

Synthesis of Cobaltabis(dicarbollyl) Complexes Incorporating Exocluster SR Substituents and the Improved Synthesis of $[3,3'\text{-Co}(1\text{-R-}2\text{-R}'\text{-}1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ Derivatives

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Introduction

In 1965 the first metallocarboranes, $[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^{n-}$ ($n = 1, 2$), were reported.¹ Due to their interesting properties and applications, their chemistry developed very quickly.^{2–6} Current applications of these novel species include (1) improvement of the solubility in electron-donating organic solvents, e.g., in solvent extraction of radionuclides;⁷ (2) isolation, separation, and characterization of organic bases, including natural substances;⁷ (3) use as radiometal carriers;^{8,9} and (4) use as electron acceptor molecules, e.g., $[3,3'\text{-Ni}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.¹⁰

In the $[7,8\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$ ion and its alkyl carbon substituted derivatives, $[7\text{-R-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9]^{2-}$, the metal may be considered to be π -bonded to the open pentagonal face of an icosahedral fragment, as in the case of the formation of ferrocene from C_5H_5^- . In so doing the metal simultaneously completes two icosahedra.^{1,11} This general structure has been confirmed for several transition metal derivatives, among them cobalt. So, cobaltabis(dicarbollyl) derivatives with noncoordinating groups on C_C had been reported.^{2–6}

The chemistry associated with ferrocene has grown continuously due to its redox properties, the extreme stability of both oxidation states Fe(II)/Fe(III), and the possibility to perform reactions on the Cp ring.¹² The cobaltabis(dicarbollyl) species $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$, a metallocarborane, also offers those possibilities in a different E° region, with the characteristic of producing anionic species. One of the main drawbacks of the

$[7,8\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$ moiety vs Cp^- is the practical impossibility to perform reactions on the $\text{C}_C\text{-H}$ group.¹³ Thus it is necessary to produce the wanted C_C substitution prior to complexation. The stability of $[3,3'\text{-Co}(1\text{-SR-}2\text{-R}'\text{-}1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ derivatives with $\text{C}_C\text{-SR}$ groups shed more doubts since *exo-nido* coordination via the $\text{C}_C\text{-SR}$ and BH groups had generally been found.¹⁴ Open-face coordination with $\text{C}_C\text{-SR}$ groups had only been found with Hg^{2+} ,¹⁵ and in a few examples with Ag^+ .¹⁶ No evidence of this coordination with transition metal ions had been encountered. In this work three main objectives are pursued: (a) to design an easy, one-pot route to these C_C -substituted cobaltabis(dicarbollyl) compounds, (b) to explore the formation of cobaltabis(dicarbollyl) species with $\text{C}_C\text{-S}$ bonds, and (c) to acquire an understanding of the influence of C_C substituents on the E° value in $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ derivatives with special emphasis on the $\text{C}_C\text{-S}$ compounds. A similar modulation, mostly by B substitution, had been described earlier by Hawthorne and co-workers.⁴

Results

The synthesis of C_C -substituted metallocarborane derivatives of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ was initially carried out following the nonaqueous method described in the literature. This is based on deprotonation of *nido*- $[7\text{-R-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ derivatives by NaH .^{3,4} Subsequent reaction with anhydrous CoCl_2 in dimethoxyethane (dme) led to the desired cobaltacarboranes (see Table I, column under B). The synthesis of cobaltacarboranes with $\text{C}_C\text{-SR}$ provided low yields when this method was followed. Thus a new method using potassium *tert*-butoxide ($\text{K-}t\text{-BuO}$) as the deprotonating agent and dimethoxyethane as the solvent was developed. This presents several advantages, among them the ease of handling *nido* carborane $[\text{NMe}_4]^+$ salts and the facts that it is a one-pot reaction, it gives a high yield, and it is quite general. The reaction is indicated in Scheme 1 for the ligand $[7\text{-SEt-}8\text{-Me-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$. To test the validity of the method, the *closo* species $1,2\text{-(Et)}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, $1\text{-(CH}_2)_2\text{-}2\text{-OMe-}2\text{-Me-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, $1\text{-SEt-}2\text{-Ph-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, and $1\text{-SEt-}2\text{-Me-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ were synthesized. The syntheses were carried out by the reaction of *o*-carborane or $1\text{-Me-}1,2\text{-C}_2\text{B}_{10}\text{H}_{11}$ with BuLi and the appropriate halide in diethyl ether to produce $1,2\text{-Et}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ and $1\text{-(CH}_2)_2\text{OMe-}2\text{-Me-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, respectively, or by reaction of $1\text{-SH-}2\text{-R-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ ($\text{R} = \text{Ph, Me}$) with KOH and EtCl in deoxygenated ethanol to yield $1\text{-SEt-}2\text{-Ph-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ and $1\text{-SEt-}2\text{-Me-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$.¹⁷ The monosubstituted derivative $1\text{-SEt-}1,2\text{-C}_2\text{B}_{10}\text{H}_{11}$ ¹⁸ was synthesized by reaction of $1\text{-SH-}1,2\text{-C}_2\text{B}_{10}\text{H}_{11}$ according to a new method developed in our group.¹⁹ Partial degradation of these species was carried out following the reported KOH/ethanol

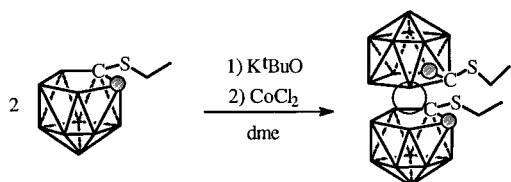
- (13) Throughout the discussion C_C will indicate one of the cluster carbon atoms.
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Scheme 1. Synthesis of $[3,3'\text{-Co}(1\text{-SEt-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$ ^a

^a The shaded circles indicate C-Me.

