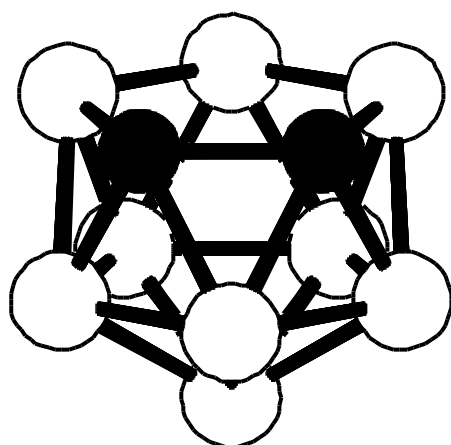


Structures of the carborane monoanions



Hydrogens not shown

Mark A. Fox, Andrew K. Hughes, Andrew L. Johnson,
Michael A.J. Paterson and Kenneth Wade

University of Durham

Why *nido*-C₂B₉ carboranes?

They are precursors to most

Carboranes

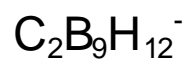
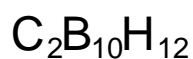
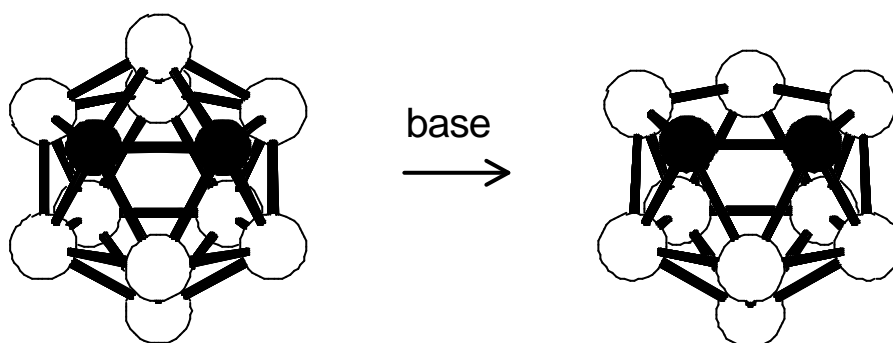
Metallacarboranes

(Andy Hughes and John Malget)

Heteroboranes

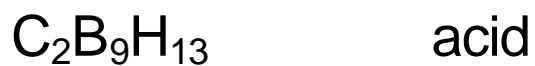
How are they made?

From the easily or commercially available icosahedral carboranes by deboronation



Hydrogens not shown

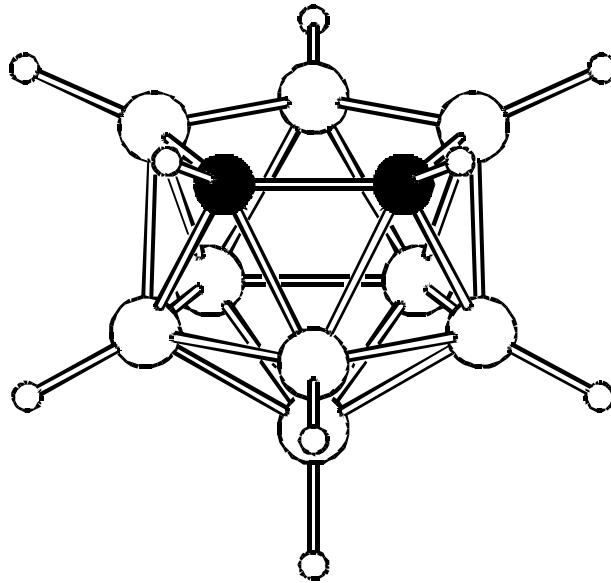
Generally



Salts of $\text{C}_2\text{B}_9\text{H}_{12}^-$ are usually obtained from deboronations of icosahedral carboranes

Structures of $C_2B_9H_{12}^-$

All cage atoms have exo-terminal hydrogens



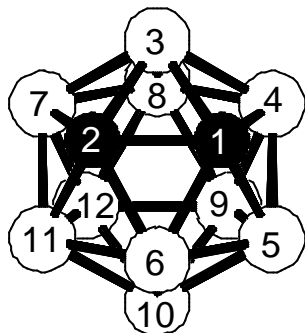
Where is the extra / twelfth / unique / non-exo terminal hydrogen ?

