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3,2,1 and stop! An innovative, straightforward and clean route for the flash synthesis of metallacarboranes†

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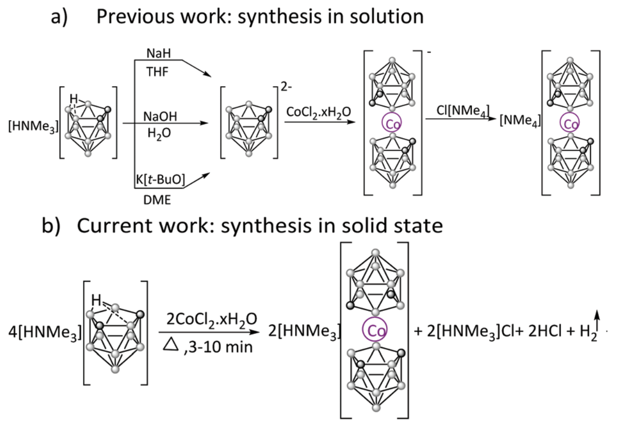
$[Co(C_2B_9H_{11})_2]^-$, analogs to metallocene, can be readily synthesised in high yield by a fast and clean solvent-free reaction of $[HNMe_3][C_2B_9H_{12}]$ with $CoCl_2{\cdot}xH_2O$. This innovative approach, applied to both *ortho* and *meta* isomers, yields the desired structures by simply heating the solid compounds to high temperature for a very short time.

Metallacarboranes are 3D boron hydride clusters that incorporate metal atoms or units in their polyhedral skeletons.[1] They find many applications in materials, sensors/biosensors and medicine, among others.[2] Metallacarboranes $[M(C_2B_9H_{11})_2]^-$ ($M = Fe^{3+}$, Co^{3+}), which were reported in 1965 [3] are the most studied. $[M(C_2B_9H_{11})_2]^-$ were synthesised from the *nido* $[C_2B_9H_{12}]^-$ cluster in two steps: (i) first, deprotonation of $[C_2B_9H_{12}]^-$ produces *nido* $[C_2B_9H_{11}]^{2-}$ which then (ii) reacts with metal-containing reagents yielding stable anionic metallacarboranes.[3] The insertion of metal into the *nido* $[C_2B_9H_{12}]^-$ ion is extremely versatile for two reasons: (i) the *nido* $[C_2B_9H_{12}]^-$ ion withstands harsh reaction conditions (*e.g.* strong bases or reflux temperatures) and (ii) completion of the icosahedron is, in general, strongly thermodynamic and kinetic favoured. The synthesis of $[M(C_2B_9H_{11})_2]^-$ has been reported in both non-aqueous and aqueous media by using NaH in dry THF or a freshly prepared hot 40% NaOH aqueous solution, respectively, to deprotonate the H_{bridge} of the *nido*-cluster.[4] The complexation reaction with MCl_2 required the reaction mixture to be stirred at reflux temperature under nitrogen for 3 hours. In both methods the work-up to isolate the pure $[M(C_2B_9H_{11})_2]^-$ is tedious.[4] A one-pot reaction method in anhydrous DME that uses K[*t*-BuO] as a base and anhydrous MCl_2 was reported to produce $[M(C_2B_9H_{11})_2]^-$ derivatives in high yield requiring much less work-up (Scheme 1a).[5] This route is, however, time consuming and implies dealing with DME, a solvent with a high boiling point and hence, difficult to remove from the reaction flask.

Solvent-free transformations are an essential approach to the sustainability of organic and organometallic synthesis[6] through the 21st century due to its efficiency in minimizing waste.[7,8] In this work, the new expeditive syntheses of $[M(C_2B_9H_{11})_2]^-$ ($M = Co^{3+}$) and their C_c-substituted derivative compounds have been established by exploring the reactivity of *nido* $[HNMe_3][C_2B_9H_{12}]$ with $CoCl_2{\cdot}xH_2O$ under solvent-free conditions in the absence of bases at high temperature during a very short time (minutes). The main objective was to design an easy, one-pot route to synthesise the pristine $[Co(C_2B_9H_{11})_2]^-$ and their C_c-substituted derivatives in a high yield in a rapid and efficient reaction.

