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Redox Potential Modulation in Mixed Sandwich Pyrrolyl/Dicarbollide Complexes

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Carbon cluster (C_c) substituents have been shown to be of essential importance in $C_c\cdots C_c$ distance, rotational energy barriers, and $^{11}B\{^1H\}$ NMR chemical shift values in mixed pyrrolyl/dicarbollide cobalt complexes. In the present work, the influence of electronic properties of *exo*-cluster substituents upon redox potential values associated to the metallic central atom in mixed pyrrolyl/dicarbollide and dimethylpyrrolyl/dicarbollide cobalt complexes is discussed. With that purpose, two new neutral sandwich species, *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(C_6H_5)_2$-1,2-$C_2B_9H_9$] (**2**) and *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-2-SCH_3-1,2-$C_2B_9H_9$] (**3**), have been synthesized and characterized by ^1H, ^{11}B, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR and IR spectroscopies, elemental analysis, and X-ray diffraction analysis. The redox potential ($E_{1/2}$) of these complexes has been measured in nonpolar media and compared to values obtained for previously reported mixed complexes, incorporating alkyl, phenyl, thiophenyl, and thiomethyl *exo*-cluster substituents. The potential shift arising from the effect of these substituents has been discussed in terms of individual and average contribution. This last point is in the case of two identical substituting groups placed on both C_c atoms, in which the contribution of the second introduced substituent has shown to be lower than that for the first one. The potential shift arising from the presence of methyl units on the pyrrolyl anion has also been determined.

Introduction

Ferrocene-like sandwich complexes containing exclusively dicarbollide moiety $[C_2B_9H_{11}]^{2-}$ ligands or their derivatives have been known since the discovery by Hawthorne and coworkers of $[Fe(C_2B_9H_{11})_2]^-$.[1] Examples with first row transition metals such as Fe(II),[2] Co(III),[2,3] Ni(III),[2,4] Ni(IV),[2,5] Cu(II),[6] Cu(III),[6] and Cr(III)[7] have been reported. Only the d^6 cations obey the 18 electron rule, the Fe(II), Co(III), and Ni(IV) should be the more stable, and of these, the Co(III) is reported to be the more robust.[8] Neutral mixed sandwich complexes incorporating the well-known Cp^- and $[C_2B_9H_{11}]^{2-}$ were reported also a long time ago, and examples with Fe(III),[2] Co(III),[2,3] and Ni(III)[9] are described. However, the syntheses leading to these compounds do not

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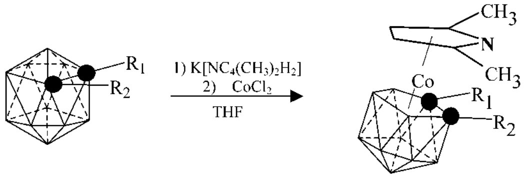
produce high yields. In 1996, the first mixed complex incorporating one pyrrolyl and one dicarbollide units, [3-Co-(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] (**1**), was reported by our research group.[10] Since then, several derivatives with substituting groups either on the α positions of the pyrrolyl unit[11] and/or on the cluster carbon atoms (C_c)[12] have been reported along with more efficient methods of syntheses. It has been proven that the $C_c \cdots C_c$ distance,[11b] the rotation energy barriers,[12d] and the ^{11}B NMR chemical shifts[11c] are dependent on the nature of the substituting groups.

With the aim of discovering the influence of substituents on the half wave potential ($E_{1/2}$) associated with the redox Co(III)/Co(II) processes, we carried out an exhaustive study on several substituted cobaltabisdicarbollide complexes.[13] It was found there that the presence of aromatic groups and sulfur atoms directly bonded to the carborane cages produces a displacement of $E_{1/2}$ to more positive values. Therefore, a way to modulate the $E_{1/2}$ was possible in highly stable compounds. The $E_{1/2}$ value for the couple Co(III)/Co(II) was, however, found at very reducing potentials; for example, [Co-$(C_2B_9H_{11})_2]^-$/[Co$(C_2B_9H_{11})_2]^{2-}$ was found at −1.028 V versus Ag/AgCl/[N$(C_4H_9)_4$]Cl (acetonitrile) 0.1 M. The reason for this highly negative potential was the negative nature of the Co(III) species and the capacity of $[C_2B_9H_{11}]^{2-}$ to stabilize high oxidation states.

Mixed sandwich complexes with one dicarbollide and one mononegative π ligand would, expectedly, shift the $E_{1/2}$ to more positive potential values. In the aim to disclose if additive contributions by substituting groups are applicable in neutral mixed sandwich complexes, we have undertaken this work on the readily available, one pot synthesis, pyrrolyl/dicarbollide cobalt complexes.

