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

Ines Bennour, Ana M. Cioran, Francesc Teixidor 🕩 and Clara Viñas 🕩 *

 $[Co(C_2B_9H_{11})_2]^-$, 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(C₂B₉H₁₁)₂]⁻ $(M = Fe^{3+}, Co^{3+})$, which were reported in 1965³ are the most studied. $[M(C_2B_9H_{11})_2]^-$ were synthesised from the *nido* [C2B9H12]⁻ 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 nidocluster.⁴ The complexation reaction with MCl₂ 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 MCl₂ 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 synthesis⁶ 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 = Co³⁺) and their C_c-substituted derivative compounds have been established by exploring the reactivity of *nido* [HNMe₃][C₂B₉H₁₂] with CoCl₂·*x*H₂O 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* [HNMe₃] [7,8-C₂B₉H₁₂] and CoCl₂·xH₂O (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 CoCl₂ reagent (anhydrous or hydrated) as well as the CoCl₂/[NHMe₃] [C₂B₉H₁₂] molar ratio were studied.



Institut de Ciència de Materials de Barcelona (ICMAB-CSIC). Campus UAB, 08193 Bellaterra, Barcelona, Spain. E-mail: clara@icmab.es

[†] Electronic supplementary information (ESI) available: Synthesis characterization of the cobaltabis(dicarbollide) complexes and X-ray studies of [HNMe₃][2,2'-Co(1,7-C₂B₉H₁₂)₂]. CCDC 1882757. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8gc03943g

