Frozen-Out Rotamers of Mixed Cobaltacarborane Complexes

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Although the existence of frozen-out rotamers in solution had been shown for mixed cobaltacarborane complexes forming adducts with BF_3 at low temperature. The existence of either one or more frozen-out conformations of these complexes in solution at room temperature, or otherwise the presence of free rotation of the pyrrolyl unit showing an average behavior, is still obscure. The reaction of 1,2-$C_2B_{10}H_{12}$ and 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ with a suspension of K[$NC_4(CH_3)_2H_2$] in THF and anhydrous $CoCl_2$ in 1:12:5 ratio yielded, respectively, *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$C_2B_9H_{11}$] (**2**) and *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**3**). ^{1}H NMR studies performed on **2**, **3**, and other mixed complexes incorporating one pyrrolyl and one dicarbollide unit (*closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-1,2-$C_2B_9H_{10}$] (**4**), *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] (**1**), *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**5**), and *closo*-[3-Co(η^5-NC_4H_4)-1-CH_3-1,2-$C_2B_9H_{10}$] (**6**)) showed the presence of resonances with atypical chemical shifts that suggested the existence of stable frozen-out conformations. This abnormal displacement of ^{1}H NMR resonances was assigned to electronic ring effects due to the presence of the phenyl unit; this electronic ring effect of the electrons of the phenyl ring on neighboring hydrogen atoms has been seen in mixed complexes for the very first time. ZINDO semiempirical calculations have been used to calculate the theoretical energy profile of the different rotamers. The obtained profiles furnish an explanation for experimental results with good qualitative concordance in all cases.

Introduction

Since the first mixed cobalt complex incorporating one pyrrolyl and one dicarbollide unit, [3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] (**1**), was described by our research group,[1] some other complexes with substituting groups on one or both cluster carbon atoms[2] (C_c) or on the α position of the nitrogen atom of the pyrrolyl unit have been described.[3] All these structures have been shown to be very similar in all the complexes, with the metal atom sandwiched by the pentagonal open faces of the pyrrolyl ion and the dicarbollide unit. The two pentagonal cycles adopt, at least in the solid state, a staggered conformation usually with the nitrogen atom placed between both C_c atoms.

Although X-ray data have shown this preferential orientation in the solid state, the behavior of these complexes in solution is still obscure. ^{13}C{^{1}H} and ^{1}H NMR experiments performed at room temperature exhibit patterns that can be explained either by the existence of a "frozen-out" rotamer or by a rapid exchange between two or more stable rotamers which would offer averaged spectra.

In recent work,[4] the existence of two stable "frozen-out" rotamers in solution at low temperature was demonstrated for [3-Co(η^5-$C_4H_4N{\rightarrow}BF_3$)-1,2-$(CH_2)_3$-1,2-$C_2B_9H_9$] and [3-Co(η^5-$C_4H_4N{\rightarrow}BF_3$)-1,2-$(CH_3)_2$-1,2-$C_2B_9H_9$]. One of the stable "frozen-out" rotamers corresponded to the nitrogen atom placed between both C_c atoms, and the second rotamer had the nitrogen atom rotated 180° from this position. Other compounds subjected to the same dynamic study such as **1**, [3-Co(η^5-NC_4H_4)-1,2-$(CH_2)_3$-1,2-$C_2B_9H_9$], [3-Co(η^5-NC_4H_4)-1,2-$(CH_3)_2$-1,2-$C_2B_9H_9$], and [3-Co(η^5-$C_4H_4N{\rightarrow}BF_3$)-1,2-$C_2B_9H_{11}$] have been shown to be based on only one stable rotamer in solution in the working temperature range (190−300 K). In all cases, ZINDO/1 was proved to be a reliable computational method to predict rotational energy barriers for mixed sandwich complexes, even to estimate the relative population between different stable rotamers.

Similar studies with the aim of elucidating the behavior of sandwich-type complexes both in solution

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Table 1. ^1H NMR Relevant Positions for Compounds 1−7

compound	C_c−H[a]	CH═C	HC−N	CH_3−C−N
[3-Co(η^5-N(CH_3)$_2$$C_4H_2$)-1-$CH_3$-1,2-$C_2B_9H_{10}$] (**4**)	3.86 (1H)	5.83/5.97		2.40 (6H)
[3-Co(η^5-N(CH_3)$_2$$C_4H_2$)-1,2-$C_2B_9H_{11}$] (**2**)	3.91 (2H)	5.96 (2H)		2.33 (6H)
[3-Co(η^5-N(CH_3)$_2$$C_4H_2$)-1-$C_6H_5$-1,2-$C_2B_9H_{10}$] (**3**)	4.58 (1H)	5.82/5.79		2.37 (3H) 1.38 (3H)
[3-Co(η^5-NC_4H_4)-1-CH_3-1,2-$C_2B_9H_{10}$] (**6**)	4.61 (1H)	6.21/6.39	6.64/6.78	
[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] (**1**)	4.36 (2H)	6.37 (2H)	6.72 (2H)	
[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**5**)	5.20 (1H)	6.16/6.23	5.31/6.73	
[3-Co(η^5-NC_4H_4)-1-C_6H_5-2-C_3H_5-1,2-$C_2B_9H_{10}$] (**7**)[b]		6.41/6.48	6.54/6.78	

[a] C_c corresponds to the cluster carbon atoms; all others correspond to pyrrolyl group. [b] In $(CD_3)_2CO$.