The solvent-free reaction between *nido* $[HNMe_3]$ $[7,8\text{-}C_2B_9H_{12}]$ and $CoCl_2{\cdot}xH_2O$ ($x = 0, 6$) was performed by heating the two solid reagents at 350 °C (also at 250 °C) into a Pyrex tube. As displayed in Table 1, several parameters such as temperature, reaction time, nature of the $CoCl_2$ reagent (anhydrous or hydrated) as well as the $CoCl_2/[NHMe_3]$ $[C_2B_9H_{12}]$ molar ratio were studied.



Scheme 1

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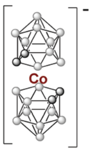
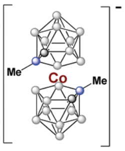
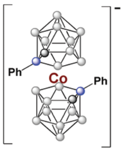
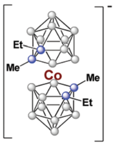
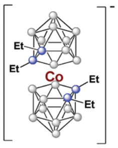
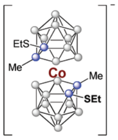
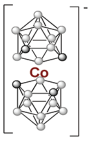
† Electronic supplementary information (ESI) available: Synthesis characterization of the cobaltabis(dicarbollide) complexes and X-ray studies of $[HNMe_3][2,2'\text{-}Co(1,7\text{-}C_2B_9H_{12})_2]$. CCDC 1882757. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8gc03943g

Table 1 Representative parameters for the complexation reaction

Cluster	Entry	Conditions		Molar ratio $CoCl_2$/ $[HNMe_3][nido\text{-}C_2B_9H_{12}]$	Yield %
		Time (min)	T (°C)		
	1	3	350	1.5 $CoCl_2$ anh.	83
	2	5	350	1.5 $CoCl_2$ anh.	85
	3	7	350	1.5 $CoCl_2$ anh.	88
	4	7	350	1.5 $CoCl_2{\cdot}6H_2O$	90
	5	8	350	1.5 $CoCl_2{\cdot}6H_2O$	88
	6	2	350	1.5 $CoCl_2$ anh.	42
	7	3	350	1.5 $CoCl_2$ anh.	46
	8	3	470	1.5 $CoCl_2$ anh.	68
	9	5	350	1.5 $CoCl_2$ anh.	75
	10	10	350	1.5 $CoCl_2$ anh.	90
	11	2 + 6	350 + 470	1.5 $CoCl_2{\cdot}6H_2O$	87
	12	2 + 6	350 + 470	1.5 $CoCl_2{\cdot}6H_2O$	88
	13	2 + 6	350 + 470	2.5 $CoCl_2{\cdot}6H_2O$	94
	14	2 + 6	350 + 470	2.5 $CoCl_2$ anh.	60
	15	10	350	5.5 $CoCl_2$ anh.	83
 mixture	16	2	350	2.5 $CoCl_2$ anh.	82[a]
	17	8	250	2.5 $CoCl_2$ anh.	68[a]
	18	8	250	2.5 $CoCl_2{\cdot}6H_2O$	78[a]
 mixture	19	2	350	2.5 $CoCl_2$ anh.	68[a]
	20	8	250	2.5 $CoCl_2$ anh.	62[a]
	21	8	250	2.5 $CoCl_2{\cdot}6H_2O$	70[a]
	22	8	470	2.5 $CoCl_2$ anh.	50
	23	5	350	2.5 $CoCl_2$ anh.	40
	24	10	350	2.5 $CoCl_2$ anh.	47
	25	15	350	2 $CoCl_2$ anh.	52
	26	15	350	2.5 $CoCl_2$ anh.	74

[a] Yield related to the cobaltabis(dicarbollide) mixture.

Upon completion of the reaction, water was added to the crude product before extracting with ethyl ether. Surprisingly, the formation of cobalt metal was not observed. This was typical in the wet methods as Co(II) dismutates to Co(III) and Co.[4] The orange organic phase was separated from the pink aqueous phase, the solvent removed in vacuum, and the residue taken up in water. This solution was treated with an aqueous solution of $Cl[NMe_4]$ to give the less soluble $[NMe_4][3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ complex, which was confirmed by ^{11}B- and ^1H NMR spectra. The yield provided in Table 1 is related to the $[NMe_4]^+$ cation in all experiments.

As demonstrated in entries 3 and 4, no significant effect on final yield was observed when using anhydrous $CoCl_2$ with respect to the $CoCl_2{\cdot}6H_2O$.

