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Usage of $(C_5R_5)Co(CO)I_2$ (R = H, Me) for the synthesis of 12-vertex *closo*-cobaltacarboranes. Unexpected formation of 10-$\{CpCo(C_5H_4)\}$-7,8-Me_2-7,8-*nido*-$C_2B_9H_9$

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Dedicated to the 70th anniversary of Prof. Narayan Hosmane in recognition of his great contribution to the metallacarborane chemistry.

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ABSTRACT

A series of 12-vertex *closo*-cobaltacarboranes 1,2-R'_2-3-(C_5R_5)-3,1,2-$CoC_2B_9H_9$ (**1a**: R = R′ = H; **1b**: R = Me, R′ = H; **2a**: R = H, R′ = Me; **2b**: R = R′ = Me) were synthesized by reactions of the carbonyl cobalt complexes $(C_5R_5)Co(CO)I_2$ with Tl[Tl(η-7,8-R'_2-7,8-$C_2B_9H_9$)]. The reaction of $CpCo(CO)I_2$ with Tl[Tl(η-7,8-Me_2-7,8-$C_2B_9H_9$)] is accompanied by side formation of the novel charge-compensated *nido*-carborane 10-$\{CpCo(C_5H_4)\}$-7,8-Me_2-7,8-*nido*-$C_2B_9H_9$ (**3**) in 19% yield. The structures of **2a**,**b** and **3** were determined by X-ray diffraction.

1. Introduction

Several applications of cobaltacarboranes such as development of effective agents for boron neutron capture therapy (BNCT) of cancer or removal of radionuclides from nuclear waste solution have been reported [1]. Bis(dicarbollide)cobalt anion $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ is among the very important cobaltacarboranes known [2]. Replacement of one dicarbollide anion by $[C_5R_5]^-$ leads to neutral cobaltacarboranes 3-(C_5R_5)-3,1,2-$CoC_2B_9H_{11}$ [2a]. The parent compound 3-Cp-3,1,2-$CoC_2B_9H_{11}$ (**1a**) was synthesized by Hawthorne et al. from Cp^-, $[7,8\text{-}C_2B_9H_{11}]^{2-}$ and anhydrous $CoCl_2$ [3,4]. However, this method limits the use of the substituted cyclopentadienyl anions, e.g. $[Cp^*]^-$. In this respect, the use of $[(C_5R_5)CoI_2]_2$ is a more general approach for incorporating of the $(C_5R_5)Co$ species into the carborane cage [5]. In particular, we prepared pentamethyl derivative 3-Cp*-3,1,2-$CoC_2B_9H_{11}$ (**1b**) in 36% yield by reaction of $[Cp^*CoI_2]_2$ with Tl[Tl(η-7,8-$C_2B_9H_{11}$)].

In the last five years, the carbonyl derivatives $(C_5R_5)Co(CO)I_2$ have attracted attention of chemists due to their extraordinary catalytic activity in numerous organic transformations [6]. In contrast to $[(C_5R_5)CoI_2]_2$, these complexes are well soluble in organic solvents that is one of the reasons of their catalytic effectivity. The good solubility of $(C_5R_5)Co(CO)I_2$ and lability of their carbonyl ligand allow to use these complexes as synthons of the $(C_5R_5)Co$ species. For example, Welch with coworkers showed that reactions of them with $[7,9\text{-}nido\text{-}C_2B_{10}H_{12}]^{2-}$ result in 13-vertex *closo*-cobaltacarboranes 4-(C_5R_5)-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ [7]. Herein we report applicability of $(C_5R_5)Co(CO)I_2$ for synthesis of 12-vertex *closo*-cobaltacarboranes.