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Table 1	Representative p	parameters for th	e complexation reaction
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Entry Time (min) T (°C) MOM TABOAC, [3, H ₁] Vield '8 1 3 50 1.5 GCl, anh. 83 3 7 350 1.5 GCl, anh. 83 3 7 350 1.5 GCl, anh. 83 3 7 350 1.5 GCl, anh. 88 5 8 350 1.5 GCl, anh. 88 7 3.50 1.5 GCl, anh. 42 7 3.50 1.5 GCl, anh. 42 7 3 350 1.5 GCl, anh. 43 9 5 350 1.5 GCl, anh. 42 10 10 10 350 1.5 GCl, anh. 43 11 2+6 350+470 2.5 GCl, anh. 68 12 2+6 350 2.5		Entry	Conditions			
$\begin{bmatrix} 1 & 3 & 50 & 15 \operatorname{Cocl} \operatorname{anh.} & 83 \\ 3 & 7 & 350 & 15 \operatorname{Cocl} \operatorname{anh.} & 83 \\ 3 & 7 & 350 & 15 \operatorname{Cocl} \operatorname{cocl} \operatorname{anh.} & 89 \\ 3 & 7 & 350 & 15 \operatorname{Cocl} \operatorname{cocl} \operatorname{anh.} & 89 \\ 5 & 8 & 350 & 15 \operatorname{Cocl} \operatorname{cocl} \operatorname{anh.} & 89 \\ 5 & 8 & 350 & 15 \operatorname{Cocl} \operatorname{cocl} \operatorname{anh.} & 42 \\ 4 & 3 & 370 & 15 \operatorname{Cocl} \operatorname{cocl} \operatorname{anh.} & 46 \\ 8 & 3 & 470 & 15 \operatorname{Cocl} \operatorname{anh.} & 46 \\ 9 & 5 & 350 & 15 \operatorname{Cocl} \operatorname{anh.} & 75 \\ 10 & 10 & 350 & 15 \operatorname{Cocl} \operatorname{cocl} \operatorname{anh.} & 75 \\ 11 & 2 + 6 & 350 + 470 & 1.5 \operatorname{Cocl} \operatorname{anh.} & 75 \\ 11 & 2 + 6 & 350 + 470 & 1.5 \operatorname{Cocl} \operatorname{cocl} \operatorname{anh.} & 69 \\ 13 & 2 + 6 & 350 + 470 & 1.5 \operatorname{Cocl} \operatorname{cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Cocl} \operatorname{anh.} & 83 \\ 14 & 2 + 6 & 350 + 470 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 83 \\ 15 & 10 & 350 & 5.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 21 & 8 & 250 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 21 & 8 & 250 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 21 & 8 & 250 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 60 \\ 15 & 21 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 70 \\ 15 & 22 & 15 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 70 \\ 15 & 25 & 25 \operatorname{Cocl} \operatorname{anh.} & 70 \\ 15 & 25 & 25 & 25 & 25 & 25 & 25 & 25 \\ 15 & 350 & 2.5 \operatorname{Cocl} \operatorname{anh.} & 70 \\ 15 & 25 & 25 & 25 & 25 & 25 & 25 & 25 &$	Cluster		Time (min)	T (°C)	Molar ratio CoCl ₂ / [HNMe ₃][<i>nido</i> -C ₂ B ₉ H ₁₂]	Yield %
$\begin{bmatrix} 2 & 5 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 85 \\ 4 & 7 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 88 \\ 4 & 7 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 49 \\ 5 & 8 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 42 \\ 6 & 2 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 42 \\ 8 & 3 & 470 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 42 \\ 8 & 3 & 470 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 46 \\ 8 & 3 & 470 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 68 \\ 9 & 5 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 68 \\ 9 & 5 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 68 \\ 9 & 5 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 68 \\ 9 & 5 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 68 \\ 10 & 0 & 350 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 69 \\ 11 & 2 & 4 & 6 & 350 + 470 & 1.5 \operatorname{CoCl} \operatorname{anh.} & 90 \\ 13 & 2 + 6 & 350 + 470 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{CoCl} \operatorname{anh.