide belt adjacent to the Co centre. The phenyl group bonded to this carbon atom may have steric and steering effects. However, the rotational barrier is generally quite low in these metallocene-type compounds and the existence of many rotamers should be presumed (for example, compare the gas-phase rotational barrier of $4(1) \text{ kJ mol}^{-1}$ between the two main rotamers of ferrocene¹⁴). The rotamers found in molecules **1** and **2** resemble those found for ferrocene in the solid state¹⁵. Noteworthy is also the stability of the title compound towards electron impact in the mass spectrometric experiment (m/z 409.35, 100%, M^+).

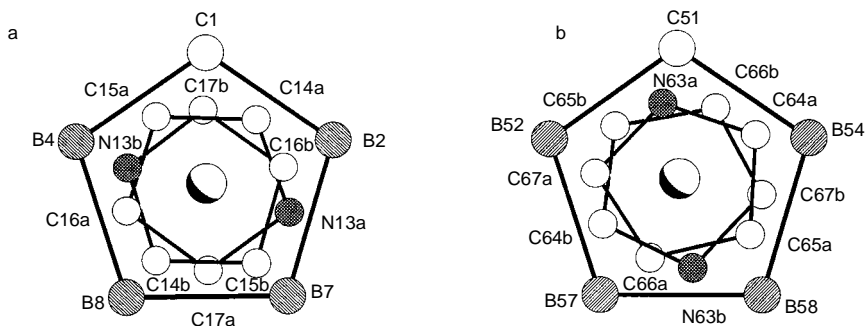


FIG. 3

Orientations of the pentagonal CB_4 and NC_4 in molecules **1** (a) and **2** (b)

The complexation mechanism is not fully understood, with respect to the moment when the rearrangement takes place (prior to the complexation or after the interaction with the metal atom), nevertheless, it is evident that the bulkiness of the phenyl substituents contributes significantly to the migration of one of the cluster carbon atoms from the original C_2B_3 face of the dicarbollide ligand¹¹. This assumption is strongly confirmed by the fact that the isomerisation in the diphenyl substituted system studied proceeds under relatively mild conditions which suggests considerable decrease in the

TABLE II

Interatomic distances (d) C(1)–C(2) for selected derivatives of 1-R-2-R'-1,2- $C_2B_{10}H_{10}$

R	R'	d_{C1-C2} , Å	Reference
H	H	1.634(3)	18
C_6H_5	C_6H_5	1.733(4)	19
H	$P(C_6H_5)_2$	1.666(9)	20
C_6H_5	$P(C_6H_5)_2$	1.755(6)	21
C_6H_5	SCH_2CH_3	1.765(7)	22

TABLE III

NMR chemical shifts (δ , ppm) and chemical shift changes ($\Delta\delta$, ppm) of the cage C-H resonances for selected 1-R-2-R'-*closo*-1,2- $C_2B_{10}H_{10}$ derivatives

R	R'	$\delta(^{13}C)$	$\Delta\delta(^{13}C)$	$\delta(^1H)$	$\Delta\delta(^1H)$
H	H	56.9	–	4.52	–
H	C_6H_5	77.9	21.0	5.30	0.78
		61.5	4.6		
C_6H_5	C_6H_5	85.8	28.9	–	–
H	$P(C_6H_5)_2$	74.0	17.1	4.44	–0.08
		64.6	7.7		
C_6H_5	$P(C_6H_5)_2$	86.9	30.0	–	–
		84.0	27.1		
H	SCH_2CH_3	75.6	18.7	4.75	0.23
		68.4	11.5		
C_6H_5	SCH_2CH_3	89.0	32.1	–	
		86.4	29.5		

activation barrier due to the presence of the two bulky phenyl substituents attached to the cluster carbons.

Previous experience from our group shows that the C–C intracluster distances tend to increase when electron-rich substituents are attached to the cage carbon atoms¹⁶. We have also proposed that the cage C–C distances in *o*-carborane derivatives can be empirically predicted, taking additive electronic and steric contributions into account¹⁷. Table II shows some C–C distances for selected *o*-carborane derivatives. Examining the results obtained, it can be concluded that the larger is the electron-withdrawing effect of the substituent, the smaller is the electronic density of the cage C–C bond and the longer is the corresponding interatomic distance. Additional data supporting the electron-withdrawing character of this type of substituents are in Table III that shows downfield shifts of the corresponding ¹³C and ¹H NMR resonances, as indicated by the calculated $\Delta\delta$ values (defined as $\delta_R - \delta_H$, where δ_H is the chemical shift for *o*-carborane) for individual substituents R. Table III suggests that the $\delta(^{13}\text{C})$ and $\delta(^1\text{H})$ chemical shifts are strongly varying with individual substituents R, the $\delta(^{13}\text{C})$ shifts being much more susceptible to the C-substitution than the corresponding $\delta(^1\text{H})$ shifts because of the different distances over which these effects are transmitted.