Isomers of $C_2B_9H_{12}^-$

Only three are known – all from deboronation of the three $C_2B_{10}H_{12}$ isomers

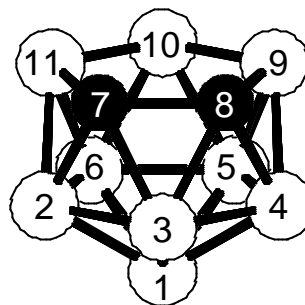
The most positive boron atom is removed

ORTHO



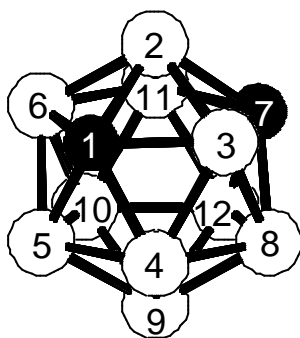
1,2-C₂B₁₀H₁₂

“-B(3)⁺”
→



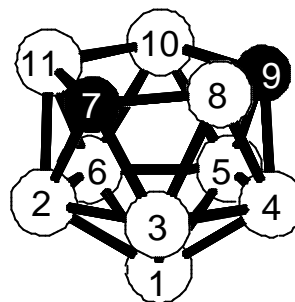
7,8-C₂B₉H₁₂⁻

META



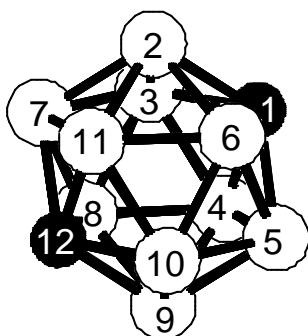
1,7-C₂B₁₀H₁₂

“-B(2)⁺”
→



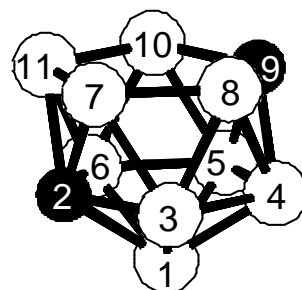
7,9-C₂B₉H₁₂⁻

PARA



1,12-C₂B₁₀H₁₂

“-B(2)⁺”
→

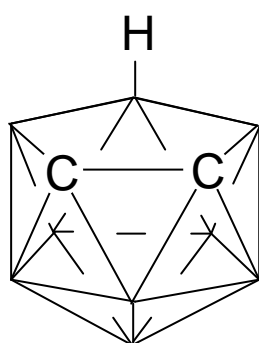


2,9-C₂B₉H₁₂⁻

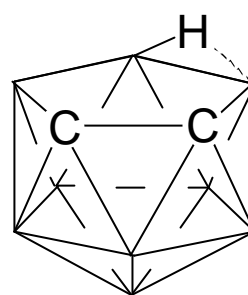
'Ortho' $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$

NMR data suggest the unique hydrogen to be bonded to the boron opposite the carbons on the open face

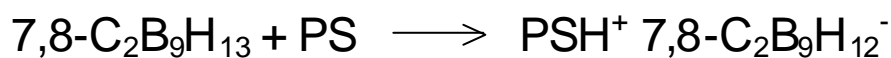
Possible geometries



symmetrical endo



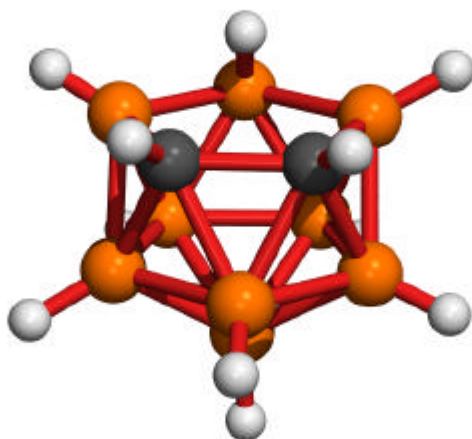
bridging and fluxional
in solution



PS = proton sponge

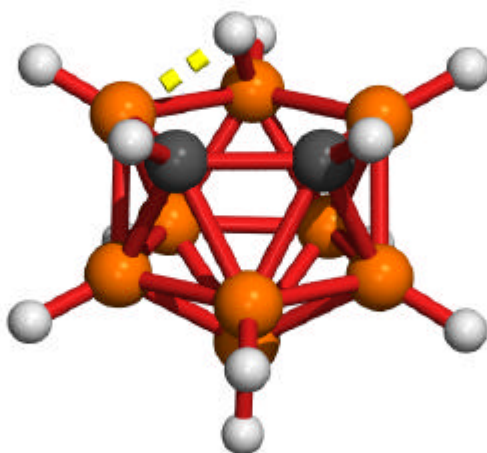
Structures determined for 3 salts of $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$
by X-ray crystallography