For purposes of comparison, and considering the peculiar cage influence of phenyl derivatives,[14] two new mixed sandwich complexes incorporating one dimethylpyrrolyl unit and one dicarbollide unit, [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(C_6H_5)_2$-1,2-$C_2B_9H_9$] (**2**) and [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-2-SCH_3-1,2-$C_2B_9H_9$] (**3**), have been synthesized. These two compounds, whose molecular structures have been determined by X-ray diffraction analysis, have been characterized electrochemically in noncoordinating solvents. With the aim of performing an exhaustive study and obtaining trustworthy data of the individual contribution of each substituting group, different already known compounds have also been studied: [3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$][11b] (**4**), [3-Co(η^5-NC_4H_4)-1-CH_3-1,2-$C_2B_9H_{10}$][12a] (**5**), [3-Co(η^5-NC_4H_4)-1,2-$(CH_3)_2$-1,2-$C_2B_9H_9$][12d] (**6**), [3-Co(η^5-NC_4H_4)-1,2-$(CH_2)_3$-1,2-$C_2B_9H_9$][12d] (**7**), [3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$][11b] (**8**), and [3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$][11b] (**9**). For the purpose of studying the influence of alkyl groups on the α positions of the pyrrolyl unit, the following compounds have also been synthesized following reported methods: [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$C_2B_9H_{11}$][12c] (**10**), [3-Co-(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-1,2-$C_2B_9H_{10}$][12d] (**11**), [3-Co(η^5-N-$C_4(CH_3)_2H_2$)-1,2-$(CH_3)_2$-1,2-$C_2B_9H_9$][11d] (**12**), [3-Co(η^5-NC_4-$(CH_3)_2H_2$)-1-C_6H_5-1,2-$C_2B_9H_{10}$][12c] (**13**), [3-Co(η^5-$NC_4(CH_3)_2$-H_2)-1,2-$(CH_2)_3$-1,2-$C_2B_9H_9$][11c] (**14**), [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$][11c] (**15**), and [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$][11c] (**16**).

Scheme 1. Synthesis of [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-r_1-2-R_2-1,2-$C_2B_9H_9$]



Results and Discussion

Synthesis of Complexes 2 and 3. The synthesis of **2** and **3** (Scheme 1) was carried out following the general one-pot method described before.[10] The pyrrolyl derivative potassium salt is used both as a nucleophile and as a base; thus, K[NC_4-$(CH_3)_2H_2$] was added to THF solutions of 1,2-$(C_6H_5)_2$-1,2-$C_2B_{10}H_{10}$ and 1-CH_3-2-SCH_3-1,2-$C_2B_{10}H_{10}$, respectively. After 4 h at reflux, anhydrous $CoCl_2$ was added, and the reactions were refluxed for 48 h more. After purification using chromatographic methods, compounds **2** and **3** were obtained.

The ^{11}B, ^1H, $^{13}C\{^1H\}$ NMR spectra of **2** showed the absence of symmetry in the molecule. This is the first example of generated asymmetry in solution found in this class of mixed sandwich complexes where, expectedly, C_s symmetry should have been found.

X-ray Diffraction Studies. Description of the Structures. From saturated solutions of **2** and **3** in dichloromethane/hexane (1:1) mixtures, good crystals were grown for X-ray diffraction analysis. Molecular structures of **2** and **3** are presented in Figures 1 and 2, and crystallographic data are summarized in Table 1. Selected bond distances are presented in Table 2. The N atom of the pyrrolyl ligand in **3** is bisecting the C1 and C2 atoms of the dicarbollide. This kind of N orientation is preferred for pyrrolyl/cobalt(III)/dicarbollide complexes. Supporting the NMR solution data, these data indicate that the nitrogen in **2** is oriented between C1 and B4 atoms. Crystallographically, this is not the first example, as in some compounds with bulky substituents at the cluster carbons, [3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-

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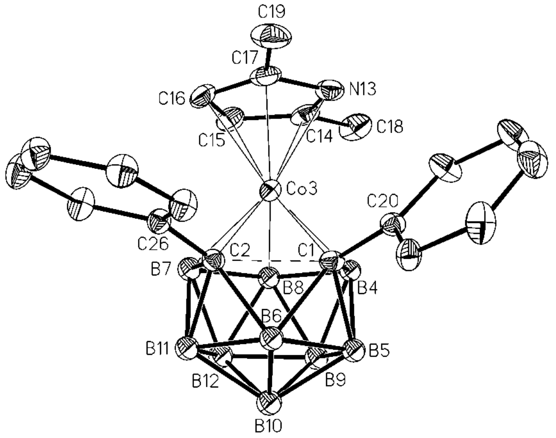

Figure 1. ORTEP drawing of *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(C_6H_5)_2$-1,2-$C_2B_9H_9$] **(2)**.