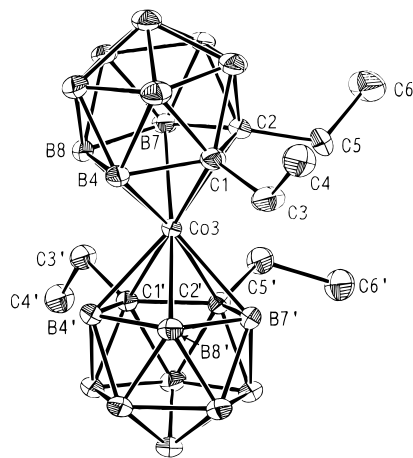
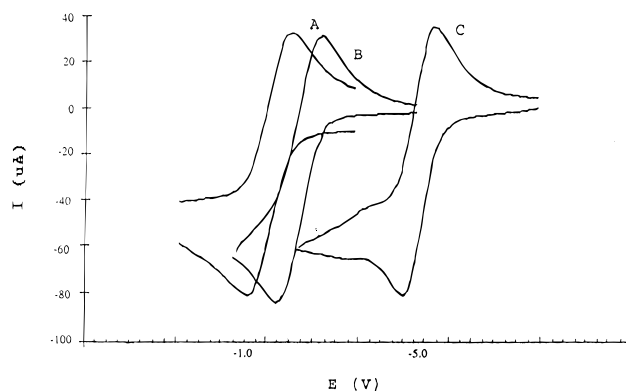
Table 1. Yields Obtained in the Synthesis of $[3,3'\text{-Co}(1\text{-R-2-R'-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$ Derivatives

compd no.	sample	%	
		A ^a	B ^b
1	$[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$	95	
2 ^c	$[3,3'\text{-Co}(1\text{-SEt-2-Ph-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	85	
3	$[3,3'\text{-Co}(1,2\text{-Et}_2\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	91	28
4	$[3,3'\text{-Co}(1\text{-(CH}_2)_2\text{OMe-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	86	40
5	$[3,3'\text{-Co}(1,2\text{-}\mu\text{-(CH}_2)_3\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	75	
6	$[3,3'\text{-Co}(1\text{-Ph-1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$	80	
7	$[3,3'\text{-Co}(1\text{-SEt-1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$	68	
8	$[3,3'\text{-Co}(1\text{-SEt-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	79	35
9	$[3,3'\text{-Co}(1\text{-Me-1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$	93	

^a A: Yield obtained by the *tert*-butoxide method. ^b B: Yield obtained by the NaH method. ^c Reference 25.

method.^{20,21} Table 1 lists the cobalt $[3,3'\text{-Co}(1\text{-R-2-R'-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$ compounds produced, the compound numbers, and the yields obtained following the method described here. As indicated earlier, the column under B indicates the yields obtained with the NaH method. Compounds **3**, **4**, and **7–9** required chromatography (column or preparative TLC) for their purification. Characterization of **1**, **5**, and **6** was carried out by comparison with authentic samples.^{4–6} The new alkyl (**3**, **4**, **9**) and C_C-SR metallacarboranes (**2**, **7**, and **8**) were characterized by elemental analysis and ¹¹B-, ¹H-, and ¹³C{¹H}-NMR spectra. The ¹¹B-NMR spectra of the sulfur and non-sulfur compounds are similar. Commonly, the spectra of the sulfur compounds display resonances at lower field, about 2 ppm, than the non-sulfur ones. The line widths of the ¹¹B-NMR spectra are wider for all nonsymmetrical compounds than for $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$. This line widening is accounted for by the lack of symmetry of most of these compounds and the existence of two geometrical isomers that we have not been able to separate: the racemic mixture and the meso form. Although the elemental analyses of the isolated TLC bands are in agreement with the proposed formulas, peak intensity analysis of the ¹¹B-NMR spectra confirms the existence of geometrical isomers in some bands. As mentioned, their extremely similar physical properties did not permit their separation. The spectrum of **3** provides evidence that the ¹¹B-NMR line widening is due to the lack of symmetry and the presence of geometrical isomers. In complex **3**, both carbon substituents are identical. Its spectrum resembles very much that of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$. Besides, good crystals of **3** have been grown which have enabled elucidation of its molecular structure (Figure 1).

Influence of Substituents on Redox Properties. The influence of C_C-R substituents on redox properties was studied by cyclic voltammetry in a three-electrode cell, with acetonitrile as the solvent, 0.1 M [NBu₄]ClO₄ as the supporting electrolyte, and platinum as the working electrode. Potentials are referenced to a Ag/AgCl electrode. In the following discussion the E°

**Figure 1.** ORTEP plot of $[\text{PMePh}_3][3,3'\text{-Co}(1,2\text{-Et}_2\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$.**Figure 2.** Cyclic voltammetry in a three-electrode, one-compartment cell. The study was carried out with 2 mM solutions of metallacarborane in acetonitrile as the solvent in the presence of 0.1 M [NBu₄]ClO₄ as the supporting electrolyte. The working electrode was Pt (diameter 2.65 mm) sealed in a glass mounting. A Pt wire was used as the counter electrode. Potentials are referenced to a Ag/AgCl (0.1 M [NBu₄]Cl) electrode at 100 mV s⁻¹. Curve A corresponds to complex **1**, B to complex **4**, and C to **8**.**Table 2.** Electrochemical Behavior of $[3,3'\text{-Co}(1\text{-R-2-R'-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$ Derivatives