and in the solid state have been carried out by others. Kuhn et al.[5] and Wayne et al.[6] calculated the energy rotation barrier in different *tert*-butyl tetrasubstituted metallocenes, obtaining frozen-out conformations at relatively high temperatures. Otherwise, studies performed on unsubstituted, monosubstituted, and 1,1′-disubstituted metallocenes showed too low energy rotation barriers to hinder free ring rotation at room temperature.[7]

In the present work, two new mixed cobalt sandwich complexes incorporating one dimethylpyrrolyl and one dicarbollide unit ([3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$C_2B_9H_{11}$] (**2**) and [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**3**)) have been synthesized. As will be shown, intramolecular interactions between different substituting groups on the C_c atoms and the α positions of the pyrrolyl allow the existence of only one rotamer in solution (compound **3**). Reinvestigation of some compounds described before ([3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-1,2-$C_2B_9H_{10}$] (**4**), [3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**5**), [3-Co(η^5-NC_4H_4)-1-CH_3-1,2-$C_2B_9H_{10}$] (**6**), and [3-Co(η^5-NC_4H_4)-1-C_6H_5-2-C_3H_5-1,2-$C_2B_9H_9$] (**7**)) and the availability of crystallographic data for compounds **1**−**7** allowed us to perform a complete structural study and obtain comparative results. These experimental results were supported by theoretical calculations performed by the ZINDO/1 method. It will also be shown the extraordinary rigidity of these rotamers. Even though there are no physical bonds besides those of the backbone between the different parts of the molecule, the resulting molecule is static even in solution, bringing a new concept of preorganization, as this is usually related to rigidity associated with bonds that prevent any movement.

Results and Discussion

Behavior in Solution. When ^1H NMR experiments were done on the parent compound **1**,[1] only two resonances with a 2:2 pattern were found in the pyrrolyl region; therefore the complex displayed a C_s symmetry. The same information was obtained when performing $^{13}C\{^1H\}$ NMR spectroscopy, and two resonances were found in the pyrrolyl region. X-ray single-crystal analysis of this complex showed the nitrogen atom being staggered between both C_c atoms with a slight displacement assigned to solid state interactions. After that early work, some other compounds such as **4**−**7** were synthesized.[2,3] As a consequence of the introduction of one substituting group on one C_c atom, C_s symmetry was lost and thus four resonances were found in the pyrrolyl region on both the ^1H and $^{13}C\{^1H\}$ NMR spectra (compounds **5** and **6**), and two and four signals, respectively, in the ^1H and $^{13}C\{^1H\}$ NMR spectra of compound **4**. To have a sufficiently large and varied basis of compounds to elucidate the effect of the substituting groups on the behavior of these complexes in solution, compounds **2** and **3** were synthesized. The reaction of the corresponding substituted *o*-carboranes, to say, 1,2-$C_2B_{10}H_{12}$ and 1-C_6H_5-1,2-$C_2B_{10}H_{11}$, with anhydrous $CoCl_2$ and K[$NC_4(CH_3)_2H_2$] in THF in 1:5:12 ratio yielded complexes **2** and **3**, which were isolated and characterized.

Compound **2** showed a symmetric ^1H NMR pattern with one resonance in the pyrrolyl region (5.96 ppm), one in the C_c-H region (3.91 ppm), and one in the methyl region (2.33 ppm). The $^{13}C\{^1H\}$ NMR spectrum of compound **2** was consistent with the former data and presented four signals at 124.20 and 89.66 ppm (pyrrolyl unit), 55.11 ppm (C_c atoms), and 14.63 ppm (methyl units).

Compound **3** exhibited a nonsymmetric pattern in the ^1H NMR spectrum due to the presence of the phenyl group on one of the C_c atoms. Two signals were found in the pyrrolyl region (5.82 and 5.79 ppm) and two others in the methyl region (2.37 and 1.38 ppm). The $^{13}C\{^1H\}$ NMR spectrum presented four resonances in the pyrrolyl region (126.09, 125.71, 89.00, and 87.62 ppm) and two in the methyl region (14.91 and 12.72 ppm).

Although $^{13}C\{^1H\}$ and ^1H NMR spectra obtained for compounds **2** and **3** would be explained either by the presence of a "frozen-out" conformation or by the existence of free rotation of the dimethylpyrrolyl unit, the clue was not found in the spectral patterns but in the position of the resonances, especially those corresponding to ^1H NMR spectroscopy. The most important chemical shifts corresponding to compounds **1**−**6** are summarized in Table 1. Focusing first on mixed complexes with a dimethylpyrrolyl unit, as is the case for **2** and **4**, the $^1H\{^{11}B\}$ NMR resonances associated with hydrogen atoms of the cluster carbon atoms and methyl units of the pyrrolyl appear, respectively, at 3.91 and 5.96 (compound **2**) and 3.86 and 5.83/5.97 (compound **4**). For compound **3**, which contains a phenyl group, the chemical shift associated with the C_c hydrogen atom appears at 4.58 ppm, that is +0.6 ppm displaced to low field with regard to the values obtained for **2** and **4**. On the other hand, two different signals appear in the methyl region, one of them very close to the values obtained for **2** and **4** (2.37 ppm) but the other largely displaced to high field ($\delta = 1.38$ ppm, $\Delta\delta \approx -1$ ppm). Therefore, an interaction between the phenyl group and the C_c hydrogen atom is likely and also between the phenyl group and the hydrogen atoms of one of the methyl groups of the pyrrolyl unit. This interaction can

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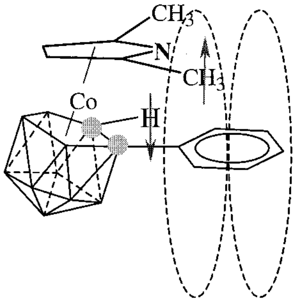

