Electronic Supplementary Material (ESI) for Green Chemistry.

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

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Contents

EXPERIMENTAL SECTION

Materials:

The 1,2-*closo*-$C_2B_{10}H_{12}$, the 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ and the 1,7-*closo*-$C_2B_{10}H_{12}$ were bought from Aldrich chemical company. All reagents ($CoCl_2$, $CoCl_2.6H_2O$, η-BuLi, Iodoethane, Bromoethane, octathiocane and the [$NHMe_3$]Cl used in this work were purchased from Sigma Aldrich excepting the KOH that was purchased from the Labkem company and the [NMe_4]Cl that was purchased from the Acros Organics company. All reagents were used without further purification.

All 1-R-2-R'-1,2-*closo*-$C_2B_9H_{10}$ clusters (R=H and R'=Ph; R=Me, Ph, Et and R' =Et; R=Me, Ph, SEt and R'= SEt) were synthesized as reported.[1] The partial degradation of all present compounds was done in ethanol using the KOH as was described previously to give the corresponding *nido*-carborane.[2]

Instrumentation and Measurements:

The ^1H-NMR, $^1H\{^{11}B\}$-NMR, (300.13 MHz), ^{11}B-NMR, $^{11}B\{^1H\}$-NMR (96.29 MHz) and $^{13}C\{^1H\}$-NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in deuterium acetone at 22ºC. The chemical shift values referenced to external BF_3-OEt_2 for ^{11}B-NMR and to the $SiMe_4$ for ^{13}C-NMR and ^1H-NMR spectra. MALDI-TOF-MS spectra were recorded in the negative ion mode using a Bruker Daltonics Biflex esquire 3000.

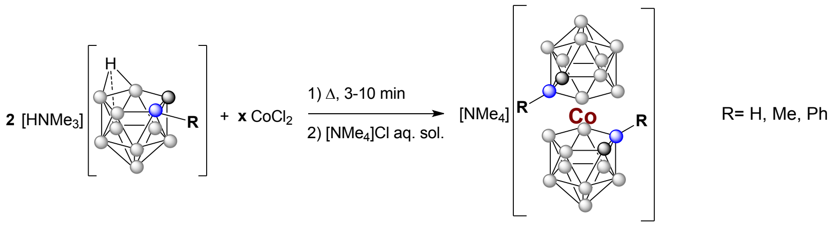
X-ray structure determination:

An orange block-like specimen of $C_7H_{32}B_{18}CoN$, approximate dimensions 0.040 mm x 0.250 mm x 0.340 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 QUEST ECO system equipped with a doubly curved silicon crystal Bruker Triumph monochromator and a Mo Kalpha sealed X-ray tube (λ = 0.71076 Å). A total of 1268 frames were collected. The total exposure time was 6.09 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 24871 reflections to a maximum θ angle of 24.14° (0.87 Å resolution), of which 856 were independent (average redundancy 29.055, completeness = 99.5%, R_{int} = 3.25%, R_{sig} = 1.52%) and 828 (96.73%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.130(11) Å, b = 10.446(10) Å, c = 11.101(9) Å, β = 106.63(4)°, volume = 1014.4(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9752 reflections above 20 $\sigma(I)$ with 6.045° < 2θ < 48.07°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.865. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7640 and 0.9670. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 1 2/m 1, with Z = 2 for the formula unit, $C_7H_{32}B_{18}CoN$. The final anisotropic full-matrix least-squares refinement on F^2 with 88 variables converged at R1 = 6.77%, for the observed data and wR2 = 17.43% for all data. The goodness-of-fit was 1.156. The largest peak in the final difference electron density synthesis was 1.142 $e^-/Å^3$ and the largest hole was -0.775 $e^-/Å^3$ with an RMS deviation of 0.092 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.257 g/cm^3 and F(000), 396 e^-.

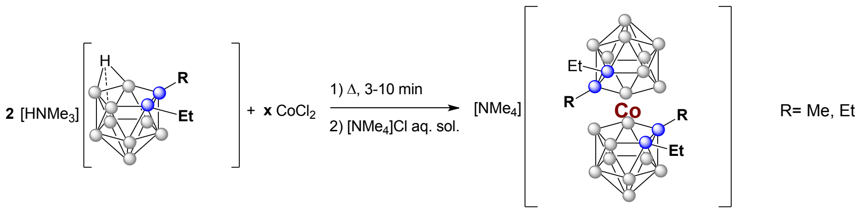
CCDC 1882757, present the crystallographic data of this new crystal structure.

Synthesis of metallabis(dicarbollide) sandwich via solid state:

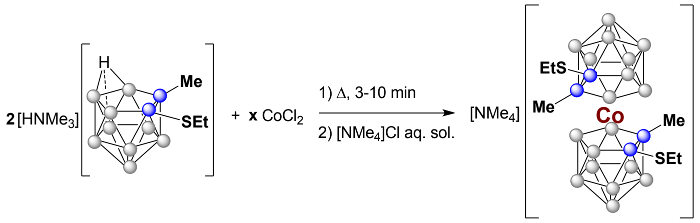
Scheme S1. Free solvent Synthesis reaction of $[3,3'\text{-Co}(1\text{-R-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ from $[\text{HNMe}_3][8\text{-R-}7,8\text{-}$*nido*$\text{-C}_2\text{B}_9\text{H}_{11}]$; R= H, Me, Ph and $\text{CoCl}_2.\text{nH}_2\text{O}$ (n=0, 6)



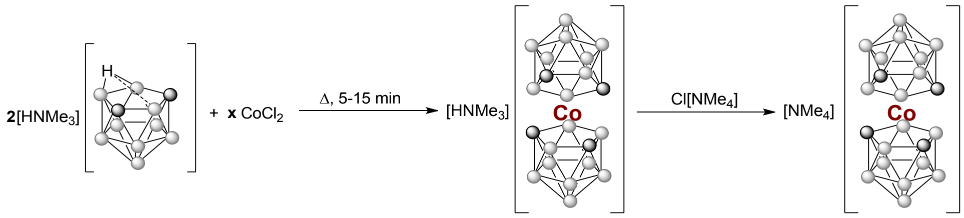
Scheme S2. Free solvent Synthesis reaction of $[3,3'\text{-Co}(1\text{-Et-}2\text{-R-}1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ from $[\text{HNMe}_3][7\text{-Et-}8\text{-R}'\text{-}7,8\text{-}$*nido*$\text{-C}_2\text{B}_9\text{H}_{10}]$; R= Me, Et and CoCl_2



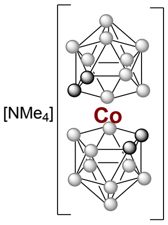
Scheme S3. Free solvent Synthesis reaction of $[3,3'\text{-Co}(1\text{-SEt-}2\text{-Me-}1,2\text{-C}_2\text{B}_9\text{H}_9)_2]^-$ from $[\text{HNMe}_3][7\text{-SEt-}8\text{-Me-}7,8\text{-}$*nido*$\text{-C}_2\text{B}_9\text{H}_{10}]$ and CoCl_2

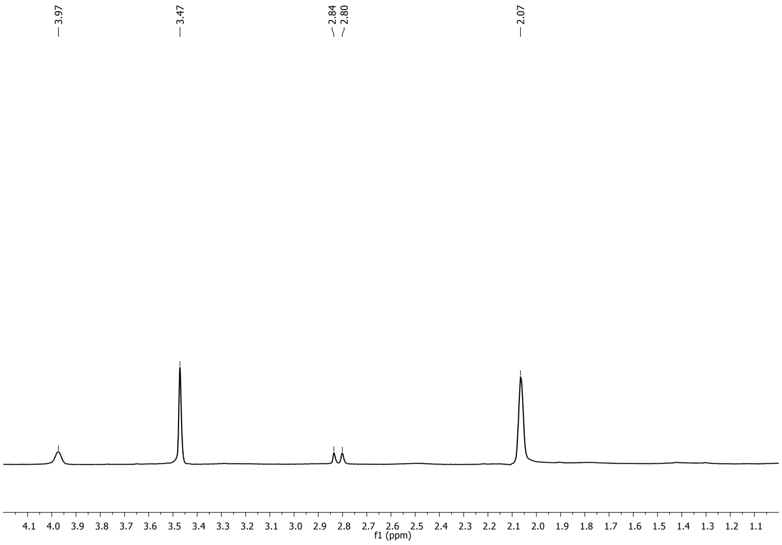


Scheme S4. Free solvent Synthesis reaction of $[2,2'\text{-Co}(1,7\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ from $[\text{HNMe}_3][7,9\text{-}$*nido*$\text{-C}_2\text{B}_9\text{H}_{12}]$

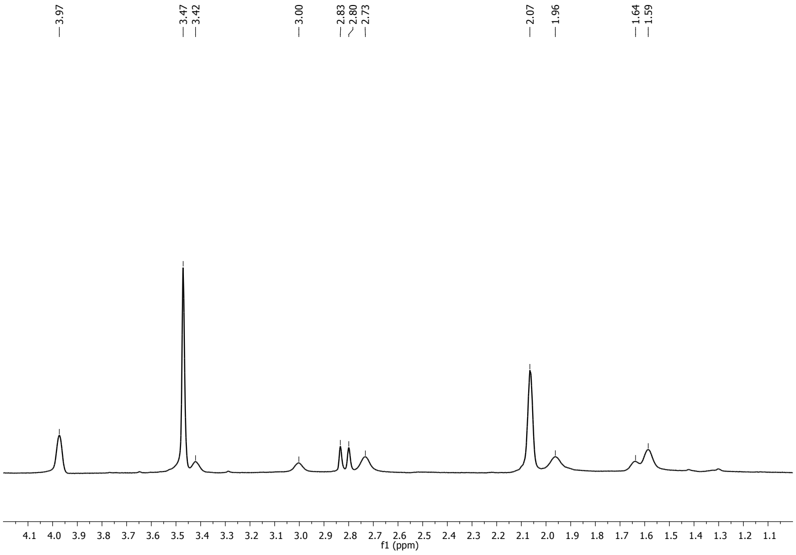


Characterization of the $[NMe_4][3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$