**Molecular structures of 7,8-C₂B₉H₁₂⁻ anions
determined by X-ray diffraction**



As (Me₂SO)₂H⁺ salt

A.J. Welch, Edinburgh, 1990



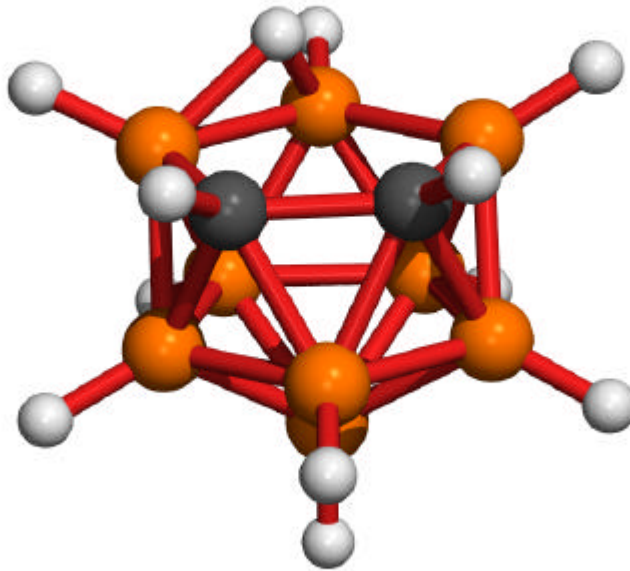
As (Me₂N)₃PNH₂⁺ salt and as PSH⁺ salt

(PS = proton sponge)

Durham 1999

Neutron diffraction is better at locating hydrogen atoms accurately.

Large crystals of the PSH^+ salt were grown and good quality neutron diffraction data obtained.

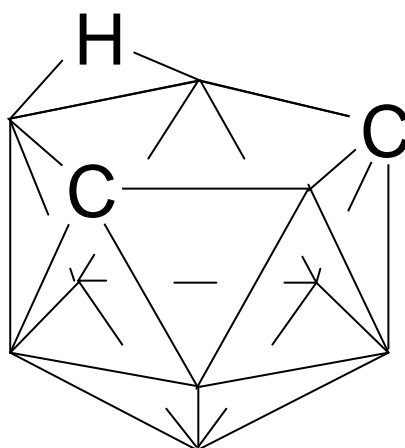


The bridging geometry is found. The unique hydrogen is asymmetrically bridged.

'Meta' $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$

NMR data suggest the unique hydrogen to be bridging to the adjacent borons on the open face

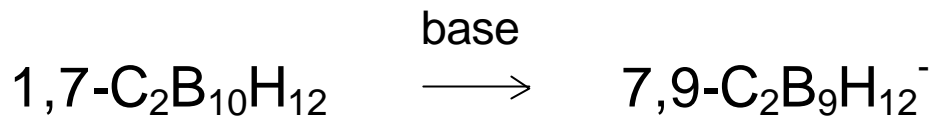
Possible geometry



symmetrical bridging

The molecular structure of $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ has not been determined experimentally

Attempts to obtain the molecular structure of 'meta' 7,9-C₂B₉H₁₂⁻ by X-ray crystallography