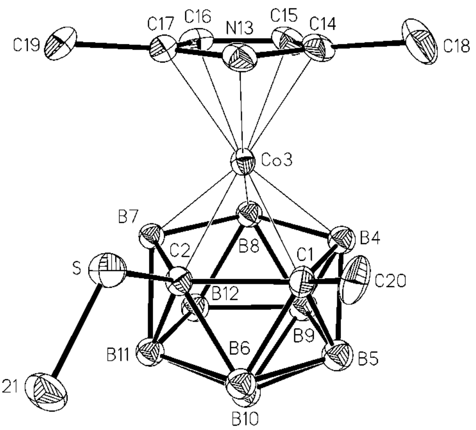

Figure 2. ORTEP drawing of *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-2-SCH_3-1,2-$C_2B_9H_9$] (**3**).

Table 1. Crystallographic Data and Structural Refinement Details for *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(C_6H_5)_2$-1,2-$C_2B_9H_9$] (**2**) and *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-2-SCH_3-1,2-$C_2B_9H_9$] (**3**)

empirical formula	$C_{20}H_{27}B_9CoN$	$C_{10}H_{23}B_9CoNS$
fw	437.65	345.57
cryst syst	monoclinic	orthorhombic
space group	*Cc*	$P2_12_12_1$
a (Å)	12.7326(11)	13.376(3)
b (Å)	11.891(2)	14.877(6)
c (Å)	15.0701(9)	8.5667(17)
β (deg)	103.170(5)	90
V (Å^3)	2221.6(5)	1704.7(9)
Z	4	4
T (°C)	21	21
λ (Å)	0.71069	0.71069
ρ (g cm^{-3})	1.309	1.346
μ (cm^{-1})	7.81	11.15
GOF	1.081	1.088
R1^a [$I > 2\sigma(I)$]	0.0357	0.0476
wR2^b [$I > 2\sigma(I)$]	0.0794	0.0991
Flack parameter *x*	-0.01(2)	0.48(3)

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

$C_2B_9H_9$][11b] and [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$],[11c] the nitrogen atom is oriented as for **2**. Had the N in **2** presented a similar orientation as in **3**, a significant repulsion between the S atoms and the methyl groups would have taken place. The angle α (deviation from strictly staggered conformation with the nitrogen atom bisecting the C1−C2 distance) for **3** is 2.3° while for **2** the angle α has got a value of 70.7° (N13 is turned 2.8° from the midpoint of C1−B4 bond toward C1, and the rotamer is a staggered one).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **2** and **3**

Co3−C1	2.051(5)	2.034(4)
Co3−C2	2.036(5)	2.032(4)
Co3−N13	2.097(5)	2.109(3)
C1−C2	2.022(7)	1.773(5)
C1−B4	1.694(8)	1.692(6)
C2−B7	1.689(8)	1.712(6)
C2−C1−B4	105.3(4)	110.1(3)
C1−C2−B7	105.4(4)	109.8(3)
C1−B4−B8	110.2(4)	106.6(3)
C2−B7−B8	110.0(4)	106.7(3)
C14−N13−C17	107.5(5)	105.0(3)

Table 3. Influence of Substituents on $E_{1/2}$ Values of [3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] Derivatives with Identical Substituents on Both C_c Atoms^a

cmpd	R	E_1/V	E_2/V	$E_{1/2}$/V	$\lvert\Delta E\rvert$/V
1	H−	−159.5	−356.5	−258.0	197.0
6	CH_3−	−240.0	−330.0	−285.0	90.0
7	−$(CH_2)_3$−	−258.0	−328.0	−293.0	70.0
8	−SCH_3	−83.0	−158.0	−120.5	75.0
9	−SC_6H_5	−53.0	−132.0	−92.5	79.0

^{a}E_1 and E_2 are forward and return potential values, $E_{1/2}$, the half wave potential (($E_1 + E_2$)/2), and ΔE, the potential shift between forward and return potentials ($E_2 - E_1$).