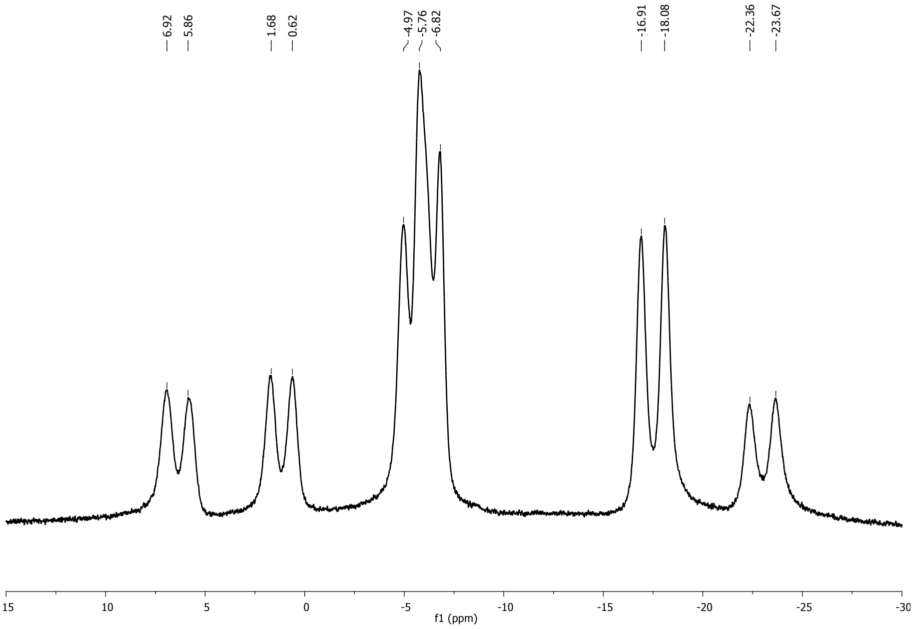




^{1}H-NMR of the $[NMe_4][3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$



^{1}H{^{11}B}-NMR of the $[NMe_4][3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$



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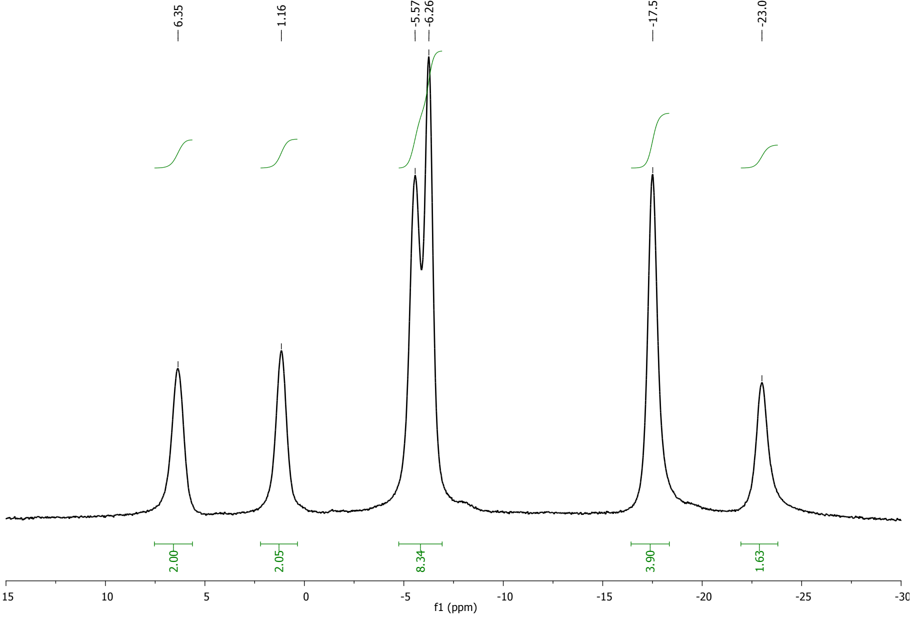
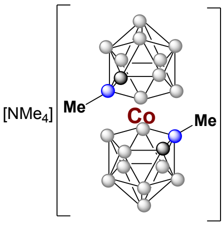
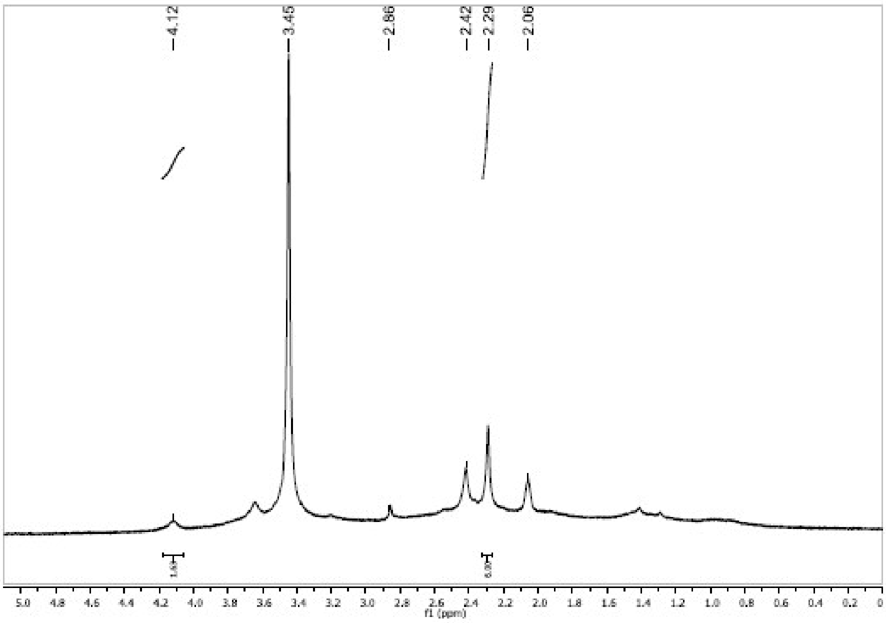


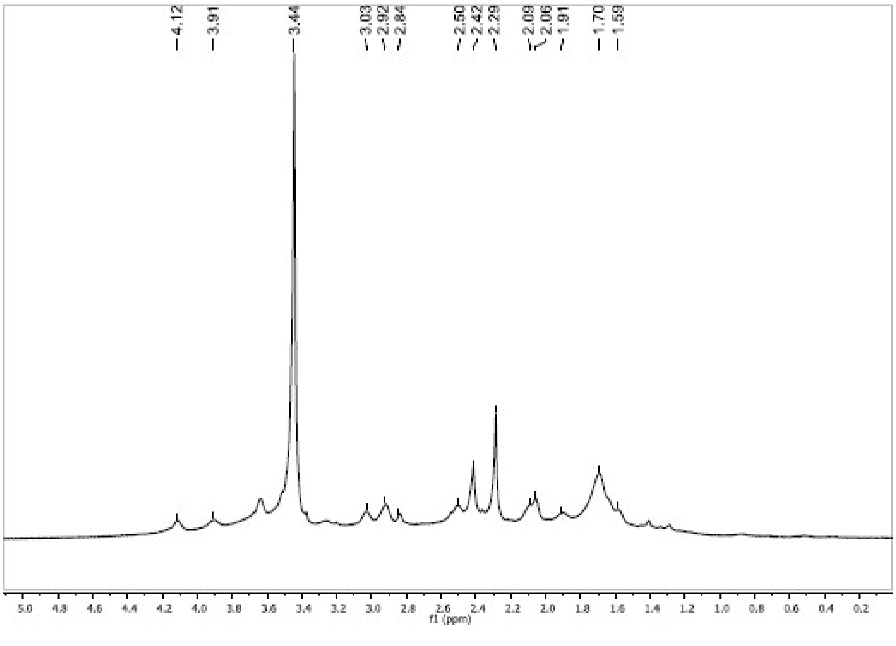
^{11}B{^{1}H}-NMR of the [NMe$_4$][3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]

Characterization of the [NMe$_4$][3,3'-Co(1-Me-1,2-C$_2$B$_9$H$_{10}$)$_2$]





^{1}H-NMR of the [NMe$_4$][3,3'-Co(1-Me-1,2-C$_2$B$_9$H$_{10}$)$_2$]



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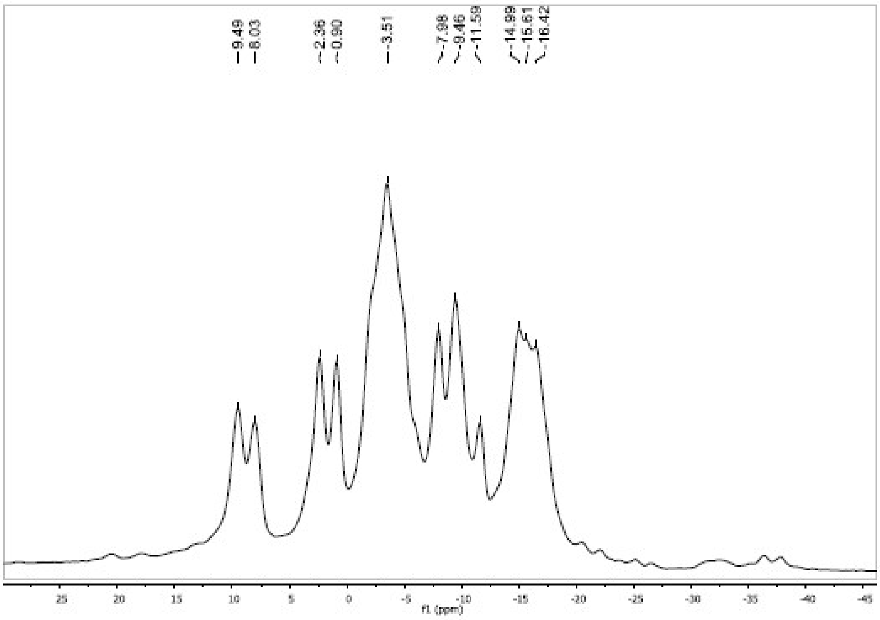