1. Fluoride ion – Bu₄NF in THF

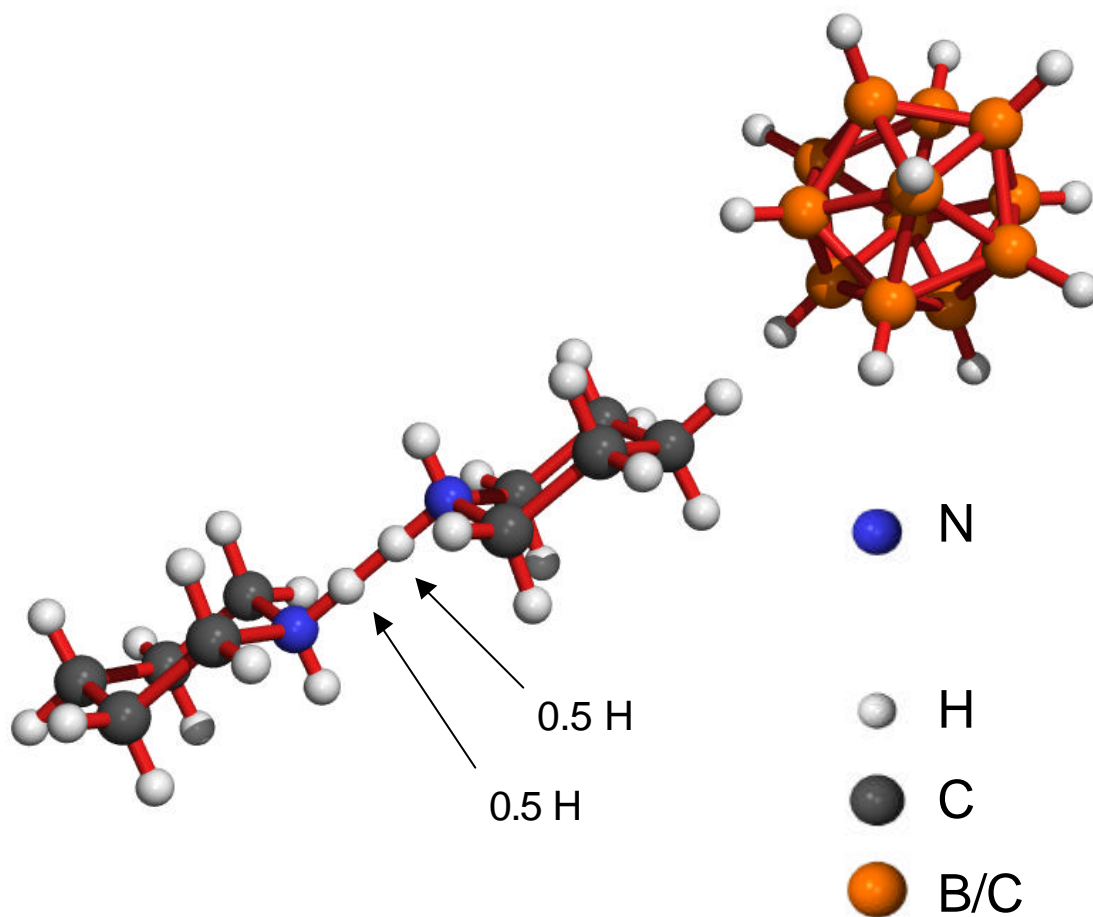
Crystals of Bu₄N⁺ 7,9-C₂B₉H₁₂⁻
- crack at low temperatures.

