

Patterns in Supraicosahedral Metallacarboranes

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Abstract

Chapter one gives an introduction into heteroborane chemistry focussing on supraicosahedral metallocarboranes.

Chapter two describes the first examples of untethered 4,1,2- MC_2B_{10} 13-vertex metallocarboranes prepared by polyhedral expansion of a tethered carborane precursor. C,C'-dimethyl 4,1,6- MC_2B_{10} compounds were afforded as co-products of the reactions. In contrast to the analogous 1,2- to 1,6- carborane rearrangement, experimental observations and DFT calculations reveal that 4,1,2- to 4,1,6- metallocarborane isomerisation does not occur under standard laboratory conditions.

Chapter three constitutes the most extensive examination to date of the relationship between ligand orientational preference and bond strength in supraicosahedral molecules. A structural study of nine 13-vertex indenyl cobaltacarboranes supplemented by DFT calculations on models of related naphthalene ferracarboranes provided information on the relative trans influences of facial cage atoms.

Chapter four describes the synthesis and characterisation of 1,14,2,9- and 1,14,2,10- $M_2C_2B_{10}$ 14-vertex cobaltacarboranes. The first unambiguous confirmation of 1,14,2,9- $M_2C_2B_{10}$ architecture from crystallographic studies and supporting spectroscopic data is presented.

A series of six asymmetric, 14-vertex, bicapped hexagonal antiprismatic bimetallocarboranes with 1,8/13,2,x- $Co_2C_2B_{10}$ atom arrangements, thought to be the results of direct electrophilic insertion reactions, are reported in chapter five. A detailed analysis of crystallographic data resulted in the identification of cage C atom positions in all six isomers.

Chapter six contains experimental procedures and characterisation details for all the new compounds reported herein. Crystallographic data is listed in appendices A and B (CD) along with structure solution and refinement details.

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I hereby declare that the work presented in this thesis was carried out by myself at Heriot-Watt University, Edinburgh, except where due acknowledgement is made, and has not been submitted for any other degree.

Amelia McAnaw Faulds (Candidate)

Prof. Alan J Welch

Date

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Published Papers

- Supraicosahedral indenyl cobaltacarboranes, *Dalton Trans.*, 2010, **39**, 5286.
- Untethered 4,1,2-MC₂B₁₀ supraicosahedral metallacarboranes, their C,C'-dimethyl 4,1,6-, 4,1,8- and 4,1,12-MC₂B₁₀ analogues, and DFT study of the (4,)1,2- to (4,)1,6-isomerisations of C₂B₁₁ carboranes and MC₂B₁₀ metallacarboranes, *Dalton Trans.*, 2012, **41**, 10957.
- The VCD method - a simple and reliable way to distinguish cage C and B atoms in (hetero)carborane structures determined crystallographically, *Dalton Trans.*, 2013, **42**, 645.
- The synthesis and characterisation of homo- and heterobimetallic 1,14,2,9- and 1,14,2,10-M₂C₂B₁₀ 14-vertex metallacarboranes, *Dalton Trans.*, 2013, **42**, 671.

Abbreviations

40-60	Boiling between 40 and 60 °C (petroleum ether)
2c-2e	Two centre two electron
3c-2e	Three centre two electron
18-crown-6	1,4,7,10,13,16-hexanoxacyclooctadecane
δ	Chemical shift in ppm
$\langle\delta(^{11}\text{B})\rangle$	Weighted average chemical shift in ppm
η	Ligand hapticity
μ	Bridging
Ω	Overall root-mean square deviation
Å	Ångström, 1×10^{-10} m
app	apparent
bha	bicapped hexagonal antiprism
BHD	B-H Distance
bipy	2,2'-bipyridine ($\text{C}_5\text{H}_4\text{N}$) ₂
BMOs	Bonding Molecular Orbitals
BNCT	Boron Neutron Capture Therapy
br	broad
CHN	Elemental analysis
Cp	Cyclopentadienyl (C_5H_5)
Cp*	Pentamethylcyclopentadienyl (C_5Me_5)
d	doublet
DFT	Density Functional Theory
dppe	1,2-bis(diphenylphosphino)ethane
DSD	Diamond-Square-Diamond
EIMS	Electron Ionisation Mass Spectrometry
Et	Ethyl group ($-\text{CH}_2\text{CH}_3$)
Et ₂ O	Diethyl ether ($\text{CH}_3\text{CH}_2\text{O}$)
FMOs	Frontier Molecular Orbitals
g	gram(s)
h	hour(s)