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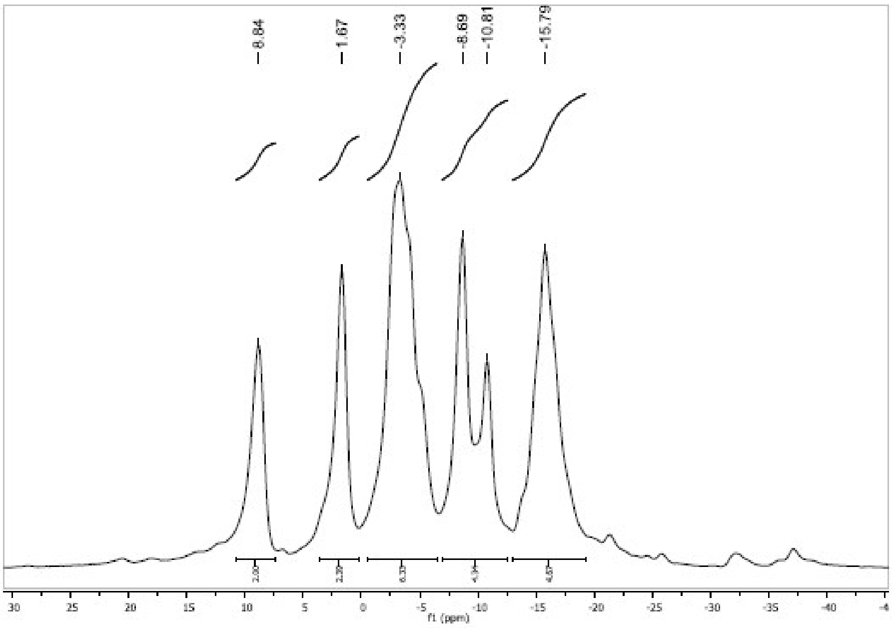
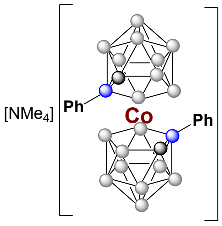
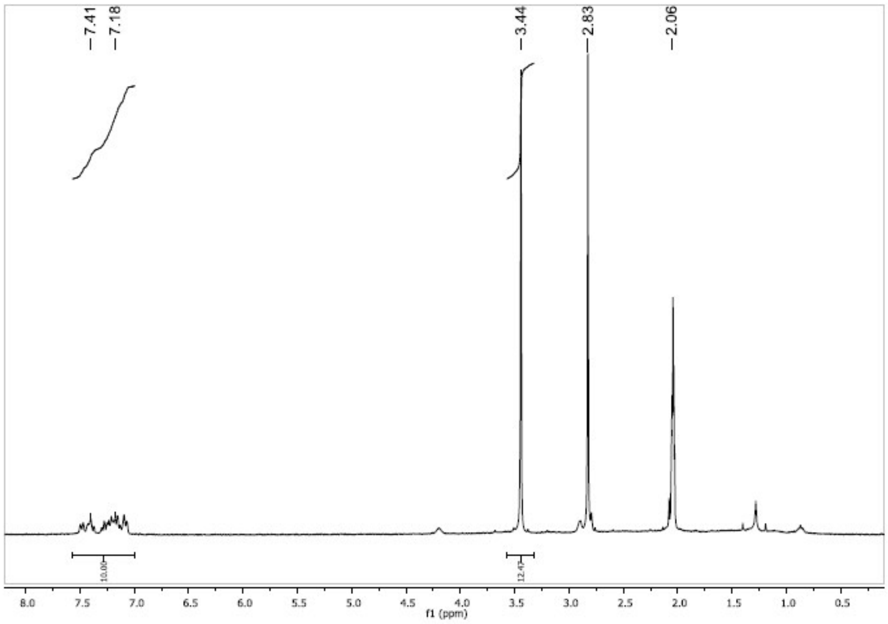


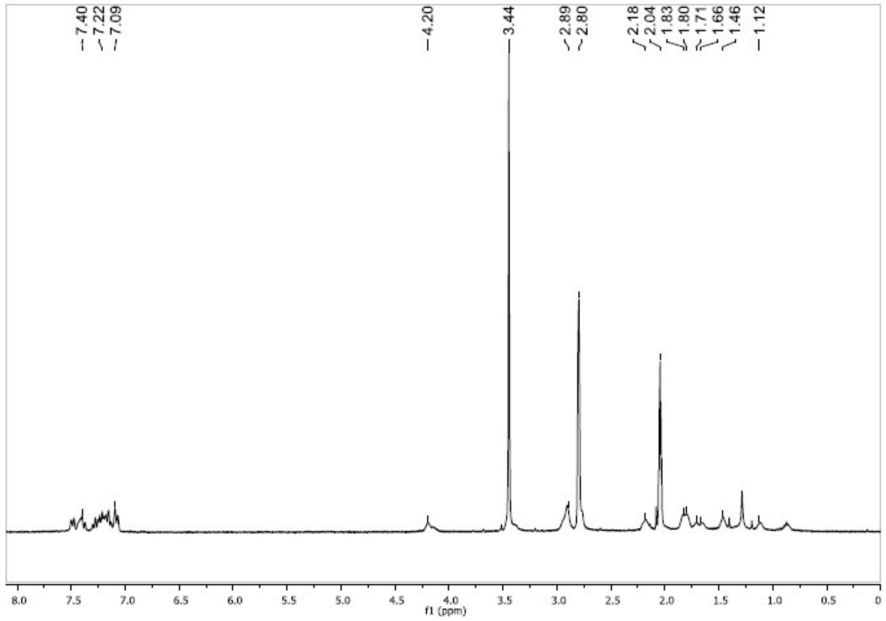
^{11}B{^{1}H}-NMR of the [NMe$_4$][3,3'-Co(1-Me-1,2-C$_2$B$_9$H$_{10}$)$_2$]

Characterization of the $[NMe_4][3,3'\text{-}Co(1\text{-}Ph\text{-}1,2\text{-}C_2B_9H_{10})_2]$





^1H-NMR of the $[NMe_4][3,3'\text{-}Co(1\text{-}Ph\text{-}1,2\text{-}C_2B_9H_{10})_2]$



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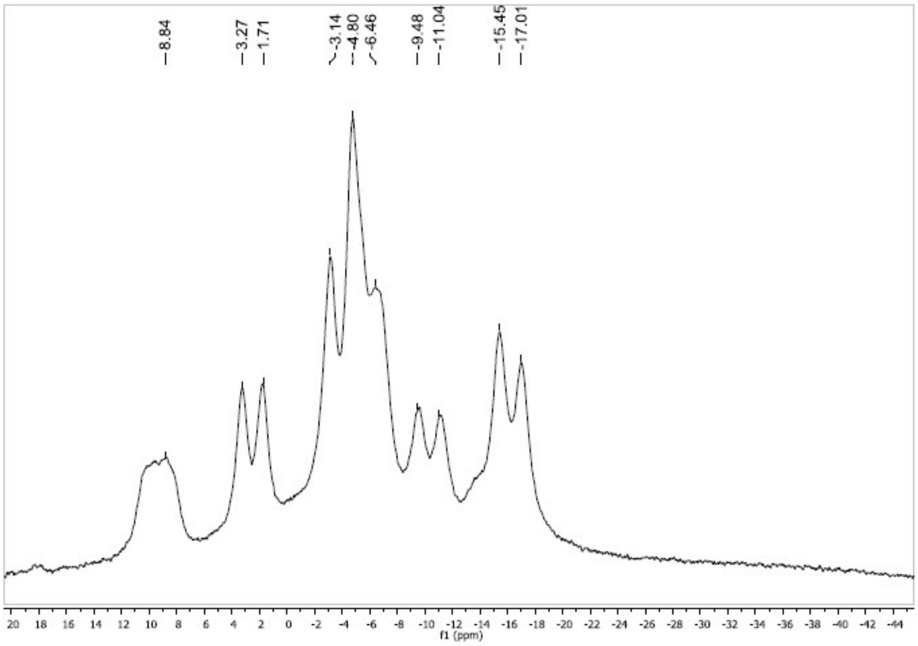
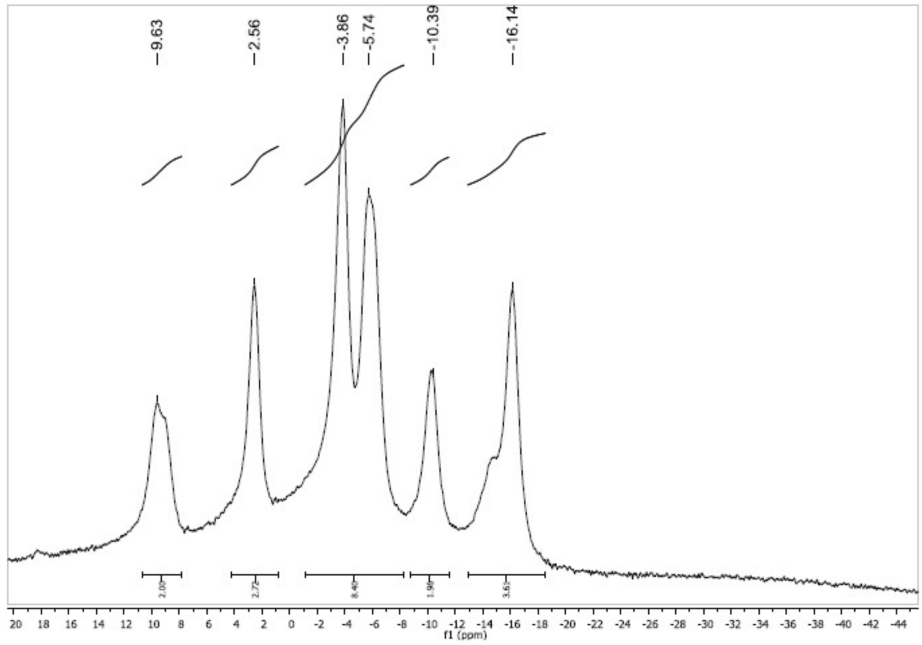
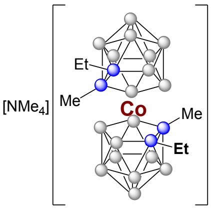