Figure 1. Electronic ring effect on CH_3 and C_c hydrogen atoms in compound **3**.

be explained with electron ring current effects. As it is well known,[8] a hydrogen atom placed on top of an aromatic ring will have a ^1H NMR chemical shift moved to high field, while it will be displaced to low field if it is placed in the plane of the ring but out of it. If electronic ring current effects can be assumed to be the cause of the observed ^1H NMR resonances' shift in **3**, this fact would imply that one of the methyl groups on the pyrrolyl unit should be on top of the phenyl ring, therefore in a zone of increased shielding resulting in a displacement to high field. The value of 1.38 ppm instead of 2.37 ppm supports this structural arrangement, which will affect the H-C_c chemical shift, too. Indeed, this is what is happening. This hydrogen will be practically in the plane of the phenyl unit (Figure 1) but out of the ring, therefore in an area of reduced shielding. Consequently, this H-C_c should be observed at lower field than that observed for other complexes with no fixed aromatic ring, e.g., complex **2**, where this H-C_c is found at 3.91 ppm.

Very similar conclusions concerning the rigidity of these mixed pyrrolyl/dicarbollide sandwich complexes can be obtained when compounds incorporating the plain pyrrolyl unit are analyzed. For **1** and **6** resonances at 4.36 and 4.61 ppm (C_c-H) and 6.72 and 6.64/6.78 (HC-N) are found, respectively. However, the resonance corresponding to the H-C_c atom is found at 5.20 ppm for compound **5**, and one of the resonances associated with the pyrrolyl unit appears at 5.31 ppm. Therefore, the presence of the phenyl unit causes a +0.8 ppm shift for the H-C_c hydrogen atom and −1.4 ppm for one of the HC-N hydrogens. Again, the phenyl ring is placed approximately as coplanar as possible with the pentagonal open face of the dicarbollide. The projection of one of the hydrogen atoms of the pyrrolyl unit is placed near the geometrical center of the ring, on top of it, leading to a displacement of its chemical shift to high field, while the C_c−H bond is approximately on the plane defined by the phenyl ring, but out of it, being subjected to a displacement to low field. The fact that only one of the hydrogen atoms of the pyrrolyl unit experiences a variation in its chemical shift proves the existence of one stable "frozen-out" conformation.

Calculation Results

All experimental data pointed to the existence of one stable rotamer in solution at room temperature, implying a preorganization of complexes **3** and **5**. To confirm these results, theoretical calculations were performed using the semiempirical ZINDO/1 computational method. Calculations were carried out for complexes **1**−**6**. From the starting position (nitrogen atom placed exactly between both C_c) rotations of 9° were performed. The first rotation was chosen to eclipse the nitrogen atom with the substituted atom in case it was present, and a single-point calculation was carried out at each point. Energetic profiles corresponding to compounds **2** and **3** are presented in Figure 2.

Compound **2** displays a symmetric profile with a very low rotational barrier. Although at room temperature fast rotation of the dymethylpyrrolyl unit should exist, the contribution of the rotamer with the nitrogen atom bisecting both C_c atoms should be absolutely dominant to the averaged ^1H and ^{13}C NMR spectra. A population analysis was carried out from the calculated curve for **2** (Figure 2). The study indicated that out of 1000 molecules only one has a rotation angle in the range $27° \leq \alpha \leq 333°$. Therefore the contribution of these rotamers to the averaged behavior observed in ^1H NMR spectra is negligible. These results confirm the hypothesis that there exists a "frozen-out" conformation in which the phenyl ring causes selective shifts of some ^1H NMR resonances.

For **3**, a clear energy maximum is distinguished in the profile, corresponding to the conformation whose dimethylpyrrolyl unit rotation angle is 99°. The more stable conformation corresponds to that where the nitrogen atom is displaced 9° from the symmetrical position. As for **2**, the relative amount of molecules with a rotation angle $27° \leq \alpha \leq 333°$ is very low, and a "frozen-out" conformation can be considered to exist.

Energetic profiles corresponding to compounds **1** and **4**−**6** are very close to those presented in Figure 2. All of them have in common only one stable conformation corresponding to the one with the nitrogen atom placed between both C_c atoms. As it was shown recently, compound **1** presents a symmetric profile;[2c] the energetic profile corresponding to compound **6** has two maxima for those conformations in which the methyl groups from the pyrrolyl and dicarbollide units are in an eclipsed conformation. Compounds **4** and **5** present almost symmetric profiles with maxima at 108° and 252°.

Solid State Behavior. As mentioned above, mixed sandwich cobalt complexes remain, in solution, in the most stable conformation, which corresponds to the one with the nitrogen atom between C_c atoms. The crystal data for compounds **1**,[1] **5**,[2c] **4**,[3] and **7**[2a] have already been published. In this paper, crystal structures corresponding to compounds **2**, **3**, and monoclinic and orthorhombic forms of **6** (labeled **6A** and **6B**) are presented (Figures 3, 4, 5, and 6, respectively). Crystallographic data corresponding to these compounds are summarized in Table 2, and selected bond lengths and angles are listed in Table 3. X-ray analyses confirmed that in all four structures the nitrogen atom locates between the cluster carbon atoms. The pyrrolyl ligand of **6B** has two different orientations in a 1:1 ratio (rotamers **6B1** and **6B2**) in solid state.