The C1−C2 distance of 2.022(7) Å in **2** is markedly longer than the distance of 1.919(6) Å in [3-Co(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$][2c] and the 1.864(5) Å distance found in [3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$].[2c] The existence of methyl units on the pyrrolyl perturb the disposition of the two phenyl rings, and these cannot relax to a vertical-parallel disposition.[15] Steric repulsion forces the carbon atoms to move apart. Substituents at pyrrolyl ring do not directly influence the C1−C2 distance. This is shown by the C1−C2 distances 1.864(5) and 1.864(7) Å found in [3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$][11b] and [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$],[11c] respectively.

Do the Substituents Significantly Influence the Redox Properties of These Mixed Cobalt Complexes? In the present work, a large number of structurally similar mixed complexes was studied with the aim to provide not only a qualitative but also a quantitative value of the influence of distinct substituting groups on $E_{1/2}$, half wave potential, calculated as the average value between oxidation and reduction wave potentials. The study was carried out by means of cyclic voltammetry in a standard double compartment-three electrode cell, using a 0.1 M solution of tetrabutylammonium hexafluorophosphate in chloroform as supporting electrolyte. A Ag/AgCl/[$N(C_4H_9)_4$]Cl 0.1 M (acetonitrile) electrode, a 4 mm diameter platinum plate, and a platinum wire were used as reference, working, and counter electrodes, respectively.

Influence of C_c Substituents on $E_{1/2}$ in Pyrrolyl/Dicarbollide Cobalt Complexes. Table 3 summarizes electrochemical data for compounds incorporating one pyrrolyl unit

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Table 4. Influence of Substituents on $E_{1/2}$ Values of [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$C_2B_9H_{11}$] Derivatives with Identical Substituents on C_c Atoms

cmpd	R	E_1/V	E_2/V	$E_{1/2}$/V	$\|\Delta E\|$/V
2	C_6H_5-	−318.0	−426.0	−372.0	108.0
10	H−	−351.0	−459.0	−405.0	108.0
12	CH_3-	−398.0	−506.0	−452.0	108.0
14	$-(CH_2)_3-$	−387.0	−486.0	−436.5	99.0
15	$-SC_6H_5$	−117.0	−226.0	−171.5	109.0
16	$-SCH_3$	−199.0	−281.0	−240.0	82.0

and one substituted dicarbollide unit, where R is the substituting group on both C_c atoms. Oxidation (E_1) and reduction (E_2) potentials, $E_{1/2}$, and ΔE (defined as $E_2 - E_1$) are reported. Taking compound **1** (which has no substituents on C_c atoms) as a reference, it can be seen that the introduction of alkyl substituents on the C_c atoms produces a displacement of $E_{1/2}$ to more negative values ($E^{6}_{1/2} - E^{1}_{1/2} = -27$ mV, $E^{7}_{1/2} - E^{1}_{1/2} = -35$ mV, being $E^{i}_{1/2}$ the value of $E_{1/2}$ for compound *i*).

Otherwise, complexes incorporating *exo*-cluster sulfur atoms directly bonded to C_c atoms produce a shift in $E_{1/2}$ to positive values; a shift of 137.5 mV is observed when $S-CH_3$ units are introduced on both C_c atoms ($E^{8}_{1/2} - E^{1}_{1/2}$, Table 3), while a more important displacement is obtained when $S-C_6H_5$ units are introduced ($E^{9}_{1/2} - E^{1}_{1/2} = 165.5$ mV).

These results can easily be explained with the capacity to stabilize Co(II) by the different groups. On one hand, alkyl groups are known to be inductive electron donors, increasing the electronic density on the carborane cluster and, thus, also on the cobalt atom; as a result, this last becomes easier to oxidize, and the value of $E_{1/2}$ is moved to more negative values. On the other hand, thiomethyl and thiophenyl substituents produce the opposite effect, decreasing electronic density on the cluster and, consequently, also on the cobalt atom; the cobalt atom becomes easier to reduce, and $E_{1/2}$ is moved to more positive values.

Influence of C_c Substituents on $E_{1/2}$ in Dimethylpyrrolyl/Dicarbollide Cobalt Complexes. Effects of substituting groups in mixed dimethylpyrrolyl cobalt complexes incorporating one dicarbollide unit are very similar to those obtained for pyrrolyl ones. Table 4 summarizes the values of $E_{1/2}$ obtained for dimethylpyrrolyl complexes with identical substituents on both C_c atoms. The introduction of alkyl substituents moves $E_{1/2}$ to negative values ($E^{12}_{1/2} - E^{10}_{1/2} = -47$ mV, $E^{14}_{1/2} - E^{10}_{1/2} = -31.5$ mV) while substituents with sulfur atoms directly bonded to C_c atoms produce displacements of $E_{1/2}$ to positive values. Thus, $E^{15}_{1/2} - E^{10}_{1/2} = 233.5$ mV while $E^{16}_{1/2} - E^{10}_{1/2} = 165.0$ mV.