^{11}B-NMR of the [NMe$_4$][3,3'-Co(1-Ph-1,2-C$_2$B$_9$H$_{10}$)$_2$]

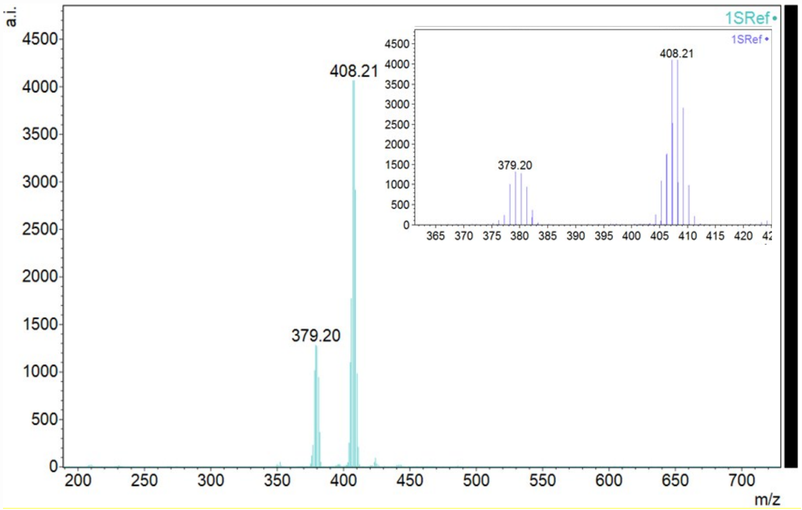


^{11}B{^{1}H}-NMR of the [NMe$_4$][3,3'-Co(1-Ph-1,2-C$_2$B$_9$H$_{10}$)$_2$]

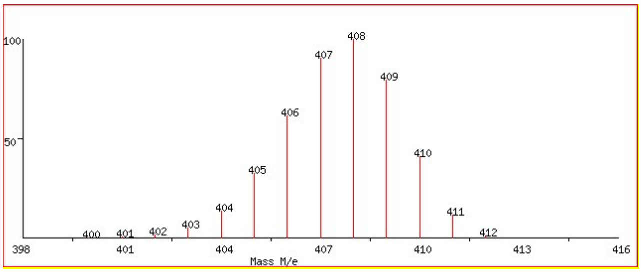
[redacted]e$_4$][3,3’-Co(1-Et-2-Me-1,2-$C_2B_9H_9$)$_2$]



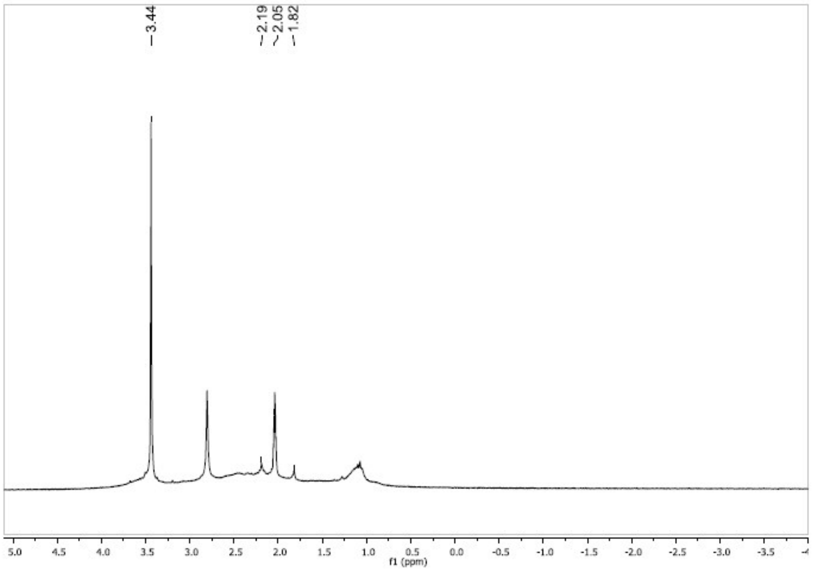
][Co(1-Me-2-Et-1,2-$C_2B_9H_9$)$_2$] in the negative ion mode displays two peaks; one centered at 408.21 (100%) that corresponds to the molecular peak ($CoC_{10}B_{18}H_{34}$) and the second one at 379.20 (31.6 %) corresponding to the complex after losing one Ethyl group. Thus, we evidenced the tendency of these metallabis(dicarbollides) to loose Ethyl but apparently not Methyl units. Methyl groups cannot undergo β-hydride elimination.



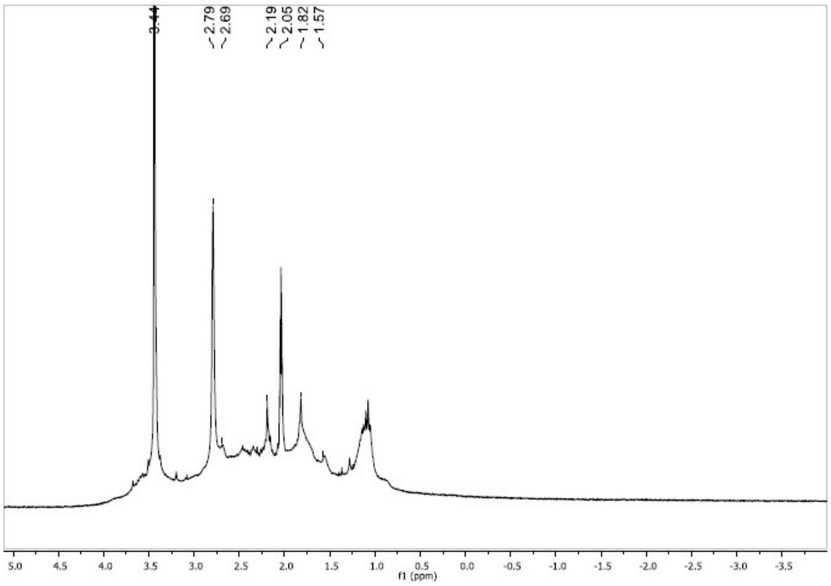
Experimental MALDI-TOF-MS spectra of [3,3’-Co(1-Et-2-Me-1,2-$C_2B_9H_9$)$_2$]$^-$



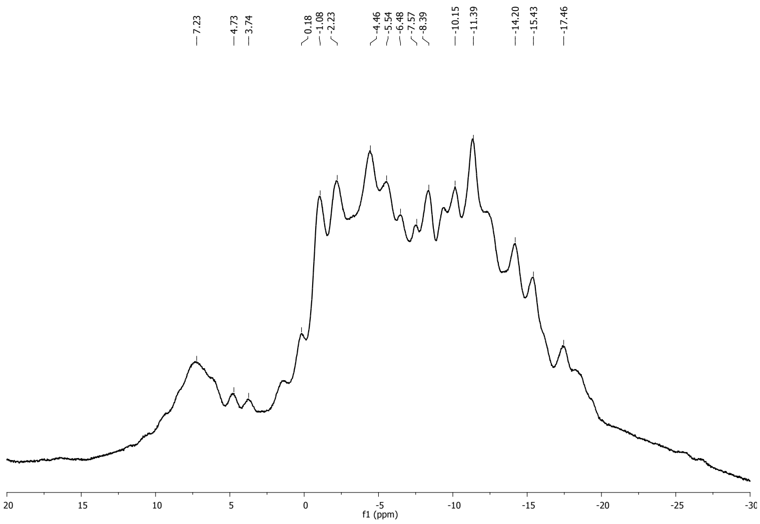
Calculated MS spectrum of [Co(1-Me-2-Et-1,2-$C_2B_9H_9$)$_2$]$^-$



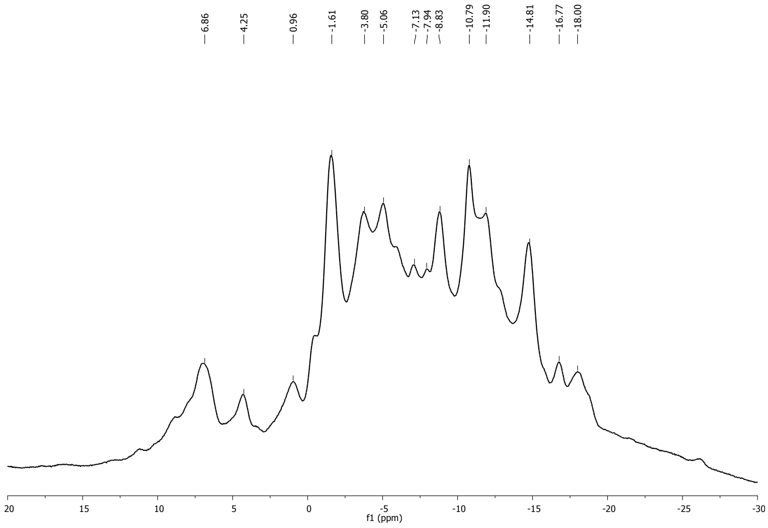
^{1}H-NMR of the [NMe$_4$][3,3'-Co(1-Et-2-Me-1,2-C$_2$B$_9$H$_9$)$_2$]