In the studied compounds there are variations in the Co ligand bond lengths (see Table 3), but no clear trend is found. The C1−C2 distance of 1.698(1) Å in **3** is longer

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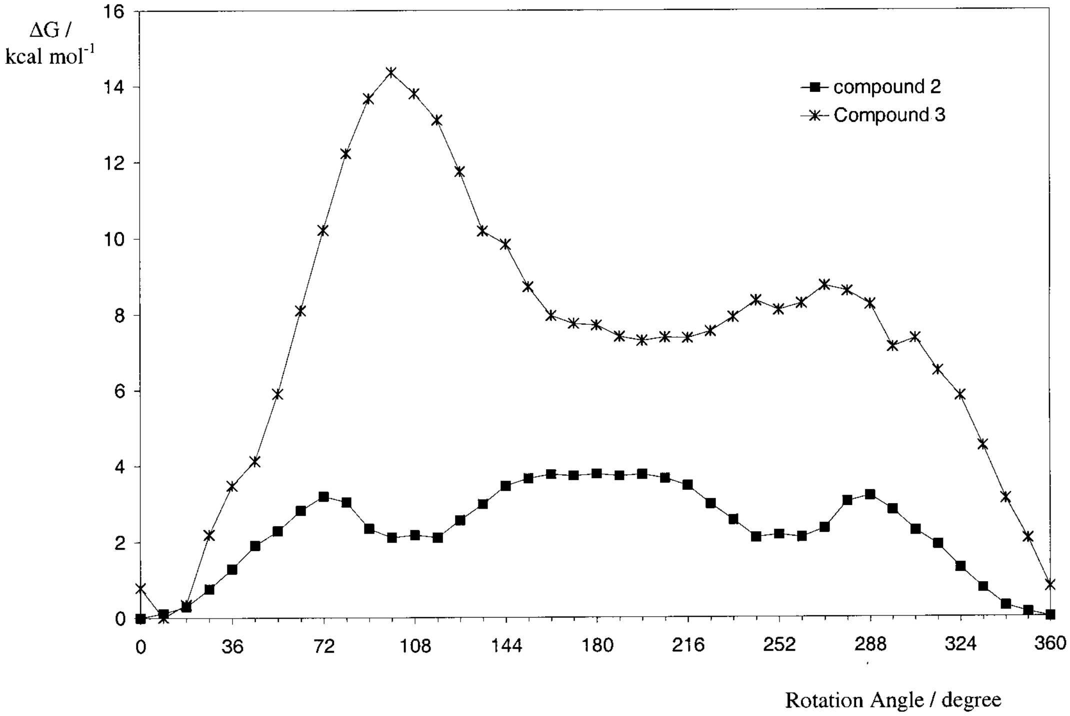


Figure 2. Calculated energy profile for **2** and **3**.

Table 2. Crystallographic Parameters for 2, 3, 6A, and 6B

	2	**3**	**6A**	**6B**
empirical formula	$C_8H_{19}B_9CoN$	$C_{14}H_{23}B_9CoN$	$C_7H_{17}B_9CoN$	$C_7H_{17}B_9CoN$
fw	285.46	361.55	271.44	271.44
cryst syst	orthorhombic	orthorhombic	monoclinic	orthorhombic
cryst habit, color	plate, yellow	plate, yellow	prism, brown	prism, brown red
space group	$Pca2_1$	$P2_12_12_1$	$P2_1/n$ (no. 14)	$P2_12_12_1$
a (Å)	11.053(2)	10.604(5)	8.022(2)	12.6346(10)
b (Å)	8.293(2)	19.212(4)	11.839(3)	13.7364(16)
c (Å)	15.861(3)	8.987(3)	14.6038(10)	7.8658(9)
β (deg)	90	90	92.385(12)	90
V (V^3)	1453.9(5)	1830.9(11)	1368.3(5)	1365.1(2)
Z	4	4	4	4
T (°C)	21	21	21	21
λ	0.71069	0.71069	0.71069	0.71069
ρ (g cm^{-3})	1.304	1.312	1.318	1.321
μ (cm^{-1})	11.54	9.32	12.22	12.25
goodness-of-fit[a] on F^2	1.080	1.021	1.005	1.037
R^b [$I > 2\sigma(I)$]	0.0355	0.0530	0.0576	0.0457
$R_w{}^c$ [$I > 2\sigma(I)$]	0.0849	0.1077	0.1352	0.0884
Flack parameter	−0.01(4)	0.07(5)		0.46(4)

[a] $S = [\sum w(F_o{}^2 - F_c{}^2)^2]/(n - p))^{1/2}$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o{}^2| - |F_c{}^2|)^2/\sum w|F_o{}^2|^2]^{1/2}$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2, 3, 6A, and 6B

	2	**3**	**6A**	**6B1**	**6B2**
C1−C2	1.633(10)	1.698(10)	1.601(10)	1.654(9)	*a*
C2−C20		1.501(10)	1.527(10)	1.538(9)	*a*
Co3−C1	2.004(6)	2.019(7)	2.004(6)	2.024(6)	*a*
Co3−C2	2.002(7)	2.048(8)	1.993(6)	2.003(6)	*a*
Co3−B8	2.093(7)	2.091(11)	2.074(7)	2.065(7)	*a*
Co3−N13	2.071(4)	2.068(6)	2.064(5)	2.079(15)	2.062(14)
Co3−C17	2.060(7)	2.091(7)	2.026(7)	2.018(11)	2.099(16)
C1−Co3−N13	106.7(2)	106.1(3)	106.3(3)	104.7(4)	108.9(4)
C2−Co3−N13	106.1(3)	108.5(3)	109.2(3)	104.6(5)	114.4(5)
C2−Co3−C17	109.1(2)	108.7(3)	110.0(3)	111.1(4)	96.1(6))

[a] Same as for **6B1**.

than the distance in the other structures. This is in line with the earlier observation that substituents at the cluster carbons increase the C1−C2 distance in *closo*-species, and a phenyl substituent increases the distance more than an alkyl substituent.[2c] Comparison of the structures of **2** and **3** reveals that owing to the phenyl substituent at the cluster carbon of **3**, the methyl group C19 is moved slightly away from the phenyl group, which is almost parallel with the C1, C2, B7, B8, B4 coordination plane. Due to steric effects the methyl carbon C19 deviates 0.155(13) Å from the mean plane of the pyrrolyl ring.