2. Results and discussion

We found that reactions of $(C_5R_5)Co(CO)I_2$ with Tl[Tl(η-7,8-$C_2B_9H_{11}$)] in boiling acetonitrile give the 12-vertex *closo*-cobaltacarboranes 3-(C_5R_5)-3,1,2-$CoC_2B_9H_{11}$ (**1a**,**b**; Scheme 1). It should be

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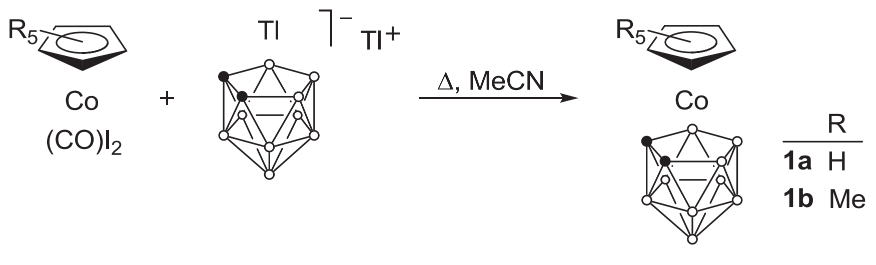


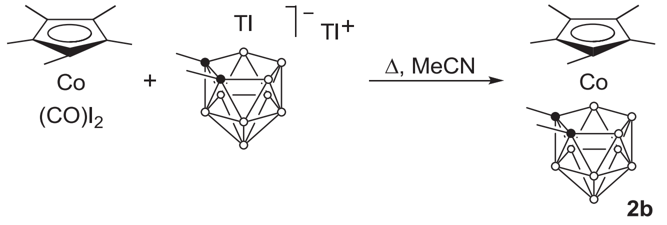
Scheme 1. Synthesis of the 12-vertex *closo*-cobaltacarboranes 3-(C_5R_5)-3,1,2-$CoC_2B_9H_{11}$ (**1a**,**b**).

noted that the yields in this case are expectedly higher than those for use of $[(C_5R_5)CoI_2]_2$ [5] as a starting materials (49 *vs.* 24% for **1a** and 48 *vs.* 36% for **1b**). Decreasing of the reaction temperature was found to have a negative impact on the product yield. For example, the pentamethyl derivative **1b** was obtained in only 36% yield when the reaction was proceeded at room temperature.

Going from the parent dicarbollide anion $[7,8\text{-}C_2B_9H_{11}]^{2-}$ to the *C*-methylated derivative $[7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9]^{2-}$, the yields of cobaltacarboranes considerably decrease that can be explained by sterical hindrance of methyl groups. For example, reaction of $Cp^*Co(CO)I_2$ with $Tl[Tl(\eta\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ gives 1,2-Me_2-3-Cp^*-3,1,2-$CoC_2B_9H_9$ (**2b**) in only 14% yield (Scheme 2).

Unexpectedly, we found that analogous synthesis of 1,2-Me_2-3-Cp-3,1,2-$CoC_2B_9H_9$ (**2a**) from $CpCo(CO)I_2$ and $Tl[Tl(\eta\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ in boiling acetonitrile is accompanied by side formation of the *B*-substituted *nido*-carborane 10-{$CpCo(C_5H_4)$}-7,8-Me_2-7,8-*nido*-$C_2B_9H_9$ (**3**, Scheme 3). The latter has zwitterionic structure and can be considered as charge-compensated dicarbollide ligand [8]. Earlier, the formation of a trace amount of the related *C*-substituted dicarbollide 7-{$CpCo(C_5H_4)$}-7,8-*nido*-$C_2B_9H_{11}$ was observed by Hawthorne and Churchill in reaction of $[7,8\text{-}C_2B_9H_{11}]^{2-}$ with excess Cp^- and $CoCl_2$ [3,9]. In the present work, we were able to synthesize complex **3** in 19% yield. It should be noted that **3** is formed even at room temperature although in low yield (5%).