compd no.	sample	$E_{\text{pa}} - E_{\text{pc}}$ (mV)	E° (V)
1	$[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$	168	-1.028
2	$[3,3'\text{-Co}(1\text{-SEt-2-Ph-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	324	-0.622
3	$[3,3'\text{-Co}(1,2\text{-Et}_2\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	168	-0.841
4	$[3,3'\text{-Co}(1\text{-(CH}_2)_2\text{OMe-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	132	-0.819
5	$[3,3'\text{-Co}(1,2\text{-}\mu\text{-(CH}_2)_3\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	120	-0.622
6	$[3,3'\text{-Co}(1\text{-Ph-1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$	205	-0.959
7	$[3,3'\text{-Co}(1\text{-SEt-1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$	180	-0.728
8	$[3,3'\text{-Co}(1\text{-SEt-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$	156	-0.510
9	$[3,3'\text{-Co}(1\text{-Me-1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$	233	-0.889

values represent the average values of the forward and return peak potentials and are indicated in Table 2. All compounds exhibited quasi-reversible behavior. A typical voltammogram is shown in Figure 2.

The most negative E° value corresponds to $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ (**1**) at -1.028 V, and the least negative corresponds to $[3,3'\text{-Co}(1\text{-SEt-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$ (**8**) with E° = -0.510 V. Throughout the discussion the E° value for **1** has been taken as the reference, so a value of ΔE° = 0.518 V has been achieved upon SR and Me substitutions on the cluster carbon atoms. As expected, the alkyl-substituted compounds $[3,3'\text{-Co}(1,2\text{-Et}_2\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$ (**3**) and $[3,3'\text{-Co}(1\text{-CH}_2\text{CH}_2\text{OMe-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$ (**4**) present E° values comparable to those of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ (**1**). On the other hand, all C_C-SR-substituted

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Table 3. Influence of SET on the E° values of $[3,3'\text{-Co}(1\text{-R-}2\text{-R}'\text{-}1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ Derivatives^a

compd no.	R	R'	E° (V)	ΔE°
1	H	H	-1.028	0.300
7	H	SEt	-0.728	
9	Me	H	-0.889	0.379
8	Me	SEt	-0.510	
6	Ph	H	-0.959	0.337
2	Ph	SEt	-0.622	

^a ΔE° is defined as $\Delta E^\circ \approx E^\circ(1) - E^\circ(2)$, where (1) and (2) designate the two compounds in the couple.

compounds present similar E° values close to -0.6 V. A minor modulation is accomplished by H, Me, or Ph substitution on the neighboring carbon.

Another perspective can be seen when comparing complexes that differ in only one substituent, such as **1** and **7**, **6** and **2**, and **9** and **8**. In each couple the two complexes differ only by the existence of a SEt group in one of them. Interestingly a value close to $\Delta E^\circ \approx 0.34$ V (see Table 3) shall be added to the E° on the non-sulfur-containing cobaltacarborane to obtain the new E° . So the sulfur influence can be estimated as $\Delta E^\circ \approx 0.34$ V. As a result we feel that the similar steric constraints originated by the C_C substituents suggest that steric factors may not be very influential in the redox potentials discussed, and only electronic effects should be considered relevant.

Hawthorne and co-workers⁴ have described a value of $\Delta E^\circ = 0.98$ V for $[3,3'\text{-Co}(8,9,12\text{-Br}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_8)_2]^-$. They also found smaller ΔE° shifts after substitution on C_C , e.g., $\Delta E^\circ = 0.29$ for $[3,3'\text{-Co}(1,2\text{-(CH}_3)_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ and $\Delta E^\circ = 0.14$ for $[3,3'\text{-Co}(1\text{-Ph-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$. So, the largest ΔE° was found for the B-hexabrominated compound $[3,3'\text{-Co}(8,9,12\text{-Br}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_8)_2]^-$. Then it may be concluded that the electron-withdrawing capacity of the B-Br substituents stabilizes $[3,3'\text{-Co}(8,9,12\text{-Br}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_8)_2]^{2-}$ vs $[3,3'\text{-Co}(8,9,12\text{-Br}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_8)_2]^-$. This is logical since Co^{2+} , being more electron rich than Co^{3+} , does prefer a less electron rich ligand. This same explanation must be true for the C_C -SR-substituted compounds. Though to a lesser extent than for three Br per cluster, the reduced species is more stabilized than the oxidized one. Thus SR groups must dissipate electron density from the cage, becoming themselves more negative and better Lewis bases. This finding is of outmost importance in this C_C -SR type of chemistry. Up to now the good coordinating capacity of the C_C -SR groups in $[7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ and $[7,8\text{-(SR)}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ compounds^{16,22,23} has been interpreted as being due to the negative charge of the cluster, able to compensate the cation's charge. The data presented here suggest that these SR moieties are themselves better coordinating groups because they become electron-enriched due to electron density dissipation from the cage. So, in these compounds the SR groups show a negative inductive effect.