HIV	Human Immunodeficiency Virus
K	Kelvin
kcal mol ⁻¹	kilocalories per mole
m	multiplet
M	Molar concentration (molarity)
M ⁺	Molecular parent ion
Me	Methyl group (-CH ₃)
mg	milligram(s)
ml	millilitre(s)
MHz	megahertz
mmol	millimole(s)
MO	Molecular Orbital
MW	Molecular Weight
<i>m/z</i>	mass-to-charge ratio
<i>n</i> -BuLi	<i>n</i> -butyl lithium, C ₄ H ₉ Li
NMR	Nuclear Magnetic Resonance
OEt	Ethoxy group (-OCH ₂ CH ₃)
<i>p</i> -cymene	1-methyl-4-isopropylbenzene
Ph	Phenyl group (-C ₆ H ₅)
ppm	parts per million
PSEPT	Polyhedral Skeletal Electron Pair Theory
q	quartet
R _f	Retention factor
s	singlet
t	triplet
TFR	Triangular Face Rotation
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
<i>U</i> _{eq}	Isotropic displacement parameter
VCD	Vertex-to-Centroid Distance

Abbreviations for Specific Compounds

Chapter 2	1	1,2-Me ₂ -4-Cp-4,1,2- <i>closo</i> -CoC ₂ B ₁₀ H ₁₀
	2	1,6-Me ₂ -4-Cp-4,1,6- <i>closo</i> -CoC ₂ B ₁₀ H ₁₀
	3	1,8-Me ₂ -4-Cp-4,1,8- <i>closo</i> -CoC ₂ B ₁₀ H ₁₀
	4	1,2-Me ₂ -4-(<i>p</i> -cymene)-4,1,2- <i>closo</i> -RuC ₂ B ₁₀ H ₁₀
	5	1,6-Me ₂ -4-(<i>p</i> -cymene)-4,1,6- <i>closo</i> -RuC ₂ B ₁₀ H ₁₀
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Chapter 3	6	4-(η-C ₉ H ₇)-4,1,6- <i>closo</i> -CoC ₂ B ₁₀ H ₁₂
	7	1,6-Me ₂ -4-(η-C ₉ H ₇)-4,1,6- <i>closo</i> -CoC ₂ B ₁₀ H ₁₀
	8	4-(η-C ₉ H ₇)-4,1,8- <i>closo</i> -CoC ₂ B ₁₀ H ₁₂ [*]
	9	1,8-Me ₂ -4-(η-C ₉ H ₇)-4,1,8- <i>closo</i> -CoC ₂ B ₁₀ H ₁₀
	10	1(or 6)-Me-4-(η-C ₉ H ₇)-4,1,6- <i>closo</i> -CoC ₂ B ₁₀ H ₁₁ [*]
	11	8-Me-4-(η-C ₉ H ₇)-4,1,8- <i>closo</i> -CoC ₂ B ₁₀ H ₁₁
	12	1-Me-4-(η-C ₉ H ₇)-4,1,8- <i>closo</i> -CoC ₂ B ₁₀ H ₁₁ [*]
	13	4-(η-C ₉ H ₇)-4,1,10- <i>closo</i> -CoC ₂ B ₁₀ H ₁₂
	14	4-(η-C ₉ H ₇)-4,1,12- <i>closo</i> -CoC ₂ B ₁₀ H ₁₂
	15	1,12-Me ₂ -4-(η-C ₉ H ₇)-4,1,12- <i>closo</i> -CoC ₂ B ₁₀ H ₁₀
16	1,2-Me ₂ -4-(η-C ₉ H ₇)-4,1,2- <i>closo</i> -CoC ₂ B ₁₀ H ₁₀	
17	1,2-μ-(CH ₂) ₃ -4-(η-C ₉ H ₇)-4,1,2- <i>closo</i> -CoC ₂ B ₁₀ H ₁₀	
<hr/>		
Chapter 4	18	1,14-Cp ₂ -1,14,2,9- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₂ [*]
	19	1-Cp-14-C ₅ H ₄ CH(OH)CH ₂ CH ₂ CH ₃ -1,14,2,9- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₂
	20	1,13-Cp ₂ -1,13,2,9- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₂
	21	2,9-Me ₂ -1,14-Cp ₂ -1,14,2,9- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₀
	22	2,10-Me ₂ -1,14-Cp ₂ -1,14,2,10- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₀ [*]
	23	1,14-(η-C ₉ H ₇) ₂ -1,14,2,9- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₂
	24	1,14-(η-C ₉ H ₇) ₂ -1,14,2,10- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₂
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Chapter 5	25	2-OEt-4-Cp-4,1,12- <i>closo</i> -CoC ₂ B ₁₀ H ₁₁
	26	3-OEt-1,8-Cp ₂ -1,8,2,10- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₁
	27	1,13-Cp ₂ -1,13,2,4- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₂
	28	1,8-Cp ₂ -1,8,2,4- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₂
	29	1,8-Cp ₂ -1,8,2,5- <i>closo</i> -Co ₂ C ₂ B ₁₀ H ₁₂