2. Piperidine – C₅H₁₀NH

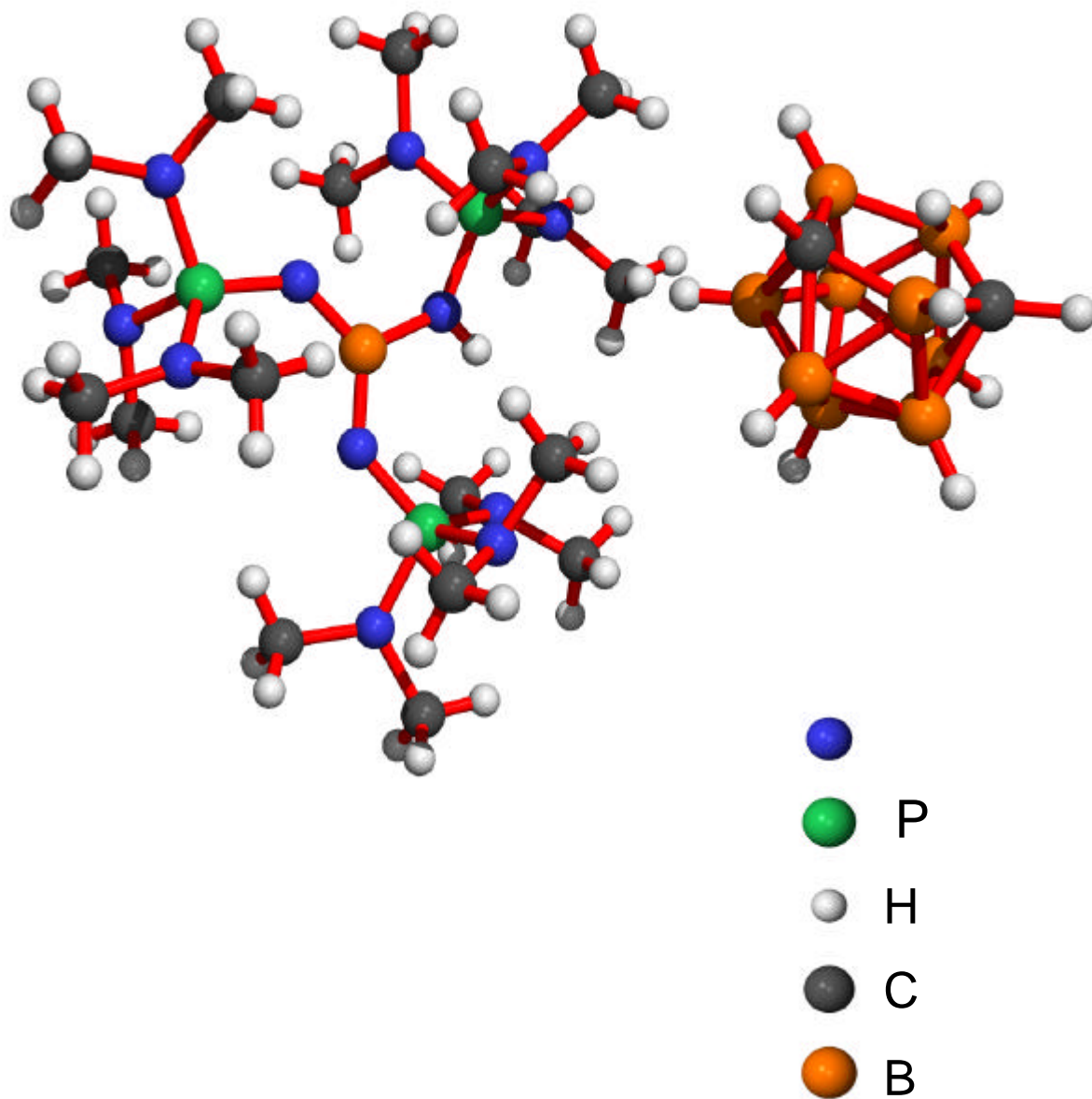
Crystals of (C₅H₁₀NH)₂H⁺ 7,9-C₂B₉H₁₂⁻
- cage distortion.

3. Iminophosphorane – (Me₂N)₃P=NH

Crystals of (Me₂N)₃PNHB[NP(NMe₂)₃]₂⁺ 7,9-C₂B₉H₁₂⁻
- cage distortion.



Crystal structure of
 $[\text{C}_5\text{H}_{10}\text{NH}]_2\text{H}^+ 7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$



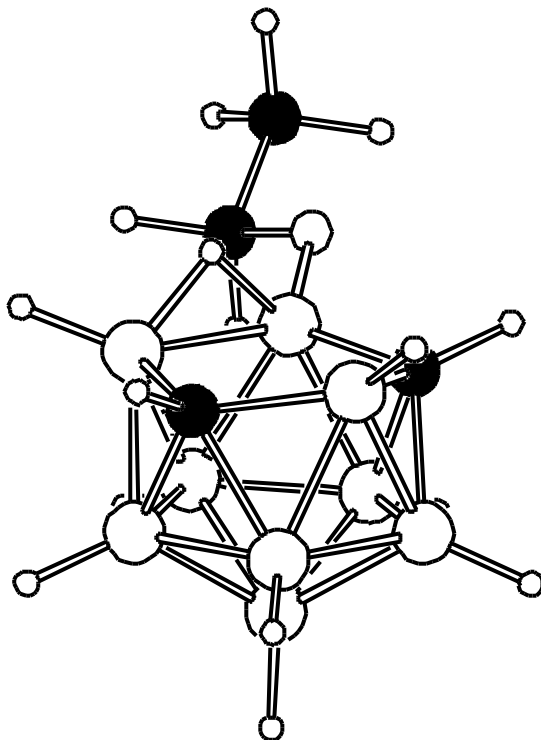
Crystal structure of
 $(\text{Me}_2\text{N})_3\text{PNHB}[\text{NP}(\text{NMe}_2)_3]_2^+ 7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$

4. Hydroxide ion – KOH in EtOH

Major product – potassium salt of 7,9-C₂B₉H₁₂⁻

Unexpected carborane side product (20%)