Accordingly, the data in Tables II and III well document the electronic component affecting the cage C–C distances together with associated carbon and proton chemical shifts. Considering the cage rearrangement discussed above, we feel that, in addition to the steric effects, the electronic contribution is also very significant as electron-withdrawing substituents deplete the electron density of the cage C–C bond, thus facilitating the cage rearrangement by lowering the energetical barrier required for the space separation of the cluster carbons. As a result, it can be concluded that the cluster rearrangement is, in general, strongly facilitated by bulky and electron-withdrawing substituents.

EXPERIMENTAL

Instrumentation

Elemental analyses were performed in our analytical laboratory using a Carlo Erba EA1108 micro-analyser. IR spectra (ν , cm^{-1} ; KBr pellets) were obtained on a Nicolet 710-FT spectrophotometer. The ¹¹B (96.29 MHz), ¹³C{¹H} (75.47 MHz) and ¹H{¹¹B} (300.13 MHz) NMR spectra (δ , ppm; *J*, Hz) were recorded on a Bruker ARX-300 spectrometer equipped with appropriate decoupling accessories. All the NMR measurements were performed in hexadeuterioacetone at 22 °C. The ¹¹B NMR shifts are referenced to external $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, while the ¹H and ¹³C NMR shifts are referenced to $\text{Si}(\text{CH}_3)_4$.

Materials

The decaborane $\text{B}_{10}\text{H}_{14}$ (Katchem Ltd., Prague) was sublimed under high vacuum prior to use and the 1,2-(C_6H_5)₂-*closo*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ was prepared according to the method reported previously²³. All other chemicals were of analytical grade and were used as purchased from commercial resources (Aldrich or Fluka). Systematic monitoring of all reaction mixtures was effected by analytical TLC on

silica gel (UV-254 tracer) plates (0.25 mm, 20 × 20 cm). All experimental manipulations were carried out using standard high-vacuum or inert-atmosphere techniques.

Synthesis of $[N(CH_3)_4][7,8-(C_6H_5)_2-nido-7,8-C_2B_9H_{10}]$

$[N(CH_3)_4][7,8-(C_6H_5)_2-nido-7,8-C_2B_9H_{10}]$ was prepared from 1,2-(C_6H_5)₂-*closo*-1,2- $C_2B_{10}H_{10}$ analogously as the unsubstituted compound²⁴. For $C_{18}H_{32}B_9N$ · 1/3 H_2O (365.7) calculated: 59.15% C, 8.94% H, 3.83% N; found: 59.11% C, 8.71% H, 3.83% N. FTIR: 3 030, 2 523, 948. ¹¹B NMR: -8.00, 2 B, ¹J(B,H) = 133; -14.30, 1 B, ¹J(B,H) = 196; -16.30, 2 B, ¹J(B,H) = 145; -18.80, 2 B, ¹J(B,H) = 151; -33.00, 1 B, ¹J(B,H) = 134; -35.30, 1 B, ¹J(B,H) = 140. ¹H{¹¹B} NMR: 7.14 m, 4 H (C_6H_5); 6.84 m, 6 H (C_6H_5); 3.41 s, 12 H ($N(CH_3)_4$). ¹³C{¹H} NMR: 142.4, 131.8, 126.2, 124.7 (C_6H_5); 55.1 ($N(CH_3)_4$).

Synthesis of $[3-(\eta^5-NC_4H_4)-1,11-(C_6H_5)_2-closo-3,1,11-CoC_2B_9H_9]$

A. From $[N(CH_3)_4][7,8-(C_6H_5)_2-nido-7,8-C_2B_9H_{10}]$: In a two-necked flask, $[N(CH_3)_4][7,8-(C_6H_5)_2-nido-7,8-C_2B_9H_{10}]$ (0.500 g, 1.39 mmol) was dissolved in a suspension of $K[NC_4H_4]$ (1.46 g, 13.9 mmol) in dry dimethoxyethane. Anhydrous $CoCl_2$ (0.900 g, 6.96 mmol) was then added and the reaction mixture refluxed for 48 h. After cooling down and filtering, the solvent was evaporated *in vacuo*. The yellow solid was extracted with hexane and purified by preparative TLC (silica gel G, dichloromethane-hexane (7 : 3)) to isolate the main band of R_f 0.52. This was isolated by extraction with CH_2Cl_2 to give an orange solid, which was identified as $[3-(\eta^5-NC_4H_4)-1,11-(C_6H_5)_2-3,1,11-closo-CoC_2B_9H_9]$ (0.22 g, 32% yield). For $C_{18}B_9H_{23}CoN$ (409.4) calculated: 52.78% C, 5.66% H, 3.42% N; found: 52.68% C, 5.37% H, 3.51% N. FTIR: 3 107, 3 050, 2 955, 2 923, 2 853, 2 571, 2 541, 1 495, 1 465, 1 444. ¹¹B NMR: -13.90, 1 B, ¹J(B,H) = 183; -12.04, 2 B, ¹J(B,H) = 131; -8.21, 1 B, ¹J(B,H) = 136; -4.63, 1 B, ¹J(B,H) = 158; 0.81, 2 B; 1.85, 1 B; 2.72, 1 B. ¹H{¹¹B} NMR: 5.99 s, 1 H (CH=); 6.13 s, 1 H (CH=); 6.19 s, 1 H (NCH=); 6.37 s, 1 H (NCH=); 7.28–7.76 m, 10 H (2 × C_6H_5). ¹³C{¹H} NMR: 93.3 (CH=); 93.9 (CH=); 112.9 (NCH=); 113.9 (NCH=); 126.9–144.1 (C_6H_5). MS: m/z 409.35 (100%, M⁺).