Once the synthesis of the pristine $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ complex was achieved, we tested if the synthesis of $C_{cluster}$-substituted cobaltabis(dicarbollide) complexes could be accomplished. Reaction was run by using the same method and conditions but starting with the monosubstituted $[HNMe_3][8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]$ (R = Me, Ph) ligands.

This new reaction led to the formation of $[NMe_4][3,3'\text{-}Co(1\text{-}Me\text{-}1,2\text{-}C_2B_9H_{10})_2]$ and $[NMe_4][3,3'\text{-}Co(1\text{-}Ph\text{-}1,2\text{-}C_2B_9H_{10})_2]$ sandwich with yields equal to 90% after 10 min and 94% after 8 min, respectively (entries 10 and 13). It was noticed that the presence of one methyl or aryl group linked to the $C_{cluster}$ decreases the reaction's yield; however, very good yields were still obtained in only 10 minutes of heating in comparison with the traditional method that takes around 1440 minutes to give rise to the same compound, but with a yield difference of approx. 5%. Time of reaction also has a positive impact on the final yield. As illustrated in Table 1, entries 7 and 9, the yield rises significantly with increase in reaction time, namely from 3 to 5 minutes. Furthermore, if temperature is increased by 120 °C (entries 7 and 8), a consequently boost in yield of about 22% is observed. Reactions with $CoCl_2{\cdot}xH_2O$ (x = 0, 6) have also been conducted at 250 °C just extending the reaction time 6 extra minutes with comparable yields to these in the table.

Based on these utmost positive results, the complexation reactions of disubstituted *nido* units ($[HNMe_3][7\text{-}R\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]$ (R = R′ = Et; R = Me, R′ = Et and R = Ph, R′ = Et)) were investigated. Our approach was shown to work with both $[HNMe_3][7\text{-}Me\text{-}8\text{-}Et\text{-}7,8\text{-}C_2B_9H_{10}]$ and $[HNMe_3][7,8\text{-}Et_2\text{-}7,8\text{-}C_2B_9H_{10}]$, leading to $[Co(C_2B_9H_{11})_2]^-$ derivatives with yields above 70%. However, the ethyl units were lost in part (*vide infra*). On the other hand, the linkage of the aryl substituent to the C_2B_3 face in the presence of the ethyl group hinders the formation of the complex. Therefore, our next step was to study the effect of the lone pair of electrons on the complexation reactions. Starting from *closo* $1\text{-}R\text{-}2\text{-}R'\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = R′ = SEt; R = Me, R′ = SEt and R = Ph, R′ = SEt), *via* a partial deboronation reaction, *nido* ligands $[HNMe_3][7\text{-}R\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]$ (R = R′ = SEt; R = Me, R′ = SEt and R = Ph, R′ = SEt)[9] were synthesised (see ESI†).

Out of these three compounds, only $[HNMe_3][7\text{-}Me\text{-}8\text{-}SEt\text{-}7,8\text{-}C_2B_9H_{10}]$, yielded 50% of the target complex, which confirms the inhibition of the solid state reaction when hindrance and/or electronic alterations exist (entry 22). Nevertheless, the yield of the $[HNMe_3][3,3'\text{-}Co(1\text{-}Me\text{-}2\text{-}SEt\text{-}C_2B_9H_9)_2]$ was low compared to the previously obtained complexes. The yield for this particular $[HNMe_3][7\text{-}Me\text{-}8\text{-}SEt\text{-}7,8\text{-}C_2B_9H_{10}]$ ligand using traditional methods was of 79% with K[*t*-BuO] and 35% when NaH was employed.[5] Having obtained such good results and satisfactory yields by using this new solid state complexation reaction on *ortho*–*nido* species, the behaviour of the *meta*–*nido* isomer, $[HNMe_3][7,9\text{-}C_2B_9H_{12}]$, was our target.

The $[NMe_4][2,2'\text{-}Co(1,7\text{-}C_2B_9H_{11})_2]$ complex was obtained in 74% yield after heating at 350 °C for 15 min. The *meta*-isomer needed more time to produce a comparable good yield to the *ortho*-isomer. Table 1 summarises the different guidelines used to find the optimal parameters for all obtained sandwich complexes. The direct isolation of the complexes having cobalt in the formal +3 oxidation state was not accompanied by the formation of cobalt metal. This observation suggests that the initially Co^{2+} is rapidly oxidized to form the more stable d^6 metallabis(dicarbollide) complex 18 e^- count avoiding reduction from Co^{2+} to Co^0. This is proof that the free-solvent synthesis of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ takes place *via* another mechanism than the previously reported synthesis in solution.