Structural information has also permitted the study of (i) the deviation from coplanarity of the pyrrolyl and C_2B_3 faces (Figure 7a) and (ii) the deviation from strictly staggered disposition with the nitrogen atom exactly between both C_c atoms (Figure 7b).

Values of 180 − θ (deviation from coplanarity of pentagonal faces) and α (deviation from strictly staggered conformation) are presented in Table 4 for complexes **1**−**7**. In all complexes the conformation is staggered, meaning that the nitrogen atom is placed between

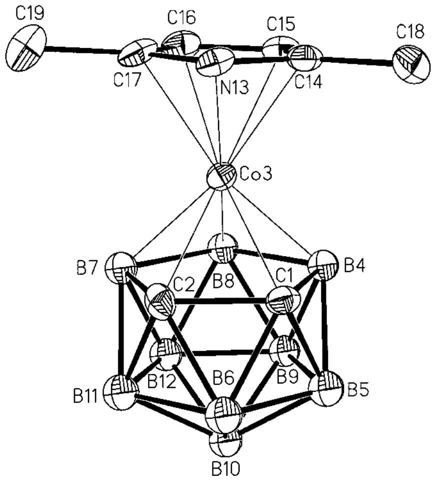


Figure 3. Molecular structure of *closo*-[3-Co(η^5-N(CH$_3$)$_2$-C$_4$H$_2$)-1,2-C$_2$B$_9$H$_{11}$] (**2**). Displacement ellipsoids are drawn at 20% probability level.

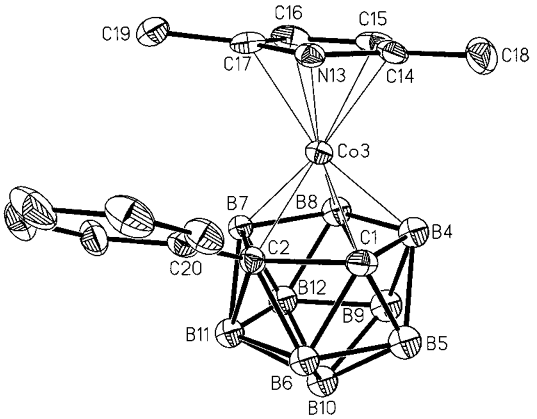


Figure 4. Molecular structure of *closo*-[3-Co(η^5-N(CH$_3$)$_2$-C$_4$H$_2$)-1-C$_6$H$_5$-1,2-C$_2$B$_9$H$_{10}$] (**3**). Displacement ellipsoids are drawn at 20% probability level.

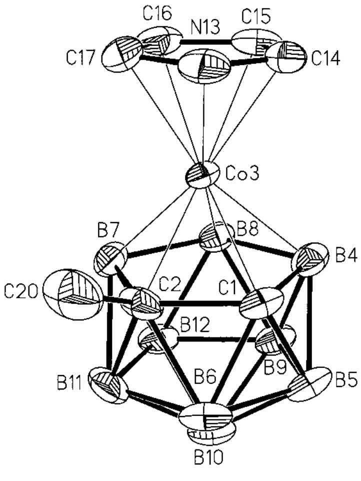


Figure 5. Molecular structure of monoclinic form of *closo*-[3-Co(η^5-NC$_4$H$_4$)-1-CH$_3$-1,2-C$_2$B$_9$H$_{10}$] (**6A**). Displacement ellipsoids are drawn at 20% probability level.

C$_c$ atoms; besides, the pyrrolyl plane and the open face of the dicarbollide unit are never coplanar, and the atom in the heterocycle most distant from the C$_2$B$_3$ plane is always the nitrogen.

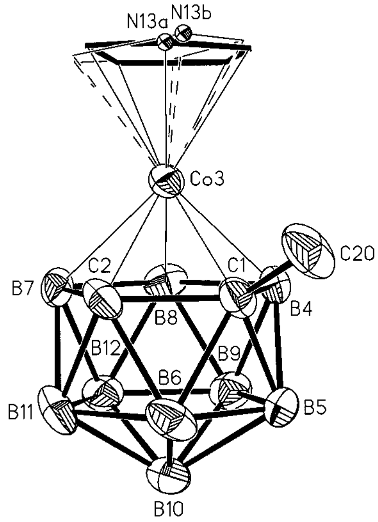


Figure 6. Simplified drawing of orthorhombic form of *closo*-[3-Co(η^5-NC$_4$H$_4$)-1-CH$_3$-1,2-C$_2$B$_9$H$_{10}$] (**6B**). Only skeletons of the two pyrrolyl positions are drawn (the rotamer **6B1** in thick black). Displacement ellipsoids of the ordered part of the molecule are drawn at 20% probability level.