Complex Stability. The introduction of substituents on cluster carbon atoms could lower the acid stability of these compounds

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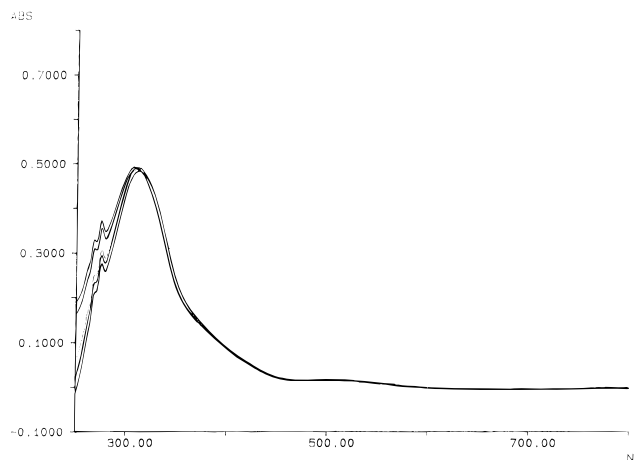


Figure 3. The UV-vis spectra of compound **8** at different acid concentrations.

with regard to that of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$. This was even more possible for the C_C -SR-substituted compounds. These studies were performed in ethanol/water (50/50) with HBF_4 and HCl . The solutions were 5×10^{-4} M in cobaltabis(dicarbollyl) derivatives and 0.4, 0.8, 2.4, 3.2, and 4 M in acid. A blank cobaltabis(dicarbollyl) derivative solution was run in every case. Figure 3 shows the UV-vis spectra of compound **8** at the different acid concentrations. As can be seen, no deterioration of the compounds took place in HBF_4 or in HCl ; however, some decomposition was found for the HBF_4 samples after 1 day of mixing, while those of HCl did not show any sign of decomposition after 1 week.

Conclusion

The synthesis of sandwich cobaltacarboranes derivatives of $[7,8\text{-C}_2\text{B}_9\text{H}_{12}]^-$ incorporating SR groups on the cluster carbon atom has been achieved for the first time. This proves that $[7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ ligands have as many types of coordination as $[7,8\text{-C}_2\text{B}_9\text{H}_{12}]^-$, in addition to this via SR. To overcome low yields in the synthesis by the NaH/THF method, a variation in which $\text{K-}t\text{-BuO}$ and dme are used has been developed. The method is quite general, provides high yields, is a one-pot reaction, and requires much less manipulation. The effect on the E° values of the C_C -SR substitution in these cobaltacarboranes has been studied. It considerably lowers the E° value with regard to $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$. This implies that cage electron density is dissipated through the SR moieties, which become more negative and better Lewis bases. This is in agreement with the good coordinating capacity of $[7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ and $[7,8\text{-(SR)}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ ligands, where the SR groups must also dissipate the cage's excess of charge. No deterioration on the acid stability of these cobaltacarboranes has been found due to SR substitution.

Experimental Section

General Methods. Commercial *o*-carborane and methyl-*o*-carborane were purified by sublimation at 0.01 mmHg. $1,2\text{-}\mu\text{-(CH}_2)_3\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ and phenyl-*o*-carborane were synthesized according to the literature.^{6,24} A 1.6 M solution of *n*-butyllithium in hexane was used as received. Dimethoxyethane (dme) was dried with Na/benzophenone . All organic and inorganic salts were analytical reagent grade and were used as received. The solvents were reagent grade. All reactions were carried

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out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed in our analytical laboratory on a Perkin-Elmer 240B microanalyzer. IR spectra of KBr pellets were obtained on a Nicolet 710-FT spectrophotometer. UV-vis measurements were made on a Cary-Varian 5 UV-vis-Nir spectrophotometer. ^{11}B -NMR (96.29 MHz), $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.47 MHz), and $^1\text{H}\{^{11}\text{B}\}$ -NMR spectra (300.13 MHz) were recorded on a Bruker ARX-300 spectrometer equipped with the appropriate decoupling accessories. All of the NMR spectroscopic data were obtained for acetone- d_6 solutions at 22 °C. Chemical shift values for ^{11}B -NMR spectra were referenced to external $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$. Chemical shift values for $^1\text{H}\{^{11}\text{B}\}$ - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were referenced to $\text{Si}(\text{CH}_3)_4$. Electrochemical measurements were made on a PAR273 potentiostat. Potentials are reported versus $\text{Ag}/\text{AgCl}/\text{Cl}^-$ (0.1 M $[\text{NBu}_4]\text{Cl}$). Metallacarborane 2 mM solutions in CH_3CN in the presence of 10^{-1} M $[\text{NBu}_4]\text{ClO}_4$ were prepared. The speed used was 100 mV s^{-1} . The electrochemical study was performed in a three-electrode, one-compartment cell. The working electrode was Pt (diameter 2.65 mm) sealed in a glass mounting. A Pt wire was used as the counter electrode. The solution was degassed by bubbling (10–15 min) dry oxygen-free dinitrogen.

Preparation of 1-R-2-R'-1,2-C₂B₁₀H₁₀. General Procedure. The starting *closa* species were synthesized according to the general procedure described in the literature.²⁰ For the following preparations only the reagents are indicated.

Preparation of 1,2-(Et)₂-1,2-C₂B₁₀H₁₀. *o*-Carborane (0.500 g, 3.47 mmol), *n*-butyllithium (6.94 mmol), and ethyl bromide (0.756 g, 6.94 mmol) afforded 1,2-(Et)₂-1,2-C₂B₁₀H₁₀ (yield 0.598 g, 87%). IR (KBr): ν (cm^{-1}) = 2980, 2945, 2889 (CH), 2587 (BH), 1462 (CH). ^1H -NMR: δ = 1.15 (t, $^1J(\text{H,H})$ = 8 Hz, 6H, CH_3), 2.32 (q, $^1J(\text{H,H})$ = 7 Hz, 4H, CH_2). ^{11}B -NMR: δ = -4.87 (d, $^1J(\text{B,H})$ = 146 Hz, 2B), -10.23 (d, $^1J(\text{B,H})$ = 128 Hz, 6B), -11.03 (d, $^1J(\text{B,H})$ = 149 Hz, 2B). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 14.04 (CH_3), 28.62 ($-\text{CH}_2-$), 81.93 (BC). Anal. Calcd for $\text{C}_6\text{H}_{20}\text{B}_{10}$: C, 35.94; H, 10.06. Found: C, 36.38; H, 10.32.

