

**REACTIONS OF ICOSAHEDRAL  
CARBORANES WITH THE  
IMINOPHOSPHORANE  $\text{HNP}(\text{NMe}_2)_3$**

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Gray, Tom G. Hibbert and Ken Wade

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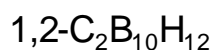
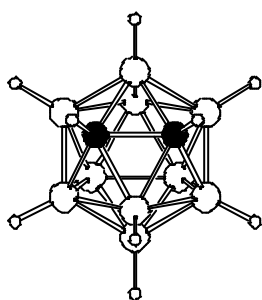
# ICOSAHEDRAL CLOSO-CARBORANES

## $C_2B_{10}H_{12}$

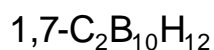
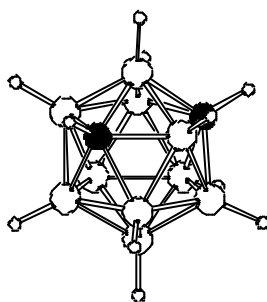
The cages are unaffected by strong acids and oxidising agents.

They are however susceptible to certain bases where one boron atom is removed (deboronated) to give the well known *nido*  $C_2B_9$  residues – they are precursors to many heteroboranes and metallocarboranes.

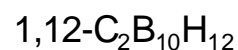
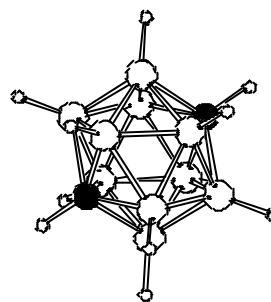
Ortho



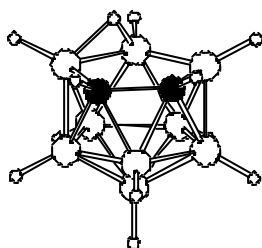
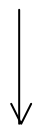
Meta



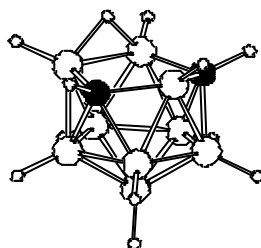
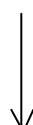
Para



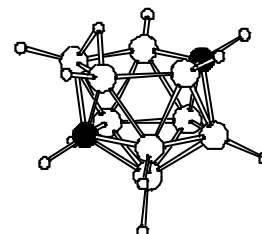
$F^-$ ,  $OR^-$ ,  
 $N_2H_4$ ,  
 $HNC_5H_{10}$



$F^-$ ,  $OR^-$ ,  
 $N_2H_4$ ,  
 $HNC_5H_{10}$



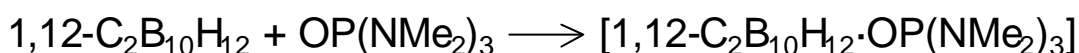
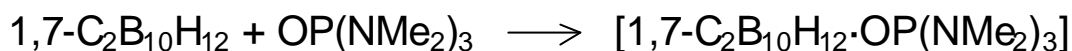
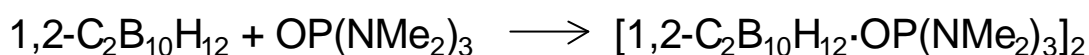
More forcing  
conditions  
than for *ortho*



KOH only

The base HMPA (hexamethylphosphoramide)  $\text{OP}(\text{NMe}_2)_3$  does not deboronate the  $\text{C}_2\text{B}_{10}\text{H}_{12}$  isomers at room temperature.

It acts as an hydrogen bond acceptor for the acidic hydrogens at the carbon atoms of these clusters to yield 1:1 carborane:HMPA adducts on crystallization.



These C-H...O hydrogen bonded supramolecular structures provide the first definitive X-ray structures of the unsubstituted carboranes.

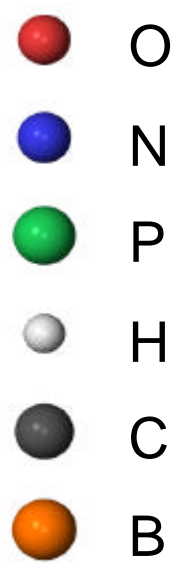