Comparison of $E^{10}_{1/2}$ and $E^{2}_{1/2}$ indicates that the presence of phenyl rings on C_c atoms also produces a shift in $E_{1/2}$ to positive values, although the displacement is less important than that found for S−R substituents.

Individual and Averaged Effects. In all examples described previously, two identical substituents were placed on both C_c atoms producing a global effect on $E_{1/2}$. Therefore, only an average contribution could be assigned to individual substituents. However, the study of nonsymmetric complexes allows us to distinguish the contribution of each substituent to the global $E_{1/2}$ shift.

Table 5. Influence of Substituents on $E_{1/2}$ Values of [3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$] and [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$C_2B_9H_{11}$] Derivatives; R and R′ Are Substituents on C_c Atoms

cmpd	R	R′	E_1/V	E_2/V	$E_{1/2}$/V	$\|\Delta E\|$/V
1*	H−	H−	−159.5	−356.5	−258.0	197.0
4*	C_6H_5-	H−	−105.0	−244.0	−174.5	139.0
5*	CH_3-	H−	−204.0	−353.0	−278.5	149.0
10**	H−	H−	−351.0	−459.0	−405.0	108.0
11**	CH_3-	H−	−401.0	−486.0	−443.5	85.0
3**	CH_3-	$-SCH_3$	−301.0	−385.0	−343.0	84.0
13**	C_6H_5-	H−	−300.0	−372.0	−336.0	72.0

* indicates complexes incorporating one pyrrolyl unit. ** indicates complexes incorporating one dimethylpyrrolyl unit.

Table 5 summarizes the values of E_1, E_2, $E_{1/2}$, and ΔE for nonsymmetric mixed cobalt complexes incorporating one pyrrolyl or one dymethylpyrrolyl and one nonsymmetric dicarbollide units. Complexes **1** and **10** are also included as reference compounds.

For pyrrolyl complexes, the effect of introducing the first methyl unit ($E^{5}_{1/2} - E^{1}_{1/2} = -20.5$ mV) is clearly higher than the effect due to the introduction of the second methyl unit ($E^{6}_{1/2} - E^{5}_{1/2} = -6.5$ mV). In mixed dimethylpyrrolyl complexes, the first SCH_3 unit produces a displacement in $E_{1/2}$ ($E^{3}_{1/2} - E^{11}_{1/2} = 100.5$ mV) which is 1.5 times the one produced by the second SCH_3 unit calculated as $E^{16}_{1/2} - E^{10}_{1/2} - 100.5 = 64.5$ mV. A similar situation is found with the introduction of the first and the second methyl units ($E^{11}_{1/2} - E^{10}_{1/2} = -38.5$ mV, $E^{12}_{1/2} - E^{11}_{1/2} = -8.5$ mV). Therefore, the introduction of the second substituent causes a smaller effect than the first but in the same sense. This fact can be explained as follows: the introduction of the first methyl unit increases the electronic density on the cobalt atom, moving $E_{1/2}$ to more negative values. This build-up of electronic density opposes a second input; therefore, when the second methyl unit is introduced, the $E_{1/2}$ shift is smaller. An identical reasoning can be used to explain the case of SCH_3 substituents.

Anomalous Effect of Phenyl Groups. Phenyl groups have been widely studied as carborane cluster substituents[14] that produce anomalous effects. As can be seen in Table 5, the introduction of one phenyl unit in mixed pyrrolyl complexes produces a displacement of $E_{1/2}$ of 83.5 mV ($E^{4}_{1/2} - E^{1}_{1/2}$).

In dimethylpyrrolyl complexes, the introduction of one phenyl unit produces a $E_{1/2}$ displacement of 69.0 mV ($E^{13}_{1/2} - E^{10}_{1/2}$), while the introduction of two phenyl units produces a global displacement of 33.0 mV ($E^{2}_{1/2} - E^{10}_{1/2}$); this value is clearly lower than that obtained for the introduction of the first substituent. The explanation must be found in the inhibition of the effect caused by the first phenyl when the second is introduced, because of steric hindering. When there is just one phenyl unit, as it was shown in a previous work,[12c] the ring remains almost in the plane of the open face of the carborane cluster, thus allowing overlapping between pπ orbitals of the phenyl ring and the tangential orbitals in the dicarbollide unit. The possibility of electronic delocalization in the aromatic ring contributes to increase the electronic withdrawing capacity of the phenyl group. When the second phenyl unit is introduced, steric overcrowding hinders them from staying in the plane of the