Preparation of 1-(CH₂)₂OMe-2-Me-1,2-C₂B₁₀H₁₀. Methyl-*o*-carborane (1.00 g, 6.23 mmol), *n*-butyllithium (6.32 mmol), and $\text{Cl}(\text{CH}_2)_2\text{OMe}$ (0.368 g, 3.90 mmol) afforded 1-(CH₂)₂OMe-2-Me-1,2-C₂B₁₀H₁₀ (yield 1.21 g, 89%). IR (KBr): ν (cm^{-1}) = 2987, 2938, 2903 (CH), 2587 (BH), 1482, 1462, 1426 (CH), 1124 (CO). ^1H -NMR: δ = 2.03 (s, 3H, CH_3), 2.46 (t, $^1J(\text{H,H})$ = 7 Hz, 2H, BCCH_2), 3.31 (s, 3H, OCH_3), 3.50 (t, $^1J(\text{H,H})$ = 7 Hz, 2H, CH_2O). ^{11}B -NMR: δ = -4.28 (d, $^1J(\text{B,H})$ = 178 Hz, 1B), -5.82 (d, $^1J(\text{B,H})$ = 167 Hz, 1B), {-9.25 (d, $^1J(\text{B,H})$ = 94 Hz), -9.90 (d, $^1J(\text{B,H})$ = 78 Hz), -10.54 (d, $^1J(\text{B,H})$ = 155 Hz), 8B}. $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 23.26 (BCCH_3), 35.06 (BCCH_2), 58.56 (OCH_3), 70.52 (CH_2O), 74.83 (BC), 75.94 (BC). Anal. Calcd for $\text{C}_8\text{H}_{20}\text{B}_{10}\text{O}$: C, 33.31; H, 9.32. Found: C, 33.55; H, 9.08.

Preparation of the Dodecahydro-7,8-dicarbaundecaborate(-1) Ions. General Procedure. The $[\text{NMe}_4][7\text{-R-8-R}'\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$ salts were prepared according to the general procedure described in the literature.^{20,21} For the following preparations only the reagents are indicated.

Preparation of $[\text{HNMe}_3][7,8\text{-(Et)}_2\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$. 1,2-(Et)₂-1,2-C₂B₁₀H₁₀ (0.330 g, 1.68 mmol) afforded $[\text{HNMe}_3][7,8\text{-(Et)}_2\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$ (yield 0.280 g, 90%). IR (KBr): ν (cm^{-1}) = 2966, 2931, 2868 (CH), 2530–2495 (BH), 1440 (CH). ^1H -NMR: δ = -2.5 (b, 1H, B-*H*-B), 1.10 (t, $^1J(\text{H,H})$ = 7 Hz, 6H, CH_3), 1.64–1.99 (m, 4H, CH_2), 3.34 (s, 9H, $\text{HN}(\text{CH}_3)_3$). ^{11}B -NMR: δ = -12.79 (d, $^1J(\text{B,H})$ = 129 Hz, 3B), -20.24 (d, $^1J(\text{B,H})$ = 108 Hz, 4B), -36.02 (d, $^1J(\text{B,H})$ = 78 Hz, 1B), -38.82 (d, $^1J(\text{B,H})$ = 134 Hz, 1B). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 15.22 (CH_3), 27.18 (CH_2), 46.57 ($\text{HN}(\text{CH}_3)_3$). Anal. Calcd for $\text{C}_9\text{H}_{30}\text{B}_9\text{N}$: C, 42.71; H, 12.13, N, 5.62. Found: C, 43.31; H, 12.00; N, 5.62.

Preparation of $[\text{HNMe}_3][7\text{-(CH}_2)_2\text{OMe-8-Me-7,8-C}_2\text{B}_9\text{H}_{10}]$. 1-(CH₂)₂OMe-2-Me-1,2-C₂B₁₀H₁₀ (1.00 g, 4.63 mmol) afforded $[\text{HNMe}_3][7\text{-(CH}_2)_2\text{OMe-8-Me-7,8-C}_2\text{B}_9\text{H}_{10}]$ (yield 1.00 g, 83%). IR (KBr): ν (cm^{-1}) = 2972, 2945, 2777 (CH), 2537 (BH), 1482, 1455 (CH), 1096 (CO). ^1H -NMR: δ = -2.50 (b, 1H, B-*H*-B), 1.42 (s, 3H, BCCH_3), 1.76–1.90 (m, 2H, BCCH_2), 3.18 (s, 9H, $\text{HN}(\text{CH}_3)_3$), 3.23 (s, 3H, OCH_3), 3.47–3.37 (m, 2H, CH_2O). ^{11}B -NMR: δ = -10.28 (d, $^1J(\text{B,H})$ = 138 Hz, 1B), -11.41 (d, $^1J(\text{B,H})$ = 143 Hz, 2B), -19.41 (d, $^1J(\text{B,H})$ = 127 Hz, 4B), -35.40 (d, $^1J(\text{B,H})$ = 127 Hz, 1B), -38.00 (d, $^1J(\text{B,H})$ = 138 Hz, 1B). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 22.12 (BCCH_3), 35.71 (BCCH_2),

45.88 ($\text{HN}(\text{CH}_3)_3$), 58.17 (OCH_3), 74.20 (CH_2O). Anal. Calcd for $\text{C}_9\text{H}_{30}\text{B}_9\text{NO}\cdot\frac{1}{2}\text{H}_2\text{O}$: C, 39.36; H, 11.38; N, 5.10. Found: C, 39.73; H, 11.02; N, 5.01.