^{1}H{^{11}B}-NMR of the [NMe$_4$][3,3'-Co(1-Et-2-Me-1,2-C$_2$B$_9$H$_9$)$_2$]

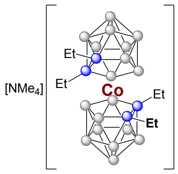


^{11}B-NMR of the [NMe$_4$][3,3'-Co(1-Et-2-Me-1,2-C$_2$B$_9$H$_9$)$_2$]

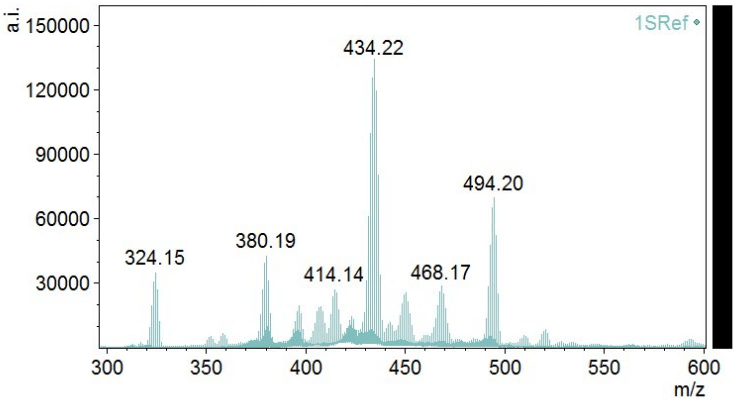


^{11}B{^{1}H}-NMR of the [NMe$_4$][3,3'-Co(1-Et-2-Me-1,2-C$_2$B$_9$H$_9$)$_2$]

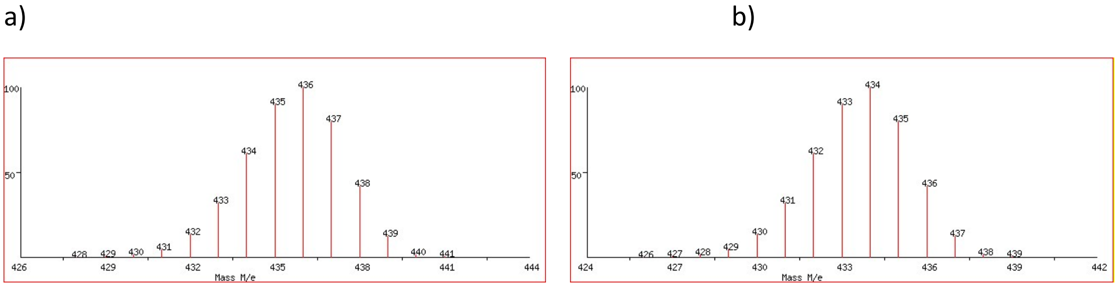
Characterization of the $[NMe_4][3,3'\text{-}Co(1,2\text{-}Et_2\text{-}1,2\text{-}C_2B_9H_9)_2]$



The MALDI-TOF-MS of $[NMe_4][Co(1,2\text{-}Et_2\text{-}1,2\text{-}C_2B_9H_9)_2]$ presents several peaks: at 434.22 (100%) corresponding to molecular peak $CoC_{12}B_{18}H_{38}$ minus 2H atoms; at 407.21 (14,4%) corresponding to molecular peak minus one Ethyl group; at 380.19 (32.0%) corresponding to molecular peak minus two Ethyl groups plus 2H atoms; at 494,20 (52.6%) corresponding to molecular peak plus two Ethyl groups. The peak at 434.22 (100%) that corresponds to the molecular peak $CoC_{12}B_{18}H_{38}$ minus 2H suggests that to our best understanding this is, or at least seems so, the first observed -hydride elimination on one branch that goes from CH_2-CH_3 to $CH{=}CH_2$ losing a H_2 in a sandwich metallacarborane. The second -hydride elimination corresponds to the loss of a·C_2H_4 group in $[NMe_4][Co(1,2\text{-}Et_2\text{-}1,2\text{-}C_2B_9H_9)_2]$. Hypothetically, this could react with a B-H vertex to produce a cobaltabis(dicarbollide) whose molecular peak corresponds to the one of the expected compound ($CoC_{12}B_{18}H_{38}$) plus two Ethyl groups.

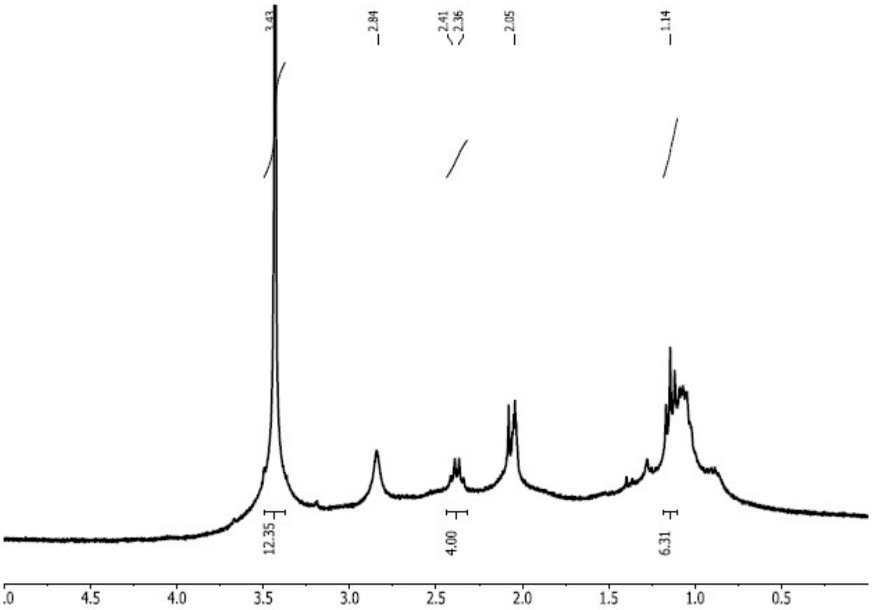


Experimental MALDI-TOF-MS spectrum of $[Co(1,2\text{-}Et_2\text{-}1,2\text{-}C_2B_9H_9)_2]^-$

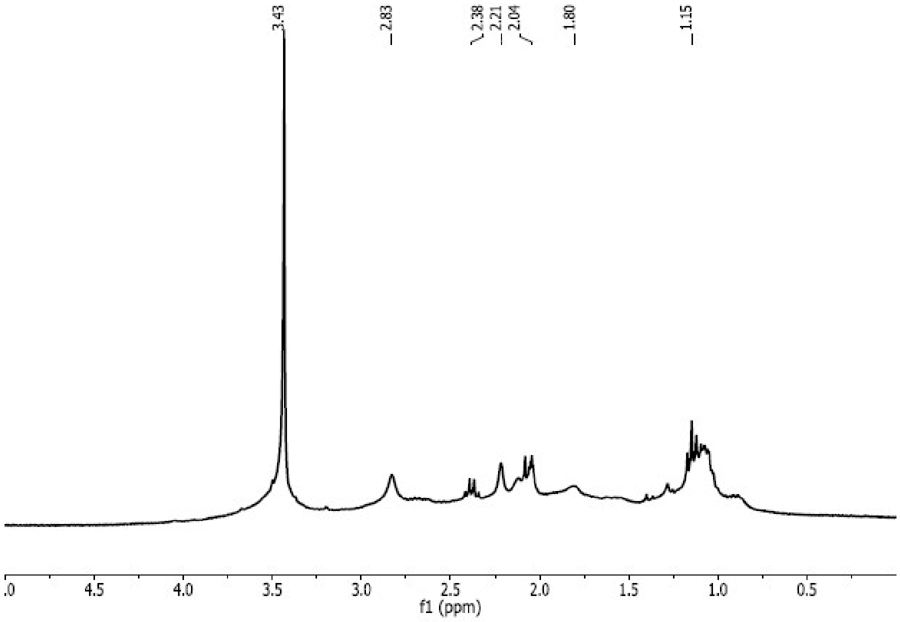

a)

b)

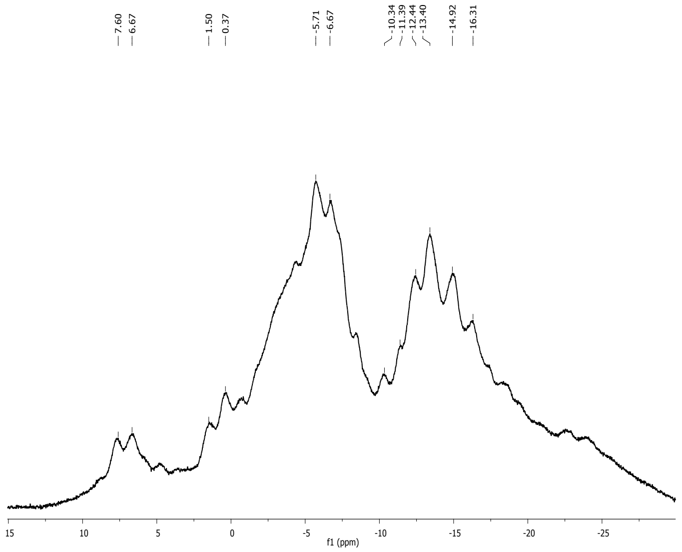
Calculated MS spectrum of $[Co(1,2\text{-}Et_2\text{-}1,2\text{-}C_2B_9H_9)_2]^-$ and b) Calculated MS spectrum of $[Co(1,2\text{-}Et_2\text{-}1,2\text{-}C_2B_9H_9)_2$ minus $2H]^-$