} & 83 \\ 16 & 2 & 350 & 470 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 83 \\ 16 & 2 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 83 \\ 16 & 2 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 66^{47} \\ 17 & 8 & 250 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 66^{47} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 66^{47} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 66^{47} \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 66^{47} \\ 22 & 8 & 470 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 67^{47} \\ 18 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 67^{47} \\ 22 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 67^{47} \\ 22 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 67^{47} \\ 22 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 67^{47} \\ 24 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 40 \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 40 \\ 42 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 40 \\ 42 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 40 \\ 42 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 15 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 4 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 4 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 4 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 4 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 & 4 & 10 & 350 & 2.5 \operatorname{CoCl} \operatorname{anh.} & 47 \\ 42 &$		1	3	350	1.5 CoCl ₂ anh.	83
$ \begin{array}{c c c c c c c } 3 & 7 & 350 & 1.5 \text{Coll} \text{ahh}, & 88 \\ 5 & 8 & 350 & 1.5 \text{Coll} \text{ahh}, & 88 \\ 5 & 8 & 350 & 1.5 \text{Coll} \text{ahh}, & 42 \\ 7 & 3 & 350 & 1.5 \text{Coll} \text{ahh}, & 42 \\ 7 & 3 & 350 & 1.5 \text{Coll} \text{ahh}, & 46 \\ 7 & 3 & 350 & 1.5 \text{Coll} \text{ahh}, & 46 \\ 9 & 5 & 350 & 1.5 \text{Coll} \text{ahh}, & 46 \\ 9 & 5 & 350 & 1.5 \text{Coll} \text{ahh}, & 75 \\ 10 & 10 & 350 & 1.5 \text{Coll} \text{ahh}, & 75 \\ 10 & 10 & 350 & 1.5 \text{Coll} \text{ahh}, & 75 \\ 11 & 2 + 6 & 350 + 470 & 1.5 \text{Coll} \text{ahh}, & 90 \\ 13 & 2 + 6 & 350 + 470 & 1.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 5.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 5.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 5.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 5.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 5.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 5.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 5.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 350 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 350 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 20 & 8 & 250 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 20 & 8 & 250 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 20 & 8 & 250 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 15 & 21 & 8 & 250 & 2.5 \text{Coll} \text{ahh}, & 60 \\ 16 & 20 & 350 & 2.5 \text{Coll} \text{ahh}, & 40 \\ 16 & 21 & 350 & 2.5 \text{Coll} \text{ahh}, & 40 \\ 16 & 21 & 350 & 2.5 \text{Coll} \text{ahh}, & 47 \\ 24 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 47 \\ 24 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 47 \\ 24 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 47 \\ 24 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 47 \\ 24 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 47 \\ 24 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 47 \\ 24 & 10 & 350 & 2.5 \text{Coll} \text{ahh}, & 47 \\ 24 & 15 & 350 & 2.5 \text{Coll} \text{ahh}, & 4$		2	5	350	1.5 CoCl ₂ anh.	85
$ \frac{4}{5} + \frac{7}{8} + \frac{350}{350} + \frac{15 \operatorname{Col}_{2}\operatorname{GH}_{2}O}{1.5 \operatorname{Col}_{2}\operatorname{GH}_{2}O} + \frac{99}{8} + \frac{4}{5} + \frac{7}{8} + \frac{350}{350} + \frac{15 \operatorname{Col}_{2}\operatorname{GH}_{2}O} + \frac{99}{8} + \frac{15 \operatorname{Col}_{2}\operatorname{GH}_{2}O} + \frac{12}{8} + \frac{2}{350} + \frac{15 \operatorname{Col}_{2}\operatorname{GH}_{2}O} + \frac{42}{8} + \frac{44}{8} + \frac{42}{8} + \frac{44}{8} + \frac{42}{8} + \frac{44}{8} + \frac{42}{8} + \frac{44}{8} + \frac{44}{$		3	7	350	$1.5 \operatorname{CoCl}_{2}$ anh.	88