Preparation of $[\text{NMe}_4][7\text{-Me-7,8-C}_2\text{B}_9\text{H}_{11}]$. Methyl-*o*-carborane (0.310 g, 1.96 mmol) afforded $[\text{NMe}_4][7\text{-CH}_3\text{-7,8-C}_2\text{B}_9\text{H}_{11}]$ (yield 0.444 g, 94%). IR (KBr): ν (cm^{-1}) = 3029, 2924, 2868 (CH), 2516 (BH), 1482 (CH), 1405, 1018. ^1H -NMR: δ = -2.68 (b, 1H, B-*H*-B), 1.35 (s, 3H, BCCH_3), 1.59 (s, 1H, BCCH), 3.44 (s, 12H, $\text{N}(\text{CH}_3)_4$). ^{11}B -NMR: δ = -9.71 (d, $^1J(\text{B,H})$ = 94 Hz, 1B), -10.61 (d, $^1J(\text{B,H})$ = 98 Hz, 1B), -13.06 (d, $^1J(\text{B,H})$ = 157 Hz, 1B), -17.69 (m, 3B), -22.09 (d, $^1J(\text{B,H})$ = 149 Hz, 1B), -33.19 (d, $^1J(\text{B,H})$ = 128 Hz, 1B), -36.43 (d, $^1J(\text{B,H})$ = 136 Hz, 1B). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 24.84 (BCCH_3), 55.24 ($\text{N}(\text{CH}_3)_4$). Anal. Calcd for $\text{C}_7\text{H}_{26}\text{B}_9\text{N}\cdot 2\text{H}_2\text{O}$: C, 32.64; H, 11.74; N, 5.44. Found: C, 32.44; H, 11.36; N, 5.48.

Preparation of $[\text{PMePh}_3][3,3'\text{-Co(1,2-Et}_2\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]$ (3). The compound was prepared by two methods. Method A: In a two-necked flask, $[\text{HNMe}_3][7,8\text{-Et}_2\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$ (0.700 g, 2.80 mmol) was dissolved in anhydrous dme (40 mL) under dinitrogen with stirring. Then, *K-t*-BuO (3.14 g, 28.0 mmol) and anhydrous CoCl_2 (3.64 g, 28.0 mmol) were added. The reaction mixture was refluxed for 24 h. Upon addition of ethanol (2 mL) and an excess of $[\text{PMePh}_3]\text{Br}$ in ethanol/water (25 mL), a solid precipitated, which was filtered and washed with water and hexane. Column chromatography (silica G, CH_2Cl_2 , R_f = 0.25) afforded $[\text{PMePh}_3][3,3'\text{-Co(1,2-Et}_2\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]$ (yield 0.908 g, 91%). Method B: According to the general procedure described in the literature,^{3,4} $[\text{HNMe}_3][7,8\text{-Et}_2\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$ (0.700 g, 2.80 mmol), NaH (0.690 g, 28.6 mmol), and anhydrous CoCl_2 (1.86 g, 14.3 mmol) in dry dme (20 mL) gave, upon addition of ethanol (2 mL) and an excess of $[\text{PMePh}_3]\text{Br}$ in ethanol/water (25 mL), $[\text{PMePh}_3][3,3'\text{-Co(1,2-Et}_2\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]$ (yield 0.279 g, 28%). Crystals suitable for an X-ray diffraction experiment were grown by slow evaporation of a concentrated methylene chloride solution. IR (KBr): ν (cm^{-1}) = 3050, 2971, 2936, 2881 (CH), 2554 (BH), 1449 (CH). ^1H -NMR: δ = 1.15–1.28 (m, 12H, CH_3), 2.70–2.73 (m, 8H, $-\text{CH}_2-$), 2.84 (d, $^2J(\text{P,H})$ = 13 Hz, 3H, CH_3P), 7.61–7.76 (m, 15H, (C_6H_5)₃P). ^{11}B -NMR: δ = 5.65 (d, $^1J(\text{B,H})$ = 133 Hz, 2B), -2.76 (d, $^1J(\text{B,H})$ = 143 Hz, 2B), -5.43 (d, $^1J(\text{B,H})$ = 138 Hz, 6B), -8.51 (d, $^1J(\text{B,H})$ = 140 Hz, 2B), -13.75 (d, $^1J(\text{B,H})$ = 138 Hz, 6B). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 9.69 (d, $^1J(\text{C,P})$ = 59 Hz, CH_3P), 16.01 (CH_3), 28.68 (BC-CH_2-), 33.10 (BC-CH_2-), 71 (BC), 117.70 (d, $^3J(\text{C,P})$ = 90 Hz, PC_{ar}), 130.70 (d, $^3J(\text{C,P})$ = 13 Hz, $m\text{-Car}$), 132.85 (d, $^2J(\text{C,P})$ = 10 Hz, $o\text{-Car}$), 135.63 ($p\text{-Car}$). Anal. Calcd for $\text{C}_{31}\text{H}_{56}\text{B}_{18}\text{CoP}$: C, 52.20; H, 7.91. Found: C, 52.13; H, 7.62.