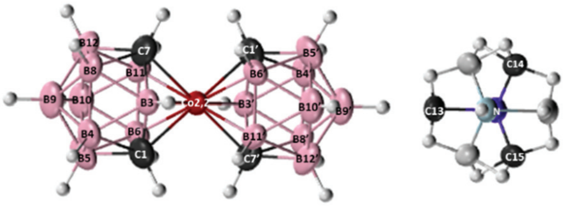


Fig. 1 Perspective view of the $[HNMe_3][2,2'\text{-}Co(1,7\text{-}C_2B_9H_{11})_2]$ unit with 50% ellipsoids. Selected bond lengths (Å): C1–B3═C7–B3 = 1.727(7) Å, C1–B6═C7–B11 = 1.683(7) Å, B11–B6 = 1.706(7) Å.

To discern on the reaction pathway, several studies were run. The solvent-free reaction's progress was controlled by the colour change of the mixture as well as liberation of gas. To determine the identity of the evolved gas, a water solution monitored by a pH meter was prepared. As the pH of this aqueous solution did not change, the generated gas was not NMe_3, but probably hydrogen. The next study was to measure the pH of the aqueous phase of the extraction process, which provided a value of 6.33 suggesting that an acid had been generated. Both experiments along with the observation that no Co^0 was produced and the ^{11}B NMR evidence that $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ was obtained, agree with the balanced equation displayed at Scheme 1(b). The solvent-free synthetic reaction takes place by an oxidation–reduction reaction that involves the two redox couples Co^{3+}/Co^{2+} and H_2O/OH^-. Moreover, X-ray diffraction of $[HNMe_3][2,2'\text{-}Co(1,7\text{-}C_2B_9H_{11})_2]$ fully supports that the cation is $[HNMe_3]^+$ (Fig. 1).[10]

The MS spectra of $[NMe_4][Co(1\text{-}Me\text{-}2\text{-}Et\text{-}1,2\text{-}C_2B_9H_9)_2]$ and $[NMe_4][Co(1,2\text{-}Et_2\text{-}1,2\text{-}C_2B_9H_9)_2]$ are clear in showing that some of the ethyl groups are lost/won during the formation of the cobaltabis(dicarbollide) cluster from the *nido* components and $CoCl_2(xH_2O)$, x = 0, 6. We do not know at what stage of the complex building the transfer of ethyl units occurs, but it is clear that at 250 °C some of the ethyl units are lost or won. Our interpretation is that at some stage of the building process β-hydride elimination occurs, (ESI†) that is consistent with NMR spectra indicating co-existence of some $[Co(C_2B_9H_{11})_2]^-$ derivatives.

Conclusions

A new, fast and environmentally-friendly solid state reaction for the syntheses of cobaltabis(dicarbollides) is presented. Our approach is a significant improvement on the traditional syntheses in solution in both speed of reaction and generated yield. We demonstrate that the $[Co(C_2B_9H_{11})_2]^-$ building reaction works well with starting plain, single or double $C_{cluster}$-substituted *nido* clusters. However, care has to be taken when β-hydride elimination may take place because in this case the resulting $[Co(C_2B_9H_{11})_2]^-$ derivative may be different to the expected one based on the precursor *nido* cluster due to the β-hydride elimination, as commonly occurs in organometallic chemistry. The presence of substituents bearing a free pair of electrons also influences the complex formation. *Meta*-isomers also give rise to the corresponding cobaltabis(dicarbollide), but in this case, the reaction time needs to be increased. A suggested mechanism of the complexation reaction is proposed, based on identifying the chemical nature of the evolved gas, the pH of the mixture, the crystal structure of the target complex and the absence of Co^{2+} dismutation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

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10 Crystal data for $C_7H_{32}B_{18}CoN$: monoclinic, space group $C2/m$, a = 9.130(11) Å, b = 10.446(10) Å, c = 11.101(9) Å, V = 1014.44 $Å^3$, Z = 2, T = 100(2) K, measured reflections 24 871, independent reflections 856, R_{int} = 0.0325, R_1 = 0.0677, wR_2 = 0.1743. CCDC 1882757.†