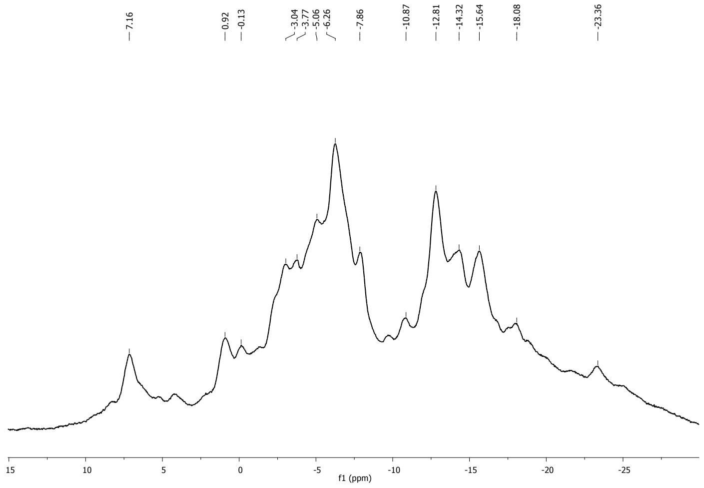
^{1}H-NMR of the $[NMe_4][3,3'-Co(1,2-Et_2-1,2-C_2B_9H_9)_2]$



$^{1}H\{^{11}B\}$-NMR of the $[NMe_4][3,3'-Co(1,2-Et_2-1,2-C_2B_9H_9)_2]$

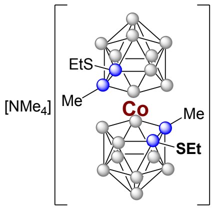


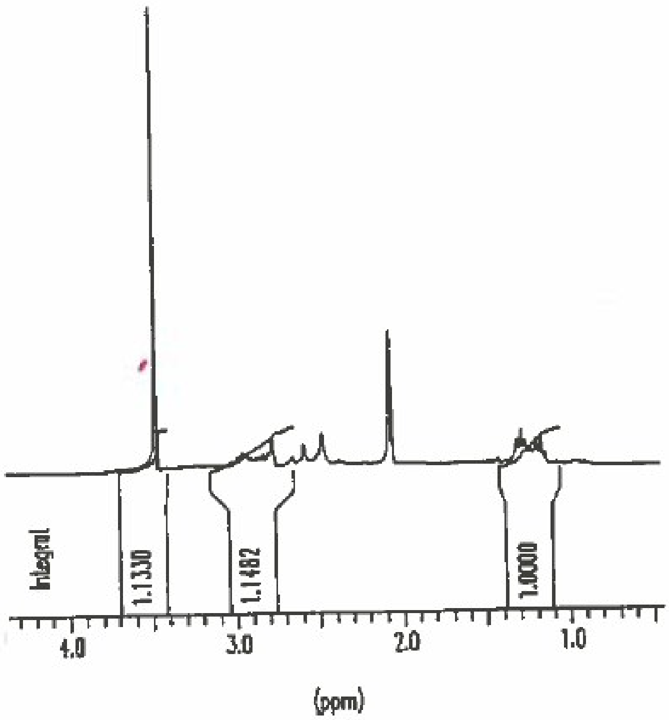
^{11}B-NMR of the $[NMe_4][3,3'\text{-}Co(1,2\text{-}Et_2\text{-}1,2\text{-}C_2B_9H_9)_2]$



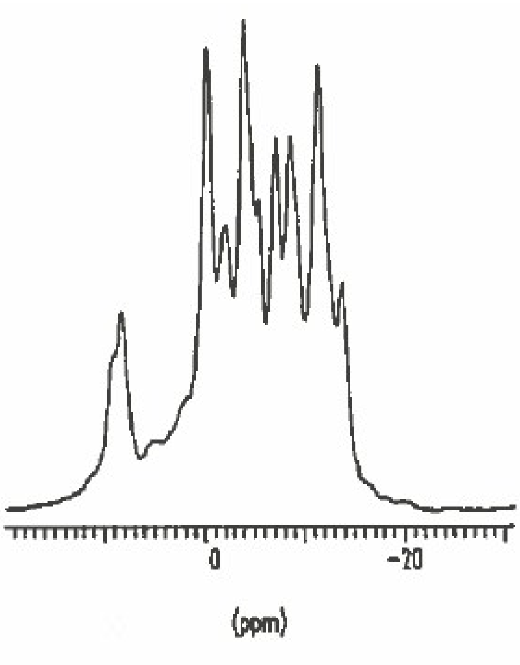
^{11}B{^{1}H }-NMR of the $[NMe_4][3,3'\text{-}Co(1,2\text{-}Et_2\text{-}1,2\text{-}C_2B_9H_9)_2]$

Characterization of the $[NMe_4][3,3'\text{-}Co(1\text{-}SEt\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_9H_9)_2]$

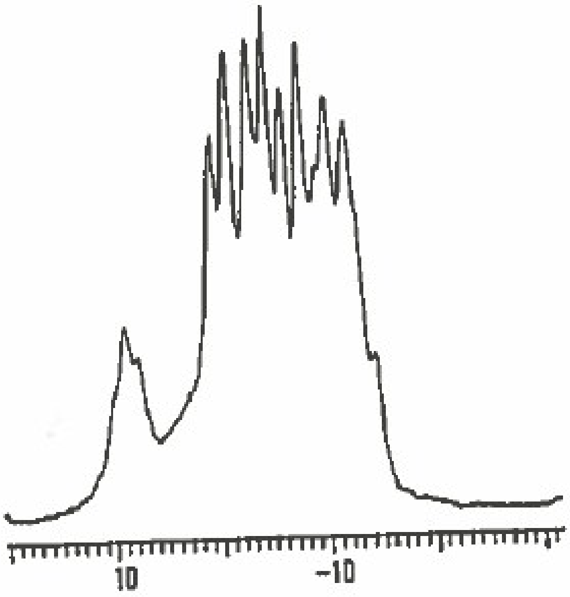




^{1}H-NMR of the $[NMe_4][3,3'\text{-}Co(1\text{-}SEt\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_9H_9)_2]$

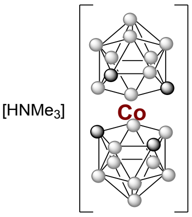


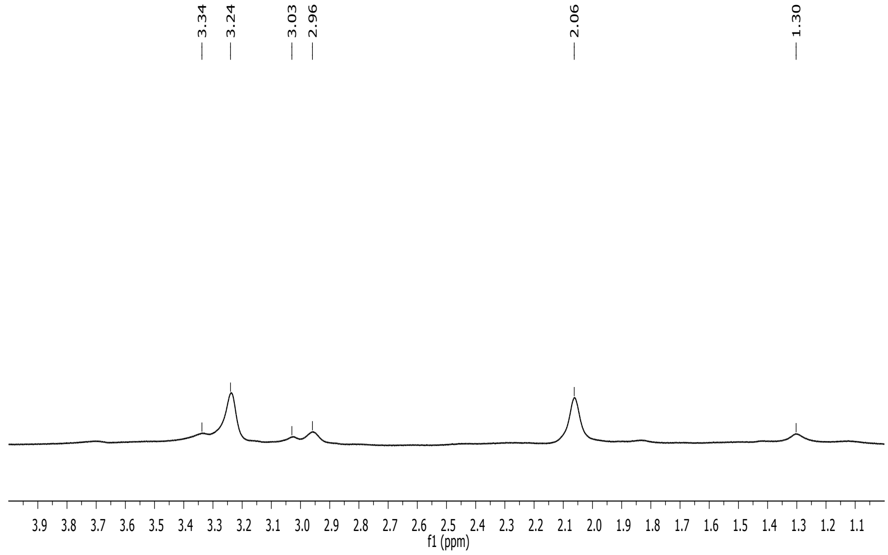
$^{11}B\{^{1}H\}$-NMR of the $[NMe_4][3,3'\text{-}Co(1\text{-}SEt\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_9H_9)_2]$



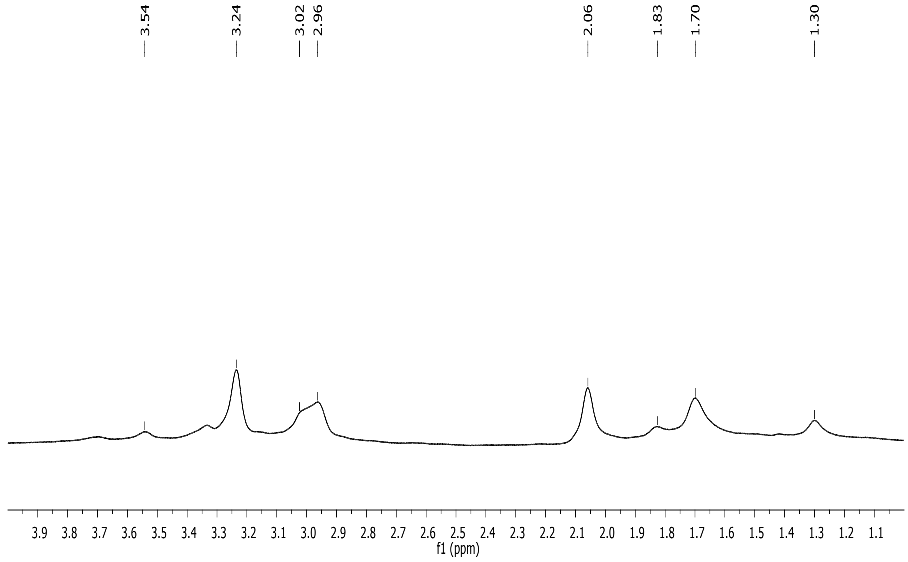
^{11}B-NMR of the $[NMe_4][3,3'\text{-}Co(1\text{-}SEt\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_9H_9)_2]$