Preparation of $[\text{PMePh}_3][3,3'\text{-Co(1-CH}_2\text{CH}_2\text{OMe-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]$ (4). The compound was prepared by the two methods indicated for compound 3. Method A: $[\text{HNMe}_3][7\text{-(CH}_2)_2\text{OMe-8-Me-7,8-C}_2\text{B}_9\text{H}_{10}]$ (0.760 g, 2.86 mmol), *K-t*-BuO (3.21 g, 28.6 mmol), and anhydrous CoCl_2 (3.72 g, 28.6 mmol) afforded, after column chromatography (silica G, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9.5/0.5), R_f = 0.57), $[\text{PMePh}_3][3,3'\text{-Co(1-CH}_2\text{CH}_2\text{OMe-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]$ (yield 0.844 g, 86%). Method B: $[\text{HNMe}_3][7\text{-(CH}_2)_2\text{OMe-8-Me-7,8-C}_2\text{B}_9\text{H}_{10}]$ (0.760 g, 2.86 mmol) with NaH (0.690 g, 28.6 mmol) afforded, after column chromatography, $[\text{PMePh}_3][3,3'\text{-Co(1-CH}_2\text{CH}_2\text{OMe-2-Me-1,2-C}_2\text{B}_9\text{H}_9)_2]$ (yield 0.393 g, 40%). IR (KBr): ν (cm^{-1}) = 3051, 2994, 2811 (CH), 2551 (BH), 1440 (CH), 1117 (CO). ^1H -NMR: δ = 2.37 (s, 3H, BCCH_3), 2.60 (s, 3H, BCCH_3), 2.79 (d, $^2J(\text{P,H})$ = 13 Hz, 3H, CH_3P), 3.26–3.61 (m, 14H, (CH_2)₂ OCH_3), 7.56–7.86 (m, 15H, (C_6H_5)₃P). ^{11}B -NMR: δ = 5.77 (2B), 2.54, -4.93, -6.55, -9.14, -10.22, -12.24, -15.57 (16B). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 9.60 (d, $^1J(\text{C,P})$ = 59 Hz, CH_3P), 27.35 (BCCH_3), 36.63 (BC-CH_2-), 40.31 (BC-CH_2-), 58.37 (OCH_3), 71.73 (CH_2O), 73.81 (BC), 117.65 (d, $^1J(\text{C,P})$ = 74 Hz, PC_{ar}), 130.69 (d, $^3J(\text{C,P})$ = 13 Hz, $m\text{-Car}$), 132.80 (d, $^2J(\text{C,P})$ = 10 Hz, $o\text{-Car}$), 135.59 ($p\text{-Car}$). Anal. Calcd for $\text{C}_{31}\text{H}_{56}\text{B}_{18}\text{CoO}_2\text{P}$: C, 54.25; H, 8.22. Found: C, 53.88; H, 7.85.

Preparation of $\text{Cs}[3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{11})_2]$ (1). Method A: $[\text{NMe}_4][7,8\text{-C}_2\text{B}_9\text{H}_{12}]$ ²¹ (1.35 g, 7.00 mmol), *K-t*-BuO (3.90 g, 35.0 mmol), and anhydrous CoCl_2 (4.50 g, 35.0 mmol) in anhydrous dme (100 mL) afforded $\text{Cs}[3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{11})_2]$ (yield 1.51 g, 95%). The NMR and IR spectra of the product compare well with those already reported in the literature.^{4,5}

Preparation of $\text{Cs}[3,3'\text{-Co(1,2-}\mu\text{-(CH}_2)_3\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]$ (5). Method A: $[\text{NMe}_4][7,8\text{-}\mu\text{-(CH}_2)_3\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$ ⁶ (0.170 g, 0.690 mmol), *K-t*-BuO (0.387 g, 3.45 mmol), and anhydrous CoCl_2 (0.445 g, 3.45 mmol) in dried dme (50 mL) afforded $\text{Cs}[3,3'\text{-Co(1,2-}\mu\text{-(CH}_2)_3\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]$

(yield 0.139 g, 75%) as a red solid. Spectra were checked against the literature.⁶

Preparation of Cs[3,3'-Co(1-Ph-1,2-C₂B₉H₁₀)₂] (6). Method A: [NMe₄][7-Ph-7,8-C₂B₉H₁₁]²⁰ (1.00 g, 3.50 mmol), K-*t*-BuO (1.90 g, 17.5 mmol), and anhydrous CoCl₂ (2.30 g, 17.5 mmol) in dried dme (50 mL) afforded Cs[3,3'-Co(1-Ph-1,2-C₂B₉H₁₀)₂] as a red solid (yield 0.850 g, 80%). Spectra were checked against the literature.⁴

Preparation of [NMe₄][3,3'-Co(1-SEt-1,2-C₂B₉H₁₀)₂] (7). To 50 mL of deoxygenated dme containing [HNMe₃][7-SEt-7,8-C₂B₉H₁₀]^{18,19} (0.347 g, 1.36 mmol) were added K-*t*-BuO (1.38 g, 12.2 mmol) and anhydrous CoCl₂ (1.60 g, 12.2 mmol). The mixture was refluxed for 24 h. When the mixture was at room temperature, it was filtered and the solvent evaporated. A water/dichloromethane (1/1) mixture was added. Stirring was continued for 10 min before the two layers were separated. The organic layer was taken to dryness. The residue was dissolved in ethanol (5 mL), and an aqueous solution of [NMe₄]Cl was slowly added, resulting in the formation of a red precipitate. This was filtered off, washed with water and hexane, and dried in vacuum. Column chromatography (silica G, CH₂Cl₂/CH₃CN (10/1.5), *R_f* = 0.76) afforded [NMe₄][3,3'-Co(1-SEt-1,2-C₂B₉H₁₀)₂] (yield 0.24 g, 68%). IR(KBr): ν (cm⁻¹) = 3060, 2971, 2924, 2855 (CH), 2570 (BH). ¹H-NMR: δ = 1.17 (t, ¹J(H,H) = 7 Hz, 6H, CH₃), 2.76 (m, 4H, SCH₂), 3.46 (s, 12H, N(CH₃)), 3.99 (s, 2H, BCH). ¹¹B-NMR: δ = 8.12 (d, ¹J(B,H) = 134 Hz), 0.96 (d, ¹J(B,H) = 175 Hz), -3.26 (d, ¹J(B,H) = 144 Hz), -6.16 (d, ¹J(B,H) = 134 Hz), -7.65 (d, ¹J(B,H) = 144 Hz), -13.39 (d, ¹J(B,H) = 199 Hz), -15.62 (d, ¹J(B,H) = 165 Hz), -19.40 (d, ¹J(B,H) = 201 Hz). ¹³C{¹H}-NMR: δ = 12.76 (CH₃), 31.69 (SCH₂), 55.16 (N(CH₃)₄), 63.84 (BC), 76.00 (BC). Anal. Calcd for C₁₂H₄₂B₁₈CoNS₂: C, 27.82; H, 8.17; S, 12.38; N, 2.70. Found: C, 28.22; H, 8.06; S, 11.19; N, 2.69.