10-EtO-7,9-C₂B₉H₁₁⁻



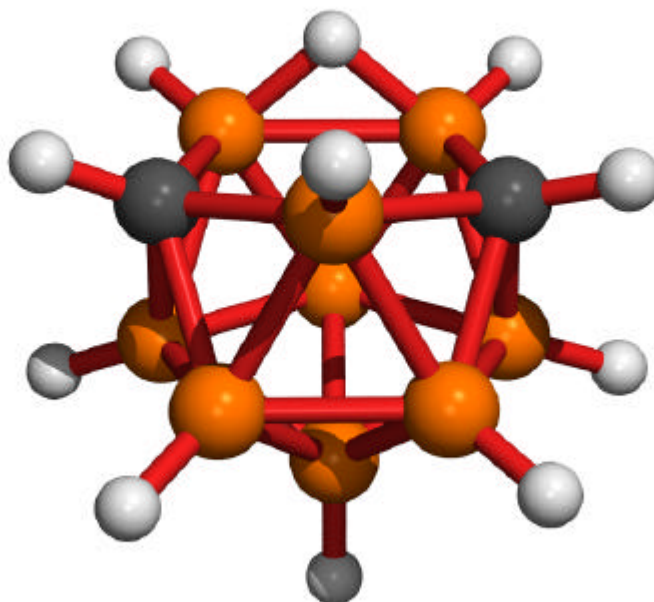
First case of cage substitution during deboronation of 1,7-C₂B₁₀H₁₂.

Add 18-crown-16 –
crystals of K(18-C-6)⁺ 7,9-C₂B₉H₁₂⁻

- cage distortion.

Add PSH⁺Cl⁻ –
Crystals of PSH⁺ 7,9-C₂B₉H₁₂⁻

**Molecular structure of the 7,9-C₂B₉H₁₂⁻ anion
determined by X-ray diffraction**



PSH⁺ salt

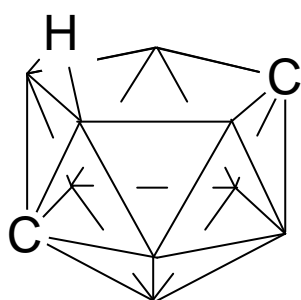
Durham 2000

Bridging geometry found as expected

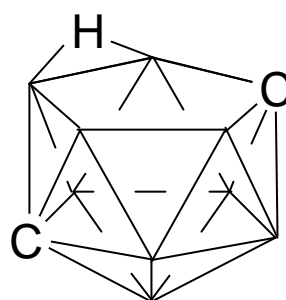
'Para' 2,9-C₂B₉H₁₂⁻

NMR data suggest the unique hydrogen to be bonded to the boron opposite the carbon on the open face

Possible geometries



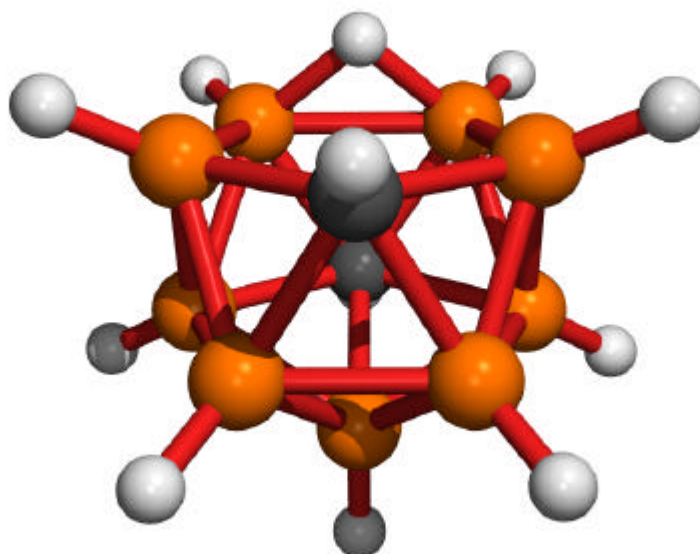
symmetrical bridging



non-symmetrical bridging
and fluxional in solution

Structure determined here for the first time for 2,9-C₂B₉H₁₂⁻ by X-ray crystallography

**Molecular structure of the 2,9-C₂B₉H₁₂⁻ anion
determined by X-ray diffraction**



PSH⁺ salt

Durham 1999

Symmetrical geometry found

The three known $C_2B_9H_{12}^-$ monoanions have been structurally characterized and the unique hydrogen located in all cases.

Acknowledgements

EPSRC

John M. Malget
Aileen M. Martin

Durham X-ray Crystallographers

Andrei S. Batsanov
Andrés E. Goeta
Judith A.K. Howard
Ivan S. Neretin