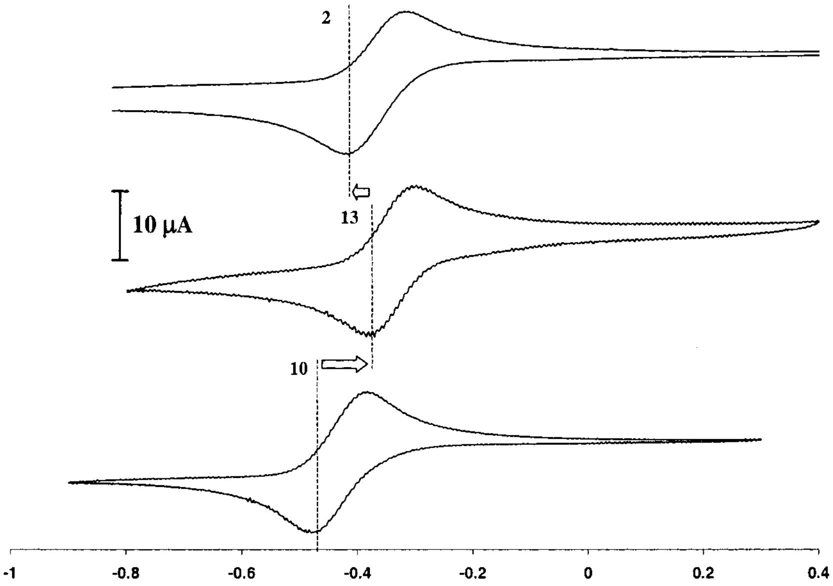

Figure 3. Voltammograms obtained for **2** (two C_6H_5 units), **10** (no substituents), and **13** (one C_6H_5 unit). Measurements performed in chloroform 0.1 M in tetrabutylammonium hexafluorophosphate. Scan rate: 40 mV/s. Reference electrode: Ag/AgCl/TBACl 0.1 M in acetonitrile.

Table 6. Influence of the Presence of Methyl Units Placed on the Pyrrolyl Unit on $E_{1/2}$ Values for $[3\text{-Co}(\eta^5\text{-NC}_4H_4)\text{-}1,2\text{-}C_2B_9H_{11}]$ Derivatives

complexes	R	R′	$E_{1/2}$/V*	$E_{1/2}$/V**	ΔE/mV
1−10	H-	H-	−258.0	−405.0	147.0
5−11	CH_3-	H-	−278.5	−443.5	165.0
6−12	CH_3-	CH_3-	−285.0	−452.0	167.0
4−13	C_6H_5-	H-	−174.5	−336.0	161.5
8−16	-SCH_3	-SCH_3	−120.5	−240.0	119.5
9−15	-SC_6H_5	-SC_6H_5	−92.5	−171.5	79.0
7−14	-$(CH_2)_3$-	-$(CH_2)_3$-	−293.0	−436.5	143.5
					140.4***

* Complexes incorporating one pyrrolyl and one dicarbollide units.
** Complexes incorporating one dimethylpyrrolyl and one dicarbollide units.
*** Average value.

pentagonal open face of the cluster (Figure 1), preventing delocalization through the π orbitals of the ring and thus lowering the electronic withdrawing properties of both substituents; the cobalt atom becomes easier to oxidize with regard to the monosubstituted complex. Thus, the effect of the first phenyl ring is inhibited because of the introduction of the second ring. In Figure 3, voltammograms obtained for compounds **2**, **10**, and **13** are shown. The different $E_{1/2}$ displacement after introduction of the first and the second phenyl units can be observed.

A similar inhibition effect as a function of cos Φ, with Φ being the dihedral angle, was observed with *ortho*-substituted biphenyl derivatives using ultraviolet photoelectron spectroscopy (PES).[16]

Influence of Pyrrolyl Substituents on $E_{1/2}$ in Pyrrolyl/Dicarbollide Cobalt Complexes. The introduction of methyl (or alkyl) units on C_c atoms has shifted $E_{1/2}$ between 8 and 40 mV toward negative values being the effect additive. In Table 6, differences in $E_{1/2}$ obtained for couples with identical substituents on C_c atoms and different substituents on the α positions of the pyrrolyl unit are compared. The introduction of methyl units produces an average shift in $E_{1/2}$ of ~140 mV to more negative values. This result is in agreement with the former explanations; electronic donor character of methyl units increases electronic density on the metallic center, displacing $E_{1/2}$ to more negative values. The displacement caused by one methyl unit on the pyrrolyl ligand (estimated to be about 70 mV) is more important than that obtained for alkyl substituents on the cluster (8−40 mV).