Preparation of [NMe₄][3,3'-Co(1-SEt-2-Me-1,2-C₂B₉H₉)₂] (8). The compound was prepared by both methods. Method A: Following the procedure described for **7**, [HNMe₃][7-SEt-8-Me-7,8-C₂B₉H₁₀]¹⁷ (0.730 g, 2.70 mmol), K-*t*-BuO (1.80 g, 16.2 mmol), and CoCl₂ (2.00 g, 16.2 mmol) afforded, after column chromatography (silica G, CH₂-Cl₂/CH₃CN (10/1), *R_f* = 0.38), [NMe₄][3,3'-Co(1-SEt-2-Me-1,2-C₂B₉H₉)₂] (yield 0.580 g, 79%). Method B: [HNMe₃][7-SEt-8-Me-

7,8-C₂B₉H₁₀]¹⁷ (0.730 g, 2.70 mmol), NaH (0.648 g, 27.0 mmol), and CoCl₂ (3.51 g, 27.0 mmol) afforded, after precipitation with [NMe₄]Cl and column chromatography, [NMe₄][3,3'-Co(1-SEt-2-Me-1,2-C₂B₉H₉)₂] (yield 0.258 g, 35%). IR(KBr): ν (cm⁻¹) = 2907, 2890 (CH), 2558 (BH). ¹H-NMR: δ = 1.13–1.27 (m, 6H, CH₃), 2.43 (s, 3H, BCCCH₃), 2.57 (s, 3H, BCCCH₃), 2.76 (m, 4H, SCH₂), 3.46 (s, 12H, N(CH₃)). ¹¹B-NMR: δ = 8.20 (d, ¹J(B,H) = 111 Hz), 0.268 (d, ¹J(B,H) = 58 Hz), -2.15, -4.07 (d, ¹J(B,H) = 143 Hz), -5.51 (d, ¹J(B,H) = 151 Hz), -7.15 (d, ¹J(B,H) = 151 Hz), -8.63 (d, ¹J(B,H) = 141 Hz), -11.41 (d, ¹J(B,H) = 168 Hz), -13.81 (d, ¹J(B,H) = 228 Hz). ¹³C{¹H}-NMR: δ = 12.87 (CH₃), 32.98 (CH₂), 55.22 (N(CH₃)₄), 72.12 and 73.23 (BC). Anal. Calcd for C₁₄H₄₆B₁₈CoNS₂: C, 30.79; H, 8.49; N, 2.56; S, 11.74. Found: C, 31.01; H, 8.34; N, 2.59; S, 11.14.

Preparation of [NMe₄][3,3'-Co(1-Me-1,2-C₂B₉H₁₀)₂] (9). Method A: [NMe₄][7-Me-7,8-C₂B₉H₁₁] (0.350 g, 1.60 mmol), K-*t*-BuO (0.898 g, 8.00 mmol), and anhydrous CoCl₂ (1.03 g, 8.00 mmol) in dry dme (30 mL) gave, upon addition of a 50% excess of aqueous [NMe₄]Cl, [NMe₄][3,3'-Co(1-Me-1,2-C₂B₉H₁₀)₂] (yield 0.315 g, 92.5%). IR (KBr): ν (cm⁻¹) = 3034, 2940 (CH), 2552 (BH), 1481, 1383 (CH). ¹H-NMR: δ = 2.42 (s, 6H, BCCCH₃), 3.45 (s, 12H, N(CH₃)₄), 4.12 (s, 2H, BCCCH₃). ¹¹B-NMR: δ = 8.33 (d, ¹J(B,H) = 130 Hz, 2B), 1.09 (d, ¹J(B,H) = 143 Hz, 2B), -3.74 (m, 6B), -9.22 (d, ¹J(B,H) = 158 Hz, 2B), -11.43 (d, ¹J(B,H) = 207 Hz, 2B), -16.40 (d, ¹J(B,H) = 149 Hz, 4B). ¹³C{¹H}-NMR: δ = 29.58 (BCCCH₃), 55.16 (N(CH₃)₄), 57.77 and 65.48 (BC). Anal. Calcd for C₉H₃₅B₁₈CoN: C, 26.31; H, 8.59; N, 3.41. Found: C, 26.70; H, 8.34; N, 3.05.

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Supporting Information Available: Tables of X-ray experimental details, positional and thermal parameters, interatomic distances and angles, anisotropic parameters, and least-squares planes for [PMePh₃]-[3,3'-Co(1,2-Et-1,2-C₂B₉H₉)₂] (15 pages). Ordering information is given on any current masthead page.

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