^{*}No crystallographic details.

- A** 1-Me-4-(PEt₃)-4,6/7-μ-{Co(PEt₃)₂-μ-(H)₂}-4,1,2-*closo*-CoC₂B₁₀H₁₀
- B** 1,2-μ-(CH₂)₃-4-Cp-4,1,2-*closo*-CoC₂B₁₀H₁₀
- C** 1,2-μ-(CH₂)₃-4-(*p*-cymene)-4,1,2-*closo*-RuC₂B₁₀H₁₀
- D** 4-Cp-4,1,6-*closo*-CoC₂B₁₀H₁₂
- E** 1,12-Me₂-4-Cp-4,1,12-*closo*-CoC₂B₁₀H₁₀
- F** 1,8-Ph₂-4-Cp-4,1,8-*closo*-CoC₂B₁₀H₁₀
- G** 2,3,5,7,9,11,12,13-Me₈-4-Cp-4,1,8-*closo*-CoC₂B₁₀H₄
- H** 1,8-Et₂-2,5,6,7,9,11,12,13-Me₈-4-Cp-4,1,8-*closo*-CoC₂B₁₀H₂
- J** 4-Cp-4,1,8-*closo*-CoC₂B₁₀H₁₂
- K** 4-Cp-4,1,12-*closo*-CoC₂B₁₀H₁₂
- L** 1-CN-4-Cp-4,1,2-*closo*-CoC₂B₁₀H₁₁
- M** 1,2-μ-(CH₂)₃-4-dppe-4,1,2-*closo*-NiC₂B₁₀H₁₀
- N** 1,2-μ-(CH₂)₃-4-(PMe₂Ph)₂-4,1,2-*closo*-PtC₂B₁₀H₁₀
- P** 4-Cp-4,1,10-*closo*-CoC₂B₁₀H₁₂
- Q** 4,5-Cp₂-4,5,1,6-*closo*-Co₂C₂B₉H₁₁
- R** 1,14-Cp₂-1,14,2,10-*closo*-Co₂C₂B₁₀H₁₂
- S** 1,13-Cp₂-1,13,2,10-*closo*-Co₂C₂B₁₀H₁₂
- T** 3-Cp-3,1,2-*closo*-CoC₂B₉H₁₁