Conclusions

Substituting groups placed on the α positions of the pyrrolyl unit and/or on C_c atoms of the carborane cluster are very important to modulate $E_{1/2}$ in mixed pyrrolyl/dicarbollide cobalt complexes.

Electronic donor substituents on C_c atoms produce a displacement of $E_{1/2}$ to more negative values, while electronic withdrawing substituents produce the opposite effect. The $E_{1/2}$ contribution due to SCH_3, SC_6H_5, and CH_3 groups is not absolutely additive, the second contribution being smaller than the first but in the same sense. For C_6H_5 substituents, the individual contribution of both phenyl units does not have the same sense, the second contribution tending to suppress the effect of the first.

The contribution of CH_3 units placed on the α positions of the pyrrolyl unit tends to be larger than the equivalent ones on the C_c.

Experimental Section

Instrumentation. Elemental analyses were performed using a Carlo Erba EA 1108 microanalyzer. IR spectra were recorded with KBr pellets on a FTIR-8300 Shimadzu spectrophotometer. ^1H NMR (300.13 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz), and ^{11}B and $^{11}B\{^1H\}$ NMR (96.29 MHz) spectra were recorded in $CDCl_3$ with a Bruker ARX 300 instrument at room temperature. Chemical shift values for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to $Si(CH_3)_4$, and those for ^{11}B and $^{11}B\{^1H\}$ NMR spectra were referenced to $(C_2H_5)_2O \rightarrow BF_3$. Chemical shifts are reported in units of part per million downfield from $Si(CH_3)_4$, and coupling constants, in hertz.

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Materials. Experiments were carried out under dry, oxygen-free dinitrogen atmosphere, using standard Schlenk 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. Potassium was refluxed in THF prior to use. 1,2-$(C_6H_5)_2$-1,2-$C_2B_{10}H_{10}$,[17] 1-SCH_3-2-CH_3-1,2-$C_2B_{10}H_{10}$,[18] [3-Co(η^5-NC_4H_4)-1,2-$C_2B_9H_{11}$][10] (**1**), [3-Co(η^5-NC_4H_4)-1-C_6H_5-1,2-$C_2B_9H_{10}$][11b] (**4**), [3-Co(η^5-NC_4H_4)-1-CH_3-1,2-$C_2B_9H_{10}$][12a] (**5**), [3-Co(η^5-NC_4H_4)-1,2-$(CH_3)_2$-1,2-$C_2B_9H_9$][12d] (**6**), [3-Co(η^5-NC_4H_4)-1,2-$(CH_2)_3$-1,2-$C_2B_9H_9$][12d] (**7**), [3-Co-(η^5-NC_4H_4)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$][11b] (**8**), [3-Co(η^5-NC_4H_4)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$][11b] (**9**), [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$C_2B_9H_{11}$][12c] (**10**), [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-1,2-$C_2B_9H_{10}$][12d] (**11**), [3-Co-(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(CH_3)_2$-1,2-$C_2B_9H_9$][11d] (**12**), [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-C_6H_5-1,2-$C_2B_9H_{10}$][12c] (**13**), [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(CH_2)_3$-1,2-$C_2B_9H_9$][11c] (**14**), [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(SC_6H_5)_2$-1,2-$C_2B_9H_9$][11c] (**15**), and [3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(SCH_3)_2$-1,2-$C_2B_9H_9$][11c] (**16**) were synthesized according to published literature.

Crystallographic Studies of 2 and 3. Single-crystal data collections were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo Kα radiation. A total of 2056 and 1727 unique reflections were collected by $\omega/2\theta$ scan mode ($2\theta_{max} = 50°$) for **2** and **3**, respectively.

The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[19] For both compounds, boron atoms were refined with isotropic displacement parameters. The rest of the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. Compounds **2** and **3** crystallize in noncentrosymmetric space groups. Absolute configuration of **2** was determined by refinement of Flack x parameter. For **3**, absolute configuration could not be reliably determined [x parameter values 0.48(3) and 0.53(3)], and the structure was refined as racemic twin. Crystallographic data and structural refinement details for compounds **2** and **3** are listed in Table 1.

Electrochemical Measurements. Electrochemical measurements were performed in a standard double-compartment three-electrode cell. A Ag/AgCl/[$N(C_4H_9)_4$]Cl (0.1 M in CH_3CN) electrode was used as reference electrode. A 4-mm^2 platinum plate and a platinum wire were used as working and counter electrodes, respectively. All measurements were performed in chloroform with tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte. Cyclic voltammograms were recorded with a scan rate of 40 mV/s. The initial potential value was applied to the working electrode for 15 s before performing voltamperometric measurements.