B. From 1,2-(C_6H_5)₂-*closo*-1,2- $C_2B_{10}H_{10}$: Following the procedure described in the preceding experiment, 1,2-(C_6H_5)₂-*closo*-1,2- $C_2B_{10}H_{10}$ (0.500 g, 1.68 mmol) and anhydrous $CoCl_2$ (1.090 g, 8.40 mmol) were added to a suspension of $K[NC_4H_4]$ (2.120 g, 20.24 mmol). The reaction mixture was worked-up similarly to afford $[3-(\eta^5-NC_4H_4)-1,11-(C_6H_5)_2-closo-3,1,11-CoC_2B_9H_9]$ (0.447 g, 65%).

X-Ray Diffraction Studies

$C_{18}H_{23}B_9CoN$, $M_r = 409.59$; triclinic, space group PI (No. 2); $a = 13.549(1)$, $b = 13.679(2)$, $c = 13.211(2)$ Å, $\alpha = 117.362(9)$, $\beta = 102.49(1)$, $\gamma = 67.755(9)^\circ$, $V = 2 010.0(5)$ Å³, $Z = 4$, $D_{calc} = 1.354$ g cm⁻³; $F(000) = 840$. A yellow prismatic crystal of dimensions 0.12 × 0.22 × 0.24 mm (grown from aqueous methanol-acetonitrile by slow evaporation), was measured at 294(2) K on a Rigaku AFC5S diffractometer using monochromatized $MoK\alpha$ radiation ($\lambda = 0.71069$ Å). The cell parameters were determined from 25 reflections in the 15.3–17.1° θ range. The intensities of reflections were measured by the $\omega - 2\theta$ scan ($h = 0-16$; $k = -16-16$; $l = -16-16$); $\sin \theta/\lambda_{max} = 0.595$ Å⁻¹. Totally 7 405 reflections were measured giving 7 072 unique reflections ($R_{int} = 0.018$) and of those 4 929 were considered as observed according to the $I \geq 2\sigma(I)$ criterion. The data were corrected for Lorentz and polarization effects. An absorption correction based on 3 ψ scans ($T = 0.942-1.000$) was also applied. Three standard reflections monitored after each 150 reflections did not show any significant variation. The data reduction was done using TEXSAN (ref.²⁵). The structure was solved by heavy atom methods²⁶ and refined on F by XTAL3.2 (ref.²⁷). The asymmetric unit contains two molecules and in both

molecules the pyrrolyl ligands are disordered. The non-hydrogen atoms were refined with anisotropic displacement parameters except the pyrrolyl atoms, which were refined with isotropic displacement parameters. Partially occupied hydrogen atoms of the pyrrolyl ligand were not included in refinements. The rest of the hydrogen atoms were placed into calculated positions with $C-H = 0.95$ and $B-H = 1.10$ Å, and $U(H)$ equal to $1.2 \times U$ of the host atom. Refinement of this atomic arrangement resulted in the final R value 0.053 ($wR = 0.053$ and $S = 1.593$, unit weights) for 516 variables and 4 929 observed reflections. The minimum and maximum residual densities were -0.4 and 0.6 e Å⁻³. Tables of observed and calculated structure factors, hydrogen atom coordinates and anisotropic thermal displacement parameters, as well as the standard CIF file produced by XTAL3.2, can be obtained on request from the authors*.

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* Complete listings of experimental details of X-ray structure determinations, coordinates, interatomic distances and angles, displacement parameters for [3-(η^5 -NC₄H₄)-1,11-(C₆H₅)₂-closo-3,1,11-CoC₂B₉H₉] (11 pages) are included in the Supplementary Information which can be received from the Authors.

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