5 8 350 1.5 CoCl_aCH_O 88 4 6 2 350 1.5 CoCl_anh, 42 42 4 8 3 350 1.5 CoCl_anh, 42 42 4 8 3 350 1.5 CoCl_anh, 42 42 4 8 3 350 1.5 CoCl_anh, 42 43 4 9 5 350 1.5 CoCl_anh, 42 44 4 9 350 1.5 CoCl_anh, 42 44 4 9 350 1.5 CoCl_anh, 470 46 11 2 + 6 350 + 470 1.5 CoCl_aCH_2O 88 13 2 + 6 350 + 470 2.5 CoCl_anh, 60 94 14 2 + 6 350 + 470 2.5 CoCl_anh, 60 94 15 10 350 2.5 CoCl_anh, 60 83 16 2 350 2.5 CoCl_anh, 66 84 10 2 350 2.5 CoCl_anh, 66 62 10 2 350 2.5 CoCl_anh, 62 62 10 2 <t< td=""><td>Co</td><td>4</td><td>7</td><td>350</td><td>1.5 CoCla6HaO</td><td>90</td></t<>	Co	4	7	350	1.5 CoCla6HaO	90
Image: state of the state		5	8	350	$1.5 \operatorname{CoCl}_2 \cdot 6H_2O$	88
$\begin{bmatrix} 6 & 2 & 350 & 1.5 \operatorname{Coch} anh. & 42 \\ 8 & 3 & 470 & 1.5 \operatorname{Coch} anh. & 46 \\ 9 & 5 & 350 & 1.5 \operatorname{Coch} anh. & 68 \\ 9 & 5 & 350 & 1.5 \operatorname{Coch} anh. & 69 \\ 10 & 10 & 350 & 1.5 \operatorname{Coch} anh. & 75 \\ 10 & 11 & 2+6 & 350+470 & 1.5 \operatorname{Coch} anh. & 90 \\ 11 & 2+6 & 350+470 & 2.5 \operatorname{Coch} anh. & 90 \\ 13 & 2+6 & 350+470 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Coch} anh. & 83 \\ 13 & 2+6 & 350+470 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Coch} anh. & 83 \\ 14 & 2+6 & 350+470 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60 \\ 15 & 20 & 8 & 250 & 2.5 \operatorname{Coch} anh. & 60^{2^{d}} \\ 20 & 8 & 250 & 2.5 \operatorname{Coch} anh. & 60^{2^{d}} \\ 21 & 8 & 250 & 2.5 \operatorname{Coch} anh. & 60^{2^{d}} \\ 21 & 8 & 250 & 2.5 \operatorname{Coch} anh. & 60^{2^{d}} \\ 22 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 60^{2^{d}} \\ 22 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 40 \\ 22 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 22 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 24 & 10 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 13 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 26 & 15 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 26 & 15 & 350 & 2.5 \operatorname{Coch} anh. & 47 \\ 25 & 25 & 25 & 25 & 25 & 25 & 25 & 25$						
$\begin{bmatrix} 7 & 3 & 350 & 1.5 \operatorname{CoCl} anh. & 46 \\ 9 & 5 & 350 & 1.5 \operatorname{CoCl} anh. & 69 \\ 9 & 5 & 350 & 1.5 \operatorname{CoCl} anh. & 75 \\ 10 & 10 & 350 & 1.5 \operatorname{CoCl} anh. & 90 \\ 11 & 2+6 & 350+470 & 1.5 \operatorname{CoCl} efH_2O & 87 \\ 13 & 2+6 & 350+470 & 2.5 \operatorname{CoCl} efH_2O & 94 \\ 14 & 2+6 & 350+470 & 2.5 \operatorname{CoCl} anh. & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{CoCl} anh. & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{CoCl} anh. & 63 \\ 16 & 2 & 350 & 2.5 \operatorname{CoCl} anh. & 68 \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl} anh. & 66^{24} \\ 22 & 8 & 470 & 2.5 \operatorname{CoCl} anh. & 60^{24} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl} anh. & 40 \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl} anh. & 40 \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl} anh. & 40 \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl} anh. & 47 \\ 25 & 15 & 350 & 2.$		6	2	350	1.5 CoCl ₂ anh.	42
$ \frac{8}{9} + \frac{3}{5} + \frac{3}{350} + \frac{470}{1.5 \text{ CoCl}_3 \text{ anh.}}{1.5 \text{ CoCl}_3 \text{ anh.}} + \frac{68}{77} + \frac{77}{75} + \frac{77}{75} + \frac{10}{10} + \frac{10}{10} + \frac{350}{350} + \frac{15 \text{ CoCl}_3 \text{ anh}}{1.5 \text{ CoCl}_3 \text{ anh}} + \frac{90}{90} + \frac{11}{11} + \frac{2}{2} + 6 + \frac{350}{350} + \frac{470}{1.5 \text{ CoCl}_3 \text{ GH}_3 O} + \frac{88}{77} + \frac{11}{11} + \frac{2}{2} + 6 + \frac{350}{350} + \frac{470}{1.5 \text{ CoCl}_3 \text{ GH}_3 O} + \frac{88}{77} + \frac{11}{14} + \frac{2}{2} + 6 + \frac{350}{350} + \frac{470}{2.5 \text{ CoCl}_3 \text{ GH}_3 O} + \frac{88}{97} + \frac{11}{14} + \frac{2}{2} + 6 + \frac{350}{350} + \frac{470}{2.5 \text{ CoCl}_3 \text{ anh}} + \frac{60}{60} + \frac{11}{15} + \frac{10}{10} + \frac{350}{350} + \frac{55}{50} \text{ CoCl}_2 \text{ anh} + \frac{82^{4}}{60} + \frac{88^{4}}{17} + \frac{88}{8} + \frac{250}{250} + \frac{2.5 \text{ CoCl}_3 \text{ anh}} + \frac{82^{4}}{68^{4}} + \frac{88^{4}}{17} + \frac{88}{8} + \frac{250}{250} + \frac{2.5 \text{ CoCl}_3 \text{ anh}} + \frac{68^{4}}{68^{4}} + \frac{68^{4}}{17} + \frac{19}{20} + \frac{2}{2} + \frac{350}{250} + \frac{2.5 \text{ CoCl}_3 \text{ anh}} + \frac{68^{4}}{62^{4}} + \frac{68^{4}}{21} + \frac{19}{8} + \frac{250}{250} + \frac{2.5 \text{ CoCl}_3 \text{ anh}} + \frac{68^{4}}{62^{4}} + \frac{68^{4}}{21} + \frac{19}{8} + \frac{250}{250} + \frac{2.5 \text{ CoCl}_3 \text{ anh}} + \frac{68^{4}}{62^{4}} + \frac{68^{4}}{21} + \frac{10}{8} + \frac{250}{250} + \frac{2.5 \text{ CoCl}_3 \text{ anh}} + \frac{68^{4}}{62^{4}} + \frac{62^{4}}{10} + \frac{10}{25} + \frac{25}{20} + \frac{2.5 \text{ CoCl}_3 \text{ anh}} + \frac{68^{4}}{20} + \frac{62^{4}}{250} + \frac{2.5 \text{ CoCl}_3 \text{ anh}} + \frac{68^{4}}{20} + \frac{10}{25} + \frac{10}{2$		7	3	350	1.5 CoCl ₂ anh.	46
$ \begin{bmatrix} 9 & 5 & 350 & 1.5 \operatorname{CoCl}_3 \operatorname{nh}_1 & 75 \\ 10 & 10 & 350 & 1.5 \operatorname{CoCl}_3 \operatorname{nh}_1 & 99 \\ 11 & 2+6 & 350 + 470 & 1.5 \operatorname{CoCl}_2 \operatorname{cH}_2 O & 88 \\ 13 & 2+6 & 350 + 470 & 2.5 \operatorname{CoCl}_2 \operatorname{cH}_2 O & 94 \\ 14 & 2+6 & 350 + 470 & 2.5 \operatorname{CoCl}_2 \operatorname{anh}_1 & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 83 \\ 16 & 2 & 350 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 82^d \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 82^d \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 10 & 8 & 250 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 62^d \\ 20 & 2.5 \operatorname{CoCl}_3 \operatorname{anh}_1 & 74^d \\ $	Me	8	3	470	1.5 CoCl ₂ anh.	68
$\begin{bmatrix} 10 & 10 & 350 & 1.5 \operatorname{CoCl}_{3} \operatorname{anh}_{4} & 90 \\ 11 & 2+6 & 350 + 470 & 1.5 \operatorname{CoCl}_{3} \operatorname{GH}_{2}O & 88 \\ 13 & 2+6 & 350 + 470 & 2.5 \operatorname{CoCl}_{2} \operatorname{GH}_{2}O & 94 \\ 14 & 2+6 & 350 + 470 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{1} & 60 \\ 15 & 10 & 350 & 5.5 \operatorname{CoCl}_{2} \operatorname{anh}_{1} & 83 \\ 15 & 10 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{1} & 88 \\ 16 & 2 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 88 \\ 17 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 18 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 68^{24} \\ 22 & 10 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 50 \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_{2} \operatorname{anh}_{2} & 70^{4} \\ 25 & 15 & 15 & 10^{4} \\ 25 & 15 & 10^{4} & 10^{4} \\ 25 & 15 $	Me Co Me	9	5	350	1.5 CoCl ₂ anh.	75
$\begin{bmatrix} 1 & 2 & 2 & 6 & 350 & 470 & 1.5 & CoCl_2 & 6H_2O & 87 \\ 1 & 2 & 2 & 6 & 350 & 470 & 1.5 & CoCl_2 & 6H_2O & 94 \\ 1 & 2 & 4 & 6 & 350 & 470 & 2.5 & CoCl_2 & 6H_2O & 94 \\ 1 & 2 & 4 & 6 & 350 & 470 & 2.5 & CoCl_2 & anh. & 60 \\ 1 & 1 & 1 & 2 & 4 & 6 & 350 & 470 & 2.5 & CoCl_2 & anh. & 60 \\ 1 & 1 & 1 & 2 & 4 & 6 & 350 & 470 & 2.5 & CoCl_2 & anh. & 83 \\ \hline & & & & & & & & & & & & & & & & & &$	X-X	10	10	350	1.5 CoCl ₂ anh.	90
122 + 6 $350 + 470$ $1.5 \text{ CoCl}_2 \text{ 6H}_2 O$ 94132 + 6 $350 + 470$ $2.5 \text{ CoCl}_2 \text{ 6H}_2 O$ 94142 + 6 $350 + 470$ $2.5 \text{ CoCl}_2 \text{ anh.}$ 601510 350 $5.5 \text{ CoCl}_2 \text{ anh.}$ 83162 350 $2.5 \text{ CoCl}_2 \text{ anh.}$ 82"178 250 $2.5 \text{ CoCl}_2 \text{ anh.}$ 82"188 250 $2.5 \text{ CoCl}_2 \text{ anh.}$ 68"192 $2.5 \text{ CoCl}_2 \text{ anh.}$ 68"1192 350 $2.5 \text{ CoCl}_2 \text{ anh.}$ 62"188 250 $2.5 \text{ CoCl}_2 \text{ anh.}$ 62"192 $2.5 \text{ CoCl}_2 \text{ anh.}$ 62"102 350 $2.5 \text{ CoCl}_2 \text{ anh.}$ 62"10 $2.5 \text{ CoCl}_2 \text{ anh.}$ $62" \text{ Cocl}_2 \text{ anh.}$ 62"10 $2.5 \text{ CoCl}_2 \text{ anh.}$ $62" \text{ Cocl}_2 \text{ Cocl}_2 \text{ anh.}$ 62"10 $2.5 \text{ Cocl}_2 \text{ anh.}$ $62" \text{ Cocl}_2 \text{ anh.}$ $62" \text{ Cocl}_2 \text{ cocl}_2 \text{ anh.}$ 10 $2.5 \text{ Cocl}_2 \text{ anh.}$ $50 \text{ Cocl}_2 \text{ cocl}_2 \text{ anh.}$ $50 \text{ Cocl}_2 \text{ cocl}_2 \text{ anh.}$ 10 2.4 10 350 $2.5 \text{ Cocl}_2 \text{ anh.}$ $47 \text{ Cocl}_2 \text{ cocl}_2 \text{ anh.}$ 10 2.4 10 350 $2.5 \text{ Cocl}_2 \text{ anh.}$ $47 \text{ Cocl}_2 \text{ cocl}_2 \text{ anh.}$ 10 2.4 10 350 $2.5 \text{ Cocl}_2 \text{ anh.}$ $47 \text{ Cocl}_2 \text{ cocl}_2 \text{ anh}.$ 10 $2.5 \text{ Cocl}_2 \text{ anh}_2 \text{ cocl}_2 $		11	2+6	350 + 470	$1.5 \text{ CoCl}_2 \cdot 6H_2O$	87