Synthesis of [3-Co(η^5-$N(CH_3)_2C_4H_2$)-1,2-$(C_6H_5)_2$-1,2-$C_2B_9H_9$)] (2). To a suspension of refluxing K[$NC_4(CH_3)_2H_2$] (1.0 g, 7.5 mmol) in 50 mL of THF, 1,2-$(C_6H_5)_2$-1,2-$C_2B_{10}H_{10}$ (0.186 g, 0.63 mmol) was added. 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 chromatographied over silica gel using dichloromethane/hexane 7:3 as mobile phase (R_f(prep) = 0.6). A pure orange air stable solid was obtained. Yield 0.15 g, 55%. IR (KBr), ν [cm^{-1}] = 3109 (υ $C_{ar}-H$), 2924 (υ C−H), 2605, 2574, 2555, 2534 (υ B−H), 1450 (δ, C−H). ^1H NMR, δ = 8.20−7.70 (m, $C_{ar}-H$, 10H), 6.33 (s, $C_{pyr}-C_{pyr}-H$, 1H), 6.31 (s, $C_{pyr}-C_{pyr}-H$, 1H), 3.62 (s, $-CH_3$, 3H), 3.28 (s, $-CH_3$, 3H).^{13}C-{^1H} NMR, δ = 142.01, 139.03, 127.85, 125.74 (s, C_{ar}), 125.05, 124.48 (s, $N-C_{pyr}$), 91.08, 89.96 (s, $C_{pyr}-C_{pyr}$), 67.57 (s, C_c), 14.33 (s, $-CH_3$), 13.36 (s, $-CH_3$). ^{11}B NMR, δ = 3.10 (1B), 1.61 (3B), −4.47 (1B), −5.83 (1B), −12.16 (d, ^1J(B,H) = 144.8, 2B), −13.50 (1B). Anal. Calcd for $C_{20}B_9H_{27}CoN$: C, 54.88; H, 6.22; N, 3.20. Found: C, 54.90; H, 6.32; N, 3.16.

Synthesis of [3-Co(η^5-$N(CH_3)_2C_4H_2$)-1-CH_3-2-SCH_3-1,2-$C_2B_9H_9$)] (3). The process was the same as that used for **2** but using 1-CH_3-2-SCH_3-1,2-$C_2B_{10}H_{10}$ (0.13 g, 0.63 mmol) as starting product. A pure orange product was obtained using the same mobile phase as for **2** (R_f(prep) = 0.6). Yield 0.11 g, 50%. IR (KBr), ν [cm^{-1}] = 2929 (υ C−H), 2603, 2575, 2545, 2526 (υ B−H), 1442, 1454 (δ C−H). ^1H NMR, δ = 5.85 (s, $C_{pyr}-C_{pyr}-H$, 1H), 5.74 (s, $C_{pyr}-C_{pyr}-H$, 1H), 2.42 (s, $-CH_3$, 6H), 2.40 (s, $-CH_3$, 3H), 2.38 (s, $-CH_3$, 3H).^{13}C{^1H} NMR, δ = 127.82 (s, $N-C_{pyr}$), 124.48 (s, $N-C_{pyr}$), 90.73 (s, $C_{pyr}-C_{pyr}$), 88.87 (s, $C_{pyr}-C_{pyr}$), 80.78 (s, C_c), 61.17 (s, C_c), 28.67 (s, $S-CH_3$), 20.75 (s, $-CH_3$), 14.89 (s, $-CH_3$), 14.78 (s, $-CH_3$). ^{11}B NMR, δ = 7.10 (d, ^1J(B,H) = 145.4, 1B), 3.29 (d, ^1J(B,H) = 149.0, 1B), 0.32 (d, ^1J(B,H) = 143.6, 1B), −1.01 (d, ^1J(B,H) = 138.8, 1B), −5.37 (d, ^1J(B,H) = 147.2, 2B), −11.63 (d, ^1J(B,H) = 161.6, 1B), −14.33 (d, ^1J(B,H) = 146.6, 2B). Anal. Calcd for $C_{10}B_9H_{23}CoNS$: C, 34.75; H, 6.71; N, 4.05. Found: C, 34.60; H, 6.81; N, 3.94.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1,2-$(C_6H_5)_2$-1,2-$C_2B_9H_9$] (**2**) and *closo*-[3-Co(η^5-$NC_4(CH_3)_2H_2$)-1-CH_3-2-SCH_3-1,2-$C_2B_9H_9$] (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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