Characterization of the $[HNMe_3][2,2'\text{-}Co(1,7\text{-}C_2B_9H_{11})_2]$

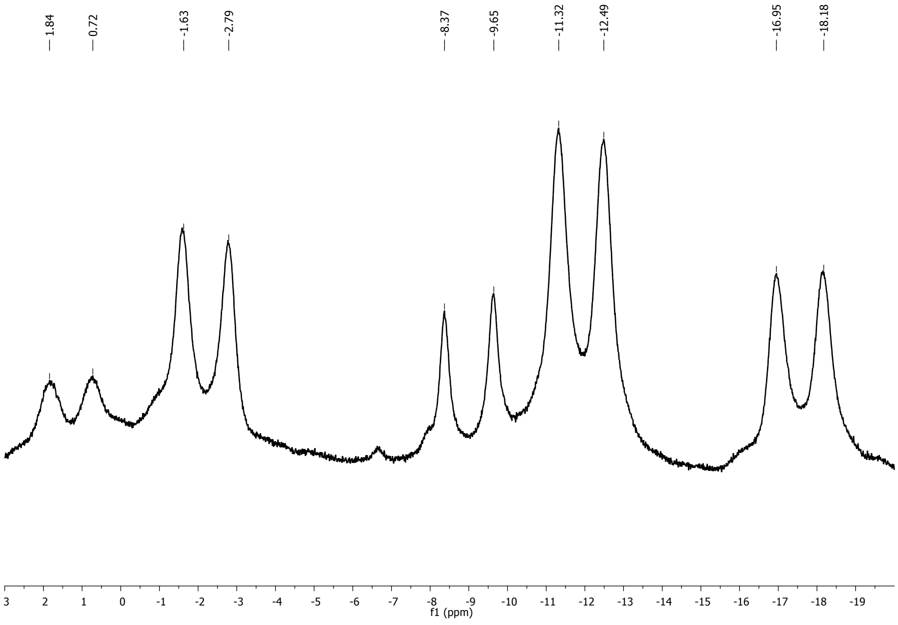




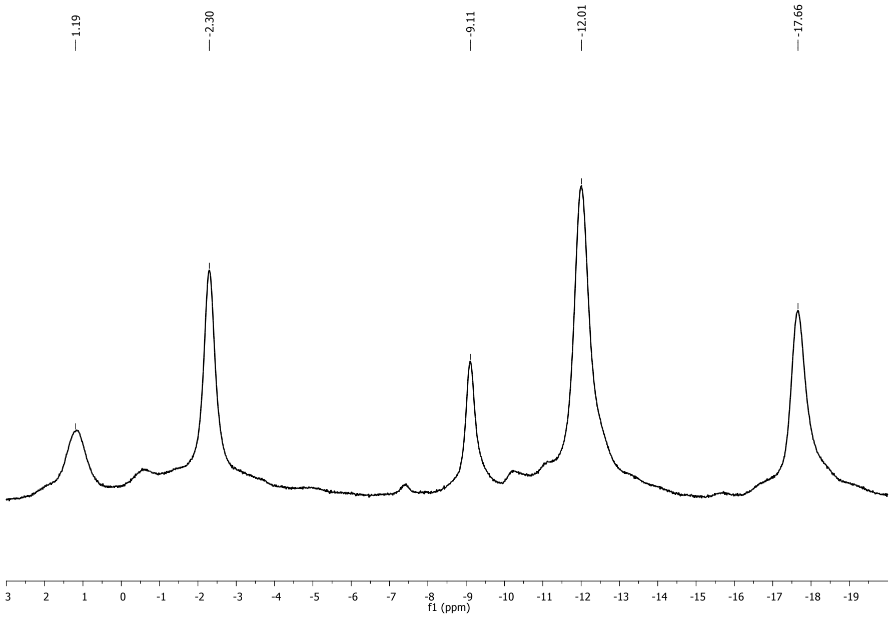
^{1}H-NMR of the $[HNMe_3][2,2'\text{-}Co(1,7\text{-}C_2B_9H_{11})_2]$



^{1}H{^{11}B}-NMR of the $[HNMe_3][2,2'\text{-}Co(1,7\text{-}C_2B_9H_{11})_2]$

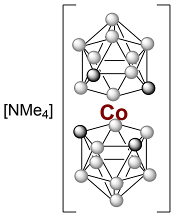


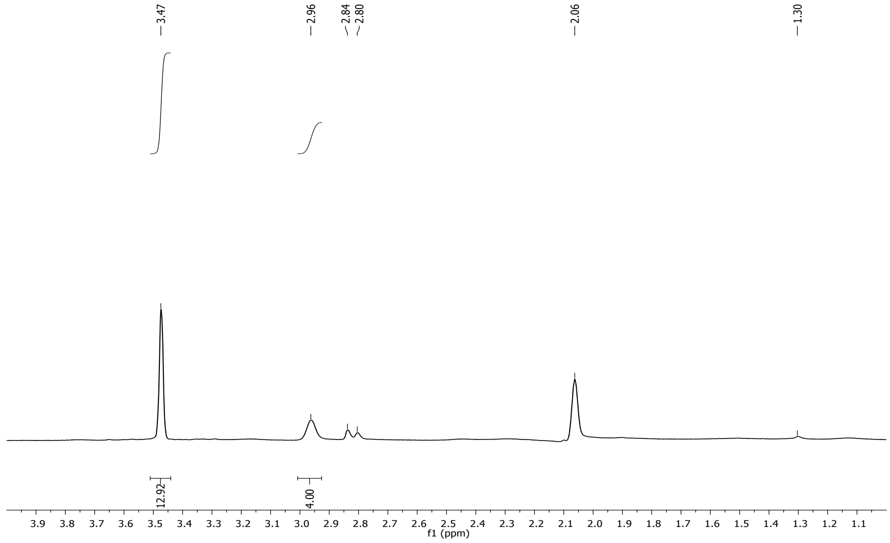
^{11}B-NMR of the [HNMe$_3$][2,2'-Co(1,7-C$_2$B$_9$H$_{11}$)$_2$]



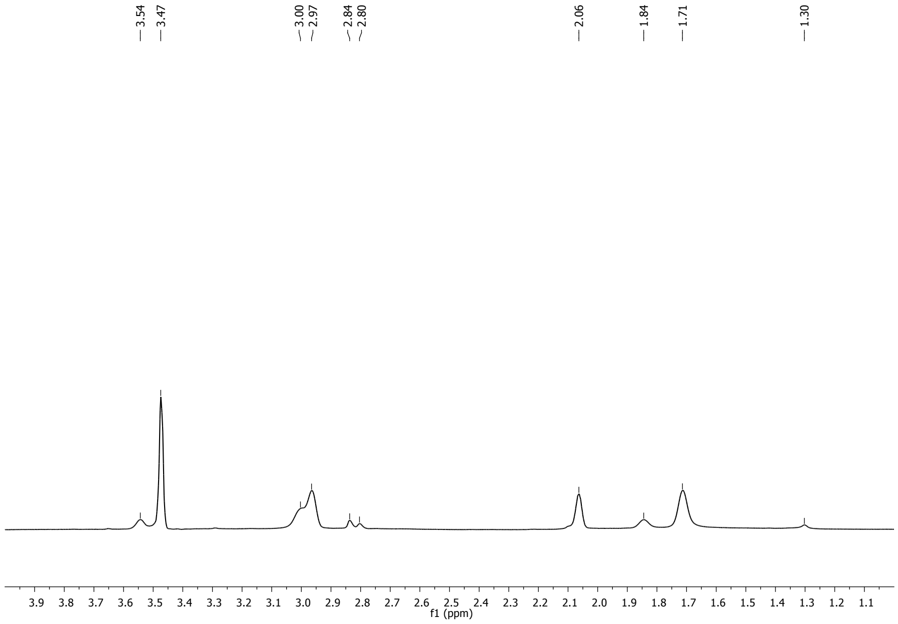
^{11}B{^{1}H }-NMR of the [HNMe$_3$][2,2'-Co(1,7-C$_2$B$_9$H$_{11}$)$_2$]

Characterization of the [NMe_4][2,2’-Co(1,7-$C_2B_9H_{11}$)$_2$]