122 + 6350 + 4701.5 CoCl ₂ 6H ₂ O88132 + 6350 + 4702.5 CoCl ₂ aH, GO94142 + 6350 + 4702.5 CoCl ₂ ah, GO6015103505.5 CoCl ₂ ah, GO831623502.5 CoCl ₂ ah, GO82°1782502.5 CoCl ₂ ah, GO68°1882502.5 CoCl ₂ ah, GO68°mixture1923502.5 CoCl ₂ ah, GO68°1882502.5 CoCl ₂ ah, GO68°1923502.5 CoCl ₂ ah, GO70°mixture1923502.5 CoCl ₂ ah, G2°68°2082502.5 CoCl ₂ ah, G2°70°mixture2182502.5 CoCl ₂ ah, G2°70°mixture2284702.5 CoCl ₂ ah, 47050102353502.5 CoCl ₂ ah, 47501024103502.5 CoCl ₂ ah, 477426153502.5 CoCl ₂ ah, 477410253502.5 CoCl ₂ ah, 4774103502.5 CoCl ₂ ah, 474725153502.5 CoCl ₂ ah, 471424103502.5 CoCl ₂ ah, 47153502.5 CoCl ₂ ah, 477414153502.5 CoCl ₂ ah, 47153502.5 CoCl ₂ ah, 47741415350						
13 2+6 350 + 470 2.5 CoCl ₂ 6H ₂ O 94 14 2+6 350 + 470 2.5 CoCl ₂ anh. 60 15 10 350 5.5 CoCl ₂ anh. 83 16 2 350 2.5 CoCl ₃ anh. 83 17 8 250 2.5 CoCl ₃ anh. 82 ^a 18 8 250 2.5 CoCl ₃ anh. 66 ^a mixture 19 2 350 2.5 CoCl ₃ anh. 66 ^a 10 8 250 2.5 CoCl ₃ anh. 66 ^a 68 ^a 10 8 250 2.5 CoCl ₃ anh. 66 ^a 62 ^a 10 8 250 2.5 CoCl ₃ anh. 66 ^a 62 ^a 62 ^b <td></td> <td>12</td> <td>2 + 6</td> <td>350 + 470</td> <td>$1.5 \operatorname{CoCl}_2 \cdot 6H_2O$</td> <td>88</td>		12	2 + 6	350 + 470	$1.5 \operatorname{CoCl}_2 \cdot 6H_2O$	88
142+6350 + 4702.5 CoCl ₂ anh.6015103505.5 CoCl ₂ anh.831623502.5 CoCl ₂ anh.8217882502.5 CoCl ₂ anh.841882502.5 CoCl ₂ anh.68°rixture1923502.5 CoCl ₂ anh.68°192082502.5 CoCl ₂ anh.68°2082502.5 CoCl ₂ anh.68°1082502.5 CoCl ₂ anh.68°102082502.5 CoCl ₂ anh.68°102082502.5 CoCl ₂ anh.68°102082502.5 CoCl ₂ anh.69°102082502.5 CoCl ₂ anh.69°102082502.5 CoCl ₂ anh.69°102082502.5 CoCl ₂ anh.70°1020103502.5 CoCl ₂ anh.40103502.5 CoCl ₂ anh.401025153502.5 CoCl ₂ anh.741025153502.5 CoCl ₂ anh.741025153502.5 CoCl ₂ anh.741025153502.5 CoCl ₂ anh.74103502.5 CoCl ₂ anh.7474103502.5 CoCl ₂ anh.74103502.5 CoCl ₂ anh.7410<	Ph Co Ph	13	2 + 6	350 + 470	$2.5 \text{ CoCl}_2 \cdot 6 \text{H}_2 \text{O}$	94
15103505.5 CoCl2 anh.831623502.5 CoCl2 anh.82°1782502.5 CoCl2 anh.66°1882502.5 CoCl2 anh.66°mixture1923502.5 CoCl2 anh.68°2082502.5 CoCl2 anh.68°2182502.5 CoCl2 anh.68°1923502.5 CoCl2 anh.68°2182502.5 CoCl2 anh.63°10502.5 CoCl2 anh.63°10502.5 CoCl2 anh.50102284702.5 CoCl2 anh.501025153502.5 CoCl2 anh.401025153502.5 CoCl2 anh.401025153502.5 CoCl2 anh.401025153502.5 CoCl2 anh.74103502.5 CoCl2 anh.5252153502.5 CoCl2 anh.52153502.5 CoCl2 anh.52153502.5 CoCl2 anh.52153502.5 CoCl2 anh.74103502.5 CoCl2 anh.74103502.5 CoCl2 anh.74103502.5 CoCl2 anh.74103502.5 CoCl2 anh.74103502.5 CoCl2 anh.74103502.5 CoCl2 anh.741035		14	2 + 6	350 + 470	2.5 CoCl ₂ anh.	60
$\begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 $		15	10	350	5.5 CoCl ₂ anh.	83
$\begin{bmatrix} 17 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \operatorname{anh}_1 & 68^a \\ 18 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \operatorname{chl}_3 O & 78^a \\ \end{bmatrix}$ mixture $\begin{bmatrix} 19 & 2 & 350 & 2.5 \operatorname{CoCl}_2 \operatorname{anh}_1 & 68^a \\ 20 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \operatorname{anh}_1 & 62^a \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \operatorname{anh}_1 & 62^a \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \operatorname{chl}_2 O & 70^a \\ \end{bmatrix}$ mixture $\begin{bmatrix} 10 & 2 & 350 & 2.5 \operatorname{CoCl}_2 \operatorname{anh}_1 & 62^a \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \operatorname{chl}_2 O & 70^a \\ \end{bmatrix}$ $\begin{bmatrix} 10 & 10 & 10 & 10 & 10 \\ 10 & 10 & 10 &$		16	2	350	$2.5 \operatorname{CoCl}_2$ anh.	82^a
$\begin{bmatrix} 18 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \operatorname{6H}_2 O & 78^a \\ mixture & & & & & & & & & & & & & & & & & & &$	Ft. T	17	8	250	2.5 CoCl_2 anh.	68^a
mixture 19 2 350 2.5 CoCl ₂ anh. 68^a 10 8 250 2.5 CoCl ₂ anh. 62^a 21 8 250 2.5 CoCl ₂ anh. 62^a mixture 21 8 250 2.5 CoCl ₂ anh. 62^a mixture 21 8 250 2.5 CoCl ₂ anh. 62^a 10 5 350 2.5 CoCl ₂ anh. 62^a 10 5 350 2.5 CoCl ₂ anh. 60^a 10 24 10 350 2.5 CoCl ₂ anh. 40^a 10 350 2.5 CoCl ₂ anh. 47^a 25^a 15^a 350^a $2.5 CoCl_2 anh.$ 40^a 10 350 2.5 CoCl ₂ anh. 47^a 25^a 15^a 350^a $2.5 CoCl_2 anh.$ 47^a 10 350 2.5 CoCl ₂ anh. 47^a 47^a 47^a 47^a 47^a 41^a 41	Me Co Me	18	8	250	$2.5 \text{ CoCl}_2 \cdot 6 \text{H}_2 \text{O}$	78 ^{<i>a</i>}
$\begin{bmatrix} 19 & 2 & 350 & 2.5 \text{ CoCl}_2 \text{ anh.} & 68^d \\ 20 & 8 & 250 & 2.5 \text{ CoCl}_2 \text{ anh.} & 62^d \\ 21 & 8 & 250 & 2.5 \text{ CoCl}_2 \text{ GH}_2 O & 70^d \\ \hline \text{mixture} & & & & & & & & & & & & & & & & & & &$	mixture					
$\begin{bmatrix} 20 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 62^a \\ 21 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \operatorname{cH}_2 O & 70^a \\ \hline mixture & & & & & & & \\ \hline mixture & & & & & & & & \\ \begin{bmatrix} 22 & 8 & 470 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 50 \\ \hline mix & s & & & & & & & \\ \hline subd & s & s & & & & & & & & & \\ \hline subd & s & s & & & & & & & & & & & \\ \hline subd & s s & & & & & & & & & & & & & \\ \hline subd & s s s & & & & & & & & & & & & & & & \\ \hline subd & s s s & & & & & & & & & & & & & & & & \\ \hline subd s s s & & & & & & & & & & & & & & & & & \\ \hline subd s s s s & & & & & & & & & & & & & & & & & & \\ \hline subd s s s s & & & & & & & & & & & & & & & & & & &$	[🔈]	19	2	350	2.5 CoCl ₂ anh.	68 ^{<i>a</i>}
$\begin{bmatrix} 1 & 21 & 8 & 250 & 2.5 \operatorname{CoCl}_2 \cdot 6H_2O & 70^a \\ mixture \\ \\ \hline mixture \\ \end{bmatrix} 22 & 8 & 470 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 50 \\ \\ \hline mixture \\ \end{bmatrix} \\ \begin{bmatrix} 22 & 8 & 470 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 50 \\ \hline mixture & 23 & 5 & 350 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 40 \\ \hline 24 & 10 & 350 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 47 \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 47 \\ 25 & 15 & 350 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 52 \\ \hline 26 & 15 & 350 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 52 \\ \hline 26 & 15 & 350 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 52 \\ \hline 26 & 15 & 350 & 2.5 \operatorname{CoCl}_2 \operatorname{anh.} & 74 \\ \hline \end{bmatrix} \\ $		20	8	250	$2.5 \operatorname{CoCl}_2$ anh.	62^a
$initure 22 8 470 2.5 CoCl2 anh. 50 initure initure initure 50 50 2.5 CoCl_2 anh. 40 initure initure initure 50 2.5 CoCl_2 anh. 52 50 initure initure initure initure 50 50 50 50 $	Et Co Et	21	8	250	$2.5 \text{ CoCl}_2 \cdot 6 \text{H}_2 \text{O}$	70^a
mixture 22 8 470 2.5 CoCl ₂ anh. 50 Image: Set in the solution of	Et					
22 8 470 2.5 CoCl ₂ anh. 50 Solution 5 350 2.5 CoCl ₂ anh. 40 23 5 350 2.5 CoCl ₂ anh. 40 24 10 350 2.5 CoCl ₂ anh. 47 25 15 350 2.5 CoCl ₂ anh. 47 26 15 350 2.5 CoCl ₂ anh. 52 Vield related to the cobatabase (discribulide) mixture 74	mixture					
Image: Set of the second set of the		22	8	470	2.5 CoCl ₂ anh.	50
Margin Go Ma 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	EtS					
Vield related to the cobaltabis (dicarbollide) mixture	Me Co Me					
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	SET					
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	Jet					
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	[<u>~</u>] ⁻	23	5	350	2.5 CoCl ₂ anh.	40
25 15 350 2 CoCl ₂ anh. 52 26 15 350 2.5 CoCl ₂ anh. 74		24	10	350	$2.5 \operatorname{CoCl}_{2}^{2}$ anh.	47
26 15 350 2.5 CoCl ₂ anh. 74 Vield related to the cobaltabis(dicarbollide) mixture		25	15	350	2 CoCl ₂ anh	52
Vield related to the cohaltabis(dicarbollide) mixture	Co	26	15	350	2.5 CoCh and	74
-		20	15	550	2.5 00012 allil.	/4
	^a Viold volated to th	a applicable	lida) mintura			

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

 $[NMe_4][3,3'-Co(1,2-C_2B_9H_{11})_2]$ complex, which was confirmed by ¹¹B- 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 $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ complex was achieved, we tested if the synthesis of $C_{cluster}$ -sub-

stituted cobaltabis(dicarbollide) complexes could be accomplished. Reaction was run by using the same method and conditions but starting with the monosubstituted $[HNMe_3][8-R-7,8-C_2B_9H_{10}]$ (R = Me, Ph) ligands.

This new reaction led to the formation of [NMe₄][3,3'-Co $(1-Me-1,2-C_2B_9H_{10})_2$ and $[NMe_4][3,3'-Co(1-Ph-1,2-C_2B_9H_{10})_2]$ 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 ([HNMe3]]7-R-8-R'-7,8- $C_2B_9H_{10}$ (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-Me-8-Et-7,8-C₂B₉H₁₀] and [HNMe₃][7,8-Et₂-7,8- $C_2B_9H_{10}$], 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-R-2-R'-1,2-C₂B₁₀H₁₀ (R = R' = SEt; R = Me, R' = SEt and R = Ph, R' = SEt), via a partial deboronation reaction, nido ligands [HNMe3]7-R-8-R'-7,8- $C_2B_9H_{10}$ (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-Me-8-SEt-7,8-C₂B₉H₁₀], 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'-Co(1-Me-2-SEt-C₂B₉H₉)₂] was low compared to the previously obtained complexes. The yield for this particular $[HNMe_3]$ [7-Me-8-SEt-7,8-C₂B₉H₁₀] 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-C₂B₉H₁₂], was our target.

The $[NMe_4][2,2'-Co(1,7-C_2B_9H_{11})_2]$ 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



Fig. 1 Perspective view of the $[HNMe_3][2,2'-Co(1,7-C_2B_9H_{11})_2]$ 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.

formation of cobalt metal. This observation suggests that the initially Co^{2+} is rapidly oxidized to form the more stable d⁶ metallabis(dicarbollide) complex 18 e⁻ count avoiding reduction from Co^{2+} to Co^{0} . This is proof that the freesolvent synthesis of $[3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ takes place *via* another mechanism than the previously reported synthesis in solution.

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 NMe₃, 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 Co⁰ was produced and the ¹¹B NMR evidence that [3,3'-Co(1,2- $C_2B_9H_{11})_2$ 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 Co³⁺/Co²⁺ and H₂O/OH⁻. Moreover, X-ray diffraction of [HNMe₃][2,2'-Co(1,7-C₂B₉H₁₁)₂] fully supports that the cation is [HNMe₃]⁺ (Fig. 1).¹⁰

The MS spectra of $[NMe_4][Co(1-Me-2-Et-1,2-C_2B_9H_9)_2]$ and $[NMe_4][Co(1,2-Et_2-1,2-C_2B_9H_9)_2]$ 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 Co²⁺ dismutation.

Conflicts of interest

There are no conflicts to declare.

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- 10 Crystal data for $C_7H_{32}B_{18}$ CoN: monoclinic, space group *C*2/ *m*, *a* = 9.130(11) Å, *b* = 10.446(10) Å, *c* = 11.101(9) Å, *V* = 1014.44 Å³, *Z* = 2, *T* = 100(2) K, measured reflections 24 871, independent reflections 856, R_{int} = 0.0325, R_1 = 0.0677, w R_2 = 0.1743. CCDC 1882757.†