A supposed pathway of the formation of **3** is illustrated in Scheme 4. Initially, complex $CpCo(CO)I_2$ undergoes disproportionation reaction with the formation of the cobaltocenium cation $[CoCp_2]^+$. The following reaction of the latter with carborane anion gives **3** as a result of electrophilic substitution at the B(10) atom. Earlier, Maitlis showed that the refluxing of complex $[CpCoI_2]_2$ (which are easily formed from $CpCo(CO)I_2$) in polar solvents leads to $[CoCp_2]^+$ [10], thus confirming our hypothesis. Moreover, Lewis and Welch observed the formation of the related indenyl rhodium complexes 9-{$(C_9H_6)Rh(C_9H_7)$}-7,8-*nido*-$C_2B_9H_{11}$ and 10-{$(C_9H_6)Rh(C_9H_7)$}-7,8-*nido*-$C_2B_9H_{11}$ in the reaction of $[(C_9H_7)RhCl_2]_n$ with $Tl[Tl(\eta\text{-}7,8\text{-}C_2B_9H_{11})]$ [11].



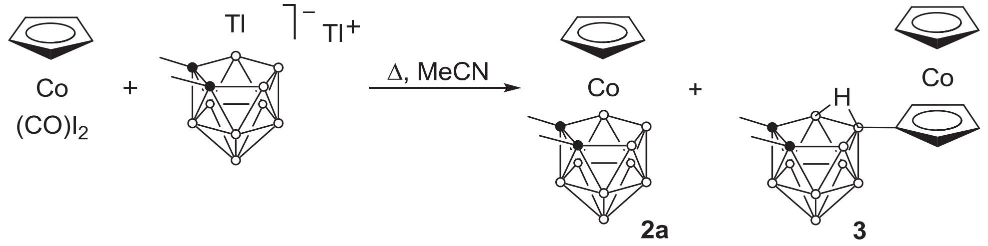
Scheme 2. Synthesis of the 12-vertex *closo*-cobaltacarborane 1,2-Me_2-3-Cp^*-3,1,2-$CoC_2B_9H_9$ (**2b**).

Complex **3** is air-stable solid. Besides singlet from the cage methyl groups, its ^1H NMR spectrum has one singlet from the unsubstituted Cp ligand (5.69 ppm) and two multiplets from the Cp ligand which attached to carborane (5.42 and 5.60 ppm). Noteworthy, these signals are shifted upfield as compared with those for the free cobaltocenium cation (5.91 ppm) that can be explained by compensation of the positive charge by the carborane anion. In the $^{11}B\{^1H\}$ NMR spectrum complex **3** reveals six broad singlets in accordance with the *Cs* symmetry. The signal of the B(10) atom is observed at $\delta = -28.1$ ppm and shifted downfield by 4.6 ppm as compared with that for the parent anion $[7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ [12].

The structures of **2a**,**b** and **3** were determined by X-ray diffraction (Figs. 1–3). The dihedral angles between C_5 and C_2B_3 planes in *closo*-cobaltacarboranes **2a**,**b** (8.4 and 10.2°) are considerably higher than those in the cage-unmethylated analogs **1a**,**b** (1.9 and 1.8°) [7,13] that is caused by the steric effect of two cage methyl groups. For the same reason, the Co···Cp* and Co···C_2B_3 distances in **2b** (1.695 and 1.439 Å, respectively) are longer than the corresponding distances in **1b** (1.664 and 1.430 Å) [7]. Noteworthy, the cage C—C bond in *closo*-cobaltacarboranes **2a**,**b** (1.663 and 1.661 Å) is considerably longer than that in *nido*-carborane **3** (1.580 Å). It is evidently connected with a loosening of all bonds in the C_2B_3 face upon coordination with the cobalt atom.

3. Conclusion

The carbonyl cobalt complexes $(C_5R_5)Co(CO)I_2$ were shown to be appropriate synthons for incorporating of the $(C_5R_5)Co$ species into



Scheme 3. Reaction of $CpCo(CO)I_2$ and $Tl[Tl(\eta\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$. The formation of 10-{$CpCo(C_5H_4)$}-7,8-$Me_2$-7,8-*nido*-$C_2B_9H_9$ (**3**).

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