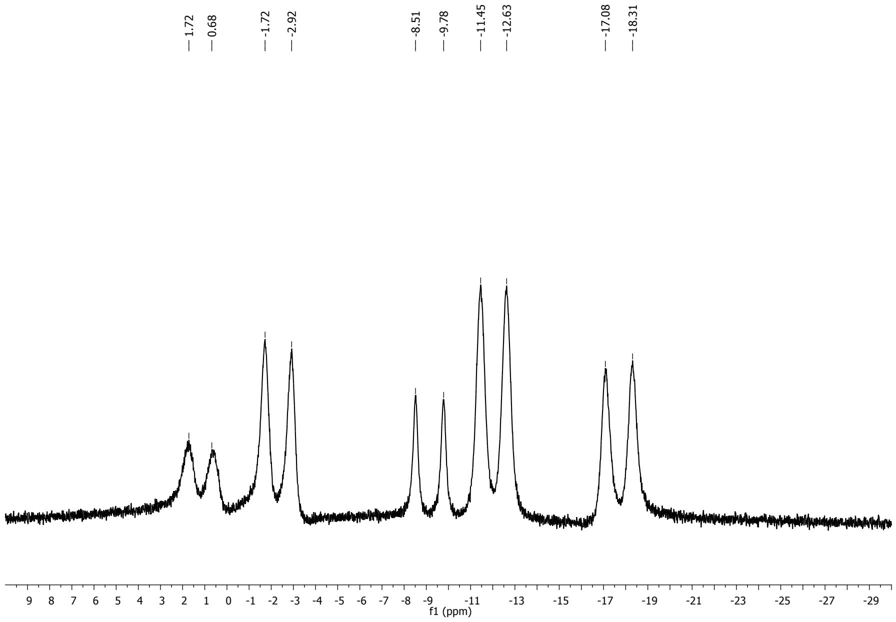




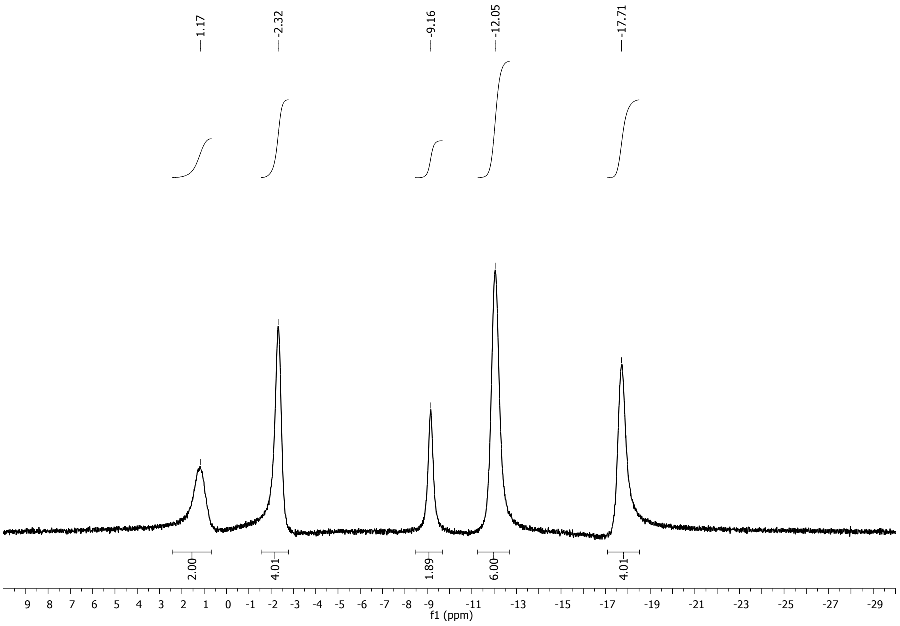
^{1}H-NMR of the [NMe_4][2,2’-Co(1,7-$C_2B_9H_{11}$)$_2$]



^{1}H{^{11}B}-NMR of the [NMe_4][2,2’-Co(1,7-$C_2B_9H_{11}$)$_2$]

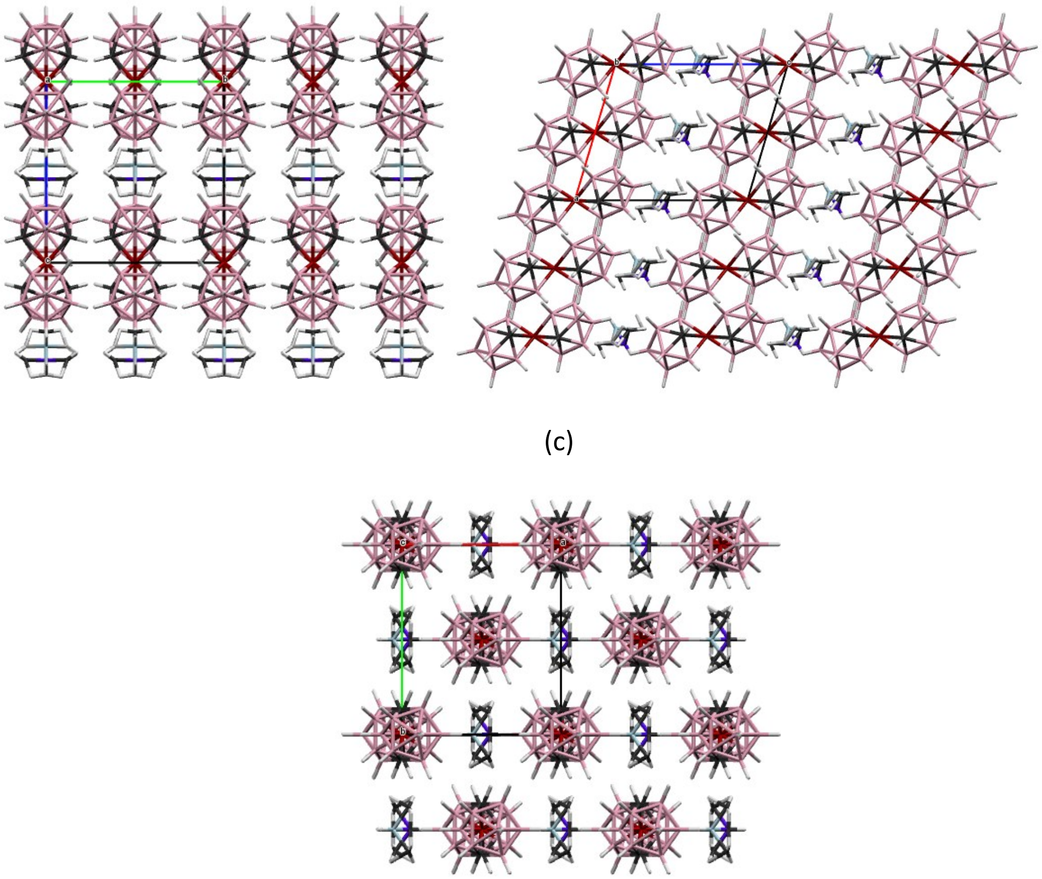


^{11}B-NMR of the [NMe$_4$][2,2'-Co(1,7-C$_2$B$_9$H$_{11}$)$_2$]



^{11}B{^{1}H }-NMR of the [NMe$_4$][2,2'-Co(1,7-C$_2$B$_9$H$_{11}$)$_2$]

Figure S 1. Packing structure of [$HNMe_3$][2,2'-Co(1,7-$C_2B_9H_{11}$)$_2$] complex along the a axis (a), b axis (b) and c axis (c)


(a)

(b)

(c)

Figure S 2. Packing arrangement of the [$HNMe_3$][2,2'-Co(1,7-$C_2B_9H_{11}$)$_2$] structure through H···B (2.788 Å) close contacts

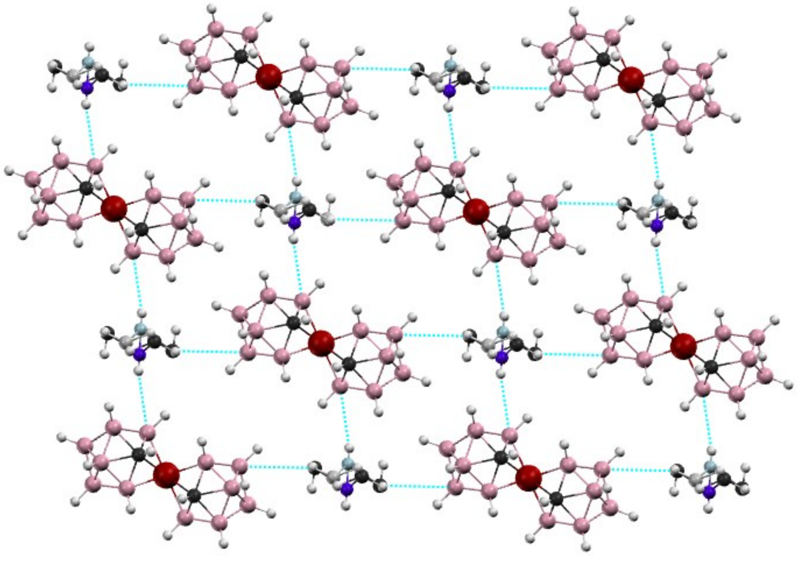


Table S1. Crystal data for X-Ray structure of the [$HNMe_3$][2,2'-Co(1,7-$C_2B_9H_{11}$)$_2$] complex

Empirical Formula	$C_7H_{32}B_{18}CoN$
Formula weight	383.84 g/mol
Crystal system	Monoclinic
Space group	C2/m
a[Å]	9.130(11)
b[Å]	10.446(10)
c[Å]	11.101(9)
α[º]=ɣ[º]	90º
β[º]	106.63
V[Å^3]	1014.4(17)
Formula unit/Cell	2
ρ_{calc}. [g cm^{-3}]	1.257
μ [mm^{-1}]	0.838
R1$^{[a]}$,[I>2σ(I)]	0.0676
wR$_2^{[b]}$ [all data]	0.1723
F(000)	396
Index ranges	-10≤h≤10
	-12≤k≤12
	-12≤l≤12

[a] R$_1$ = $\sum \left\| F_0 \right| - \left| F_c \right\| \Big/ \sum \left| F_0 \right|$

[b] wR$_2$ = $\left[\sum \left\{w(F_0^2 - F_c^2)^2\right\} / \sum \left\{w(F_0^2)^2\right\}\right]^{1/2}$, where w= 1/ $\left[\sigma^2\left(F_0^2\right) + (0.0075P)^2 + 5.6143P\right]$ $and\ P = (F_0^2 + 2F_C^2)/3$

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