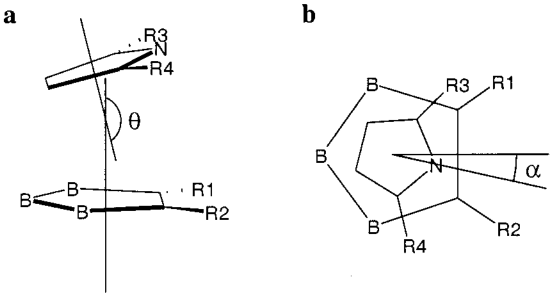


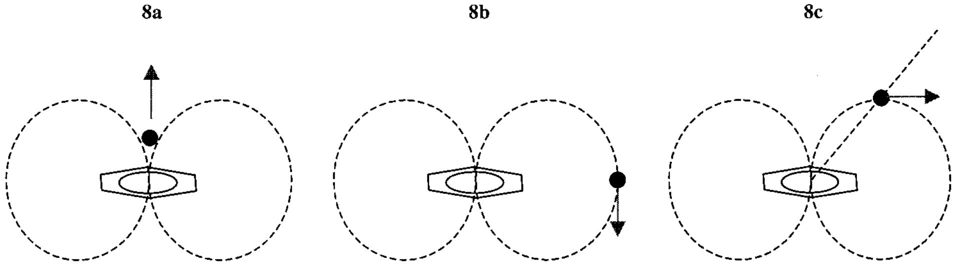
Figure 7. Deviation from coplanarity and from complete staggered configuration found in solid state structures.

Table 4. Deviation from Planarity of the Pyrrolyl and C$_2$B$_3$ Faces and Deviation from Strictly Staggered Disposition of the Three Different Complexes

compound	α	180 − *θ*
[3-Co(η^5-N(CH$_3$)$_2$C$_4$H$_2$)-1-C$_6$H$_5$-1,2-C$_2$B$_9$H$_{10}$] (**3**)	7.6	6.9
[3-Co(η^5-N(CH$_3$)$_2$C$_4$H$_2$)-1,2-C$_2$B$_9$H$_{11}$] (**2**)	5.2	3.7
[3-Co(η^5-N(CH$_3$)$_2$C$_4$H$_2$)-1-CH$_3$-1,2-C$_2$B$_9$H$_{10}$] (**4**)	1.0	6.3
[3-Co(η^5-NC$_4$H$_4$)-1-CH$_3$-1,2-C$_2$B$_9$H$_{10}$] (**6A**)	3.8	4.9
[3-Co(η^5-NC$_4$H$_4$)-1-CH$_3$-1,2-C$_2$B$_9$H$_{10}$] (**6B1**)	3.7	4.2
[3-Co(η^5-NC$_4$H$_4$)-1-CH$_3$-1,2-C$_2$B$_9$H$_{10}$] (**6B2**)	21.8	7.5
[3-Co(η^5-NC$_4$H$_4$)-1,2-C$_2$B$_9$H$_{11}$] (**1**)	3.8	3.4
[3-Co(η^5-NC$_4$H$_4$)-1-C$_6$H$_5$-1,2-C$_2$B$_9$H$_{10}$] (**5**)	7.5	4.5
[3-Co(η^5-NC$_4$H$_4$)-1-C$_6$H$_5$-2-C$_3$H$_5$-1,2-C$_2$B$_9$H$_9$] (**7**)	1.9	6.3

On the other hand, α is not 0° in any of the complexes **1**−**7**. In principle complexes **1** and **2** should present C_s symmetry, but probably due to packing forces in the solid state both compounds present a twisted structure and **2** forms chiral crystals.

A Case of Study. Non-Freezing-Out or Ring Current Effect Cancellation? As already discussed, mixed complexes incorporating a phenyl unit on one of the C$_c$ atoms have proved the existence of (i) frozen-out rotamers in solution and (ii) Ph/C-H interaction between the phenyl ring and substituting hydrogen atoms, either on C$_c$ atoms or on the pyrrolyl unit. A reinvestigation of a former mixed complex [3-Co(η^5-NC$_4$H$_4$)-1-C$_6$H$_5$-2-C$_3$H$_5$-1,2-C$_2$B$_9$H$_{10}$] (**7**) incorporating two bulky groups in the cluster carbon atoms revealed that no electronic ring effects were detected despite the presence of a phenyl ring. No major shift of the ^{1}H NMR signals associated with the cyclopropyl or pyrrolyl units were found in **7**.



Displacement of the resonance to high field

Displacement of the resonance to low field

Effect cancellation. No displacement of the resonance

Figure 8. Effect of ring orientation on ^{1}H NMR chemical shift.

ZINDO/1 calculations when performed on **7** indicated that practically there existed only one isomer which contained again the nitrogen between both C_c.

A careful investigation of crystallographic data corresponding to **7** provided the clue to the problem. The angle between the phenyl ring and the plane defined by the pyrrolyl ring or the pentagonal open face of the dicarbollide unit was almost 45°. In this way, positive and negative effects on the hydrogen atoms of the pyrrolyl and cyclopropyl units were canceled. This cancellation is shown schematically in Figure 8. If the hydrogen atom is placed on top of the ring, there is a maximum shift of the resonance to high field (Figure 8a). If the hydrogen atom is placed in the plane of the ring but out of it, there is a maximum shift of the resonance to low field (Figure 8b). If the line that joins the hydrogen atom of interest with the center of the ring and the plane of the ring form an angle of about 45°, both effects cancel (Figure 8c), as it happens in **7**. To our knowledge, this is the only clear case where both effects are canceled.

Conclusions

The presence of selective interaction between the phenyl ring and the neighboring hydrogen atoms has proven the existence of a frozen-out conformation for compounds *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**3**) and *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**5**). Theoretical calculations performed on **3**, **5**, *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-1,2-$C_2B_9H_{10}$] (**4**), *closo*-[3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] (**1**), *closo*-[3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$] (**5**), and *closo*-[3-Co(η^5-NC_4H_4)-1-CH_3-1,2-$C_2B_9H_{10}$] (**6**) have shown that all these mixed cobalt complexes have a frozen-out conformation in solution with the nitrogen atom between the two C_c atoms.

X-ray analyses performed on **1**−**3** and **5**,**6** have shown the existence of just one rotamer in the solid state, which corresponds to that with the nitrogen atom placed between C_c's, slightly displaced from the medium position due to solid state interactions.

The study of [3-Co(η^5-NC_4H_4)-1-C_6H_5-2-C_3H_5-1,2-$C_2B_9H_9$] (**7**) has shown that steric crowding avoids the adequate orientation of the phenyl ring and interaction with the α hydrogen atoms of the pyrrolyl unit is not observed, so positive and negative effects cancel each other and no net result is observed.

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. ^{1}H and ^{1}H{^{11}B} NMR (300.13 MHz), ^{13}C{^{1}H} NMR (75.47 MHz), and ^{11}B and ^{11}B{^{1}H} NMR (96.29 MHz) spectra were recorded in $CDCl_3$ with a Bruker ARX 300 instrument at room temperature. Chemical shift values for ^{1}H, ^{1}H{^{11}B}, and ^{13}C{^{1}H} NMR spectra were referenced to $Si(CH_3)_4$, and those for ^{11}B and ^{11}B{^{1}H} NMR spectra were referenced to $BF_3 \rightarrow O(C_2H_5)_2$. Chemical shifts are reported in units of part per million downfield from Me_4Si and coupling constants in hertz.

Materials. Experiments were carried out under dry, oxygen-free dinitrogen atmosphere, using standard Slenck techniques, with some subsequent manipulation in the open laboratory. THF was freshly distilled from sodium benzophenone. The rest of the solvents were of reagent grade quality and were used without further purification. 2,5-Dimethylpyrrole (Aldrich) was freshly distilled prior to use. Hexahydrated cobalt(II) chloride (Aldrich) was heated under vacuum overnight to obtain the anhydrous form. Potasium was refluxed in THF prior to use. 1-C_6H_5-1,2-$C_2B_{10}H_{11}$, 1-CH_3-1,2-$C_2B_{10}H_{11}$, and 1,2-$C_2B_{10}H_{12}$ (Katchem) were used as received. [3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$)] (**1**),[1] [3-Co(η^5-NC_4H_4)-1-CH_3-1,2-$C_2B_9H_9$] (**6**),[2a] [3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$)] (**5**),[2c] and [3-Co(η^5-$N(CH_3)_2C_4H_2$)-1-CH_3-1,2-$C_2B_9H_{10}$)] (**4**)[3] were prepared according to literature methods.

Synthesis of [3-Co(η^5-$N(CH_3)_2C_4H_2$)-1,2-$C_2B_9H_{10}$)] (2). To a suspension of refluxing K[$NC_4(CH_3)_2H_2$] (1.0 g, 7.5 mmol) in 50 mL of THF was added 1,2-$C_2B_{10}H_{12}$ (0.091 g, 0.63 mmol). After 4 h of refluxing, anhydrous $CoCl_2$ (0.41 g, 3.13 mmol) was added. The reaction mixture was refluxed for 48 h. After cooling, the solvent was vacuum-dried, and the resultant green-black solid was extracted with 50 mL of dichloromethane. The suspension was filtered over molecular sieves, and the resulting dark liquid was evaporated to 1 mL and chromatographed over silica gel using 6:4 dichloromethane/hexane as mobile phase (R_f(prep) = 0.4). A pure orange solid, stable to air, was obtained. Yield: 0.110 g, 58%. IR (KBr): ν [cm^{-1}] 3082 (ν C_c-H), 3039 (ν C−H), 2601, 2570, 2532 (ν B−H), 1454 (δ, C−H). ^{1}H NMR: δ 5.96 (s, C_{pyr}-C_{pyr}-H, 2H), 3.91 (s, C_c-H, 2H), 2.33 (s, −CH_3, 6H). ^{1}H{^{11}B} NMR: δ 5.96 (s, C_{pyr}-C_{pyr}-H, 2H), 3.91 (s, C_c-H, 2H), 3.17 (br s, B-H, 1H), 2.94 (br s, B-H, 3H), 2.33 (s, −CH_3, 6H), 1.95 (br s, B-H, 2H), 1.75 (br s, B-H, 3H). ^{13}C{^{1}H} NMR: δ 124.20 (s, N-C_{pyr}), 89.66 (s, C_{pyr}-C_{pyr}), 55.11 (s, C_c), 14.63 (s, −CH_3). ^{11}B NMR: δ 7.46 (d, ^{1}J(B,H) = 145, 1B), 3.57 (d, ^{1}J(B,H) = 146, 1B), −3.49 (d, ^{1}J(B,H) = 148, 4B), −15.30 (d, ^{1}J(B,H) = 161, 2B), −20.98 (d, ^{1}J(B,H) = 169, 1B). Anal. Calcd for $C_8B_9H_{19}CoN$: C, 33.66; H, 6.71; N, 4.91. Found: C, 33.69; H, 6.85; N, 4.99.

Synthesis of [3-Co(η^5-$N(CH_3)_2C_4H_2$)-1-C_6H_5-1,2-$C_2B_9H_{10}$)] (3). The process was the same of that used for **2** but using 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ (0.14 g, 0.63 mmol) as starting product. In this case, 7:3 methylene chloride/hexane was used as mobile phase, obtaining a pure orange product (R_f(prep) = 0.4). Yield: 0.160 g, 69%. IR (KBr): ν [cm^{-1}] = 3101 (ν C_c−H), 3055 (ν C−H), 2617, 2570, 2540 (ν B−H), 1452 (δ, C−H). ^{1}H NMR: δ 7.40−7.20 (m, C_{ar}, 5H), 5.82 (s, C_{pyr}-C_{pyr}-H, 1H), 5.79 (s, C_{pyr}-

C_{pyr}-H, 1H), 4.58 (s, C_c-H, 1H), 2.37 (s, $-CH_3$, 3H), 1.38 (s, $-CH_3$, 3H). $^1H\{^{11}B\}$ NMR: δ 7.40−7.20 (m, C_{ar}, 5H), 5.82 (s, C_{pyr}-C_{pyr}-H, 1H), 5.79 (s, C_{pyr}-C_{pyr}-H, 1H), 4.58 (s, C_c-H, 1H), 3.38 (br s, B-H, 1H), 3.16 (br s, B-H, 2H), 2.37 (s, $-CH_3$, 3H), 2.02 (br s, B-H, 2H), 1.97 (br s, B-H, 2H), 1.83 (br s, B-H, 2H), 1.38 (s, $-CH_3$, 3H). $^{13}C\{^1H\}$ NMR: δ 141.98−126.43 (C_{ar}), 126.09 (s, N-C_{pyr}), 125.71 (s, N-C_{pyr}), 89.00 (s, C_{pyr}-C_{pyr}), 87.62 (s, C_{pyr}-C_{pyr}), 53.36 (s, C_c-H), 14.91 (s, $-CH_3$), 12.72 (s, $-CH_3$). ^{11}B NMR: δ 7.18 (d, $^1J(B,H) = 147$, 1B), 4.59 (d, $^1J(B,H) = 150$, 1B), −2.61 (1B), −4.31 (3B), −11.45 (d, $^1J(B,H) = 164$, 1B), −14.95 (1B), −16.52 (1B). Anal. Calcd for $C_{14}B_9H_{23}CoN$: C, 46.506; H, 6.411; N, 3.874. Found: C, 46.40; H, 6.48; N, 3.93.

Computational Details

All calculations were performed using the Hyperchem 5.0 package (Version 5.0, Hypercube Inc.) installed on a PC-Pentium III 700 MHz computer. Internal coordinates obtained from X-ray diffraction analysis for complexes **1**−**7** were used as starting ones, performing the following geometrical operations before calculations: (i) the pyrrolyl plane and the pentagonal open face of the cluster were forced to be parallel and (ii) the nitrogen atom was placed exactly in the middle of the C_c atoms.

From starting position, rotations of 9° were performed (from 9° to 180° for compounds **1** and **2** and from 9° to 360° for **3**−**7**. At each point, a single-point calculation was performed using the ZINDO/1 semiempirical method. Previously to ZINDO calculations, the cluster carbons and the exo-cluster substituents were allowed to relax by means of molecular mechanics geometry optimization. All energy values correspond to free enthalpy referred to the lowest energetic rotamer.

X-ray Diffraction Studies. X-ray Structure Determinations of 2, 3, 6A, and 6B. Compound **6** crystallizes in two different crystal systems, monoclinic (**6A**) and orthorhombic (**6B**). Single-crystal data collections were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite-monochromatized Mo Kα radiation. A total of 1330, 1857, 2411, and 2401 unique reflections were collected by $\omega/2\theta$ scan mode ($2\theta_{max} = 50°$) for **2**, **3**, **6A**, and **6B**, respectively. Crystallographic data are presented in Table 2.

The structures were solved by direct methods and refined on F^2 by the SHELX-97 program.[9] The pyrrolyl ligand of **6B** is disordered assuming two orientations (rotamers **6B1** and **6B2)** with site occupation parameters 0.543(17) and 0.457(17). The identification of an actual rotamer is not easy, and the rotamers presented here are those that are according to calculations the most probable ones. Boron atoms of **2** and **3** and non-hydrogen atoms of the disordered pyrrolyl ligand of **6B** were refined with isotropic displacement parameters. The rest of the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms for all the structures were placed at calculated positions and treated as riding atoms. **2**, **3**, and **6B** crystallize in non-centrosymmetric space groups. Absolute configurations of **2**, **3**, and **6B** were determined by refinement of Flack's x parameter. For **6B** the configuration could not be very reliably determined, as absolute structure parameters for the two different configurations are 0.46(4) and 0.55(4).

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal displacement parameters, and bond distances and angles for *closo*-[3-Co(η^5-N(CH$_3$)$_2$C$_4$H$_2$)-1,2-C$_2$B$_9$H$_{10}$)] (**2**), [3-Co(η^5-N(CH$_3$)$_2$C$_4$H$_2$)-1-C$_6$H$_5$-1,2-C$_2$B$_9$H$_{10}$)] (**3**), and monoclinic and orthorhombic forms of [3-Co(η^5-NC$_4$H$_4$)-1-CH$_3$-1,2-C$_2$B$_9$H$_{11}$] (**6A** and **6B**). This material is available free of charge via the Internet at http://pubs.acs.org.

OM010711L

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[9] Sheldrick, G. M. *SHELX-97*; University of Göttingen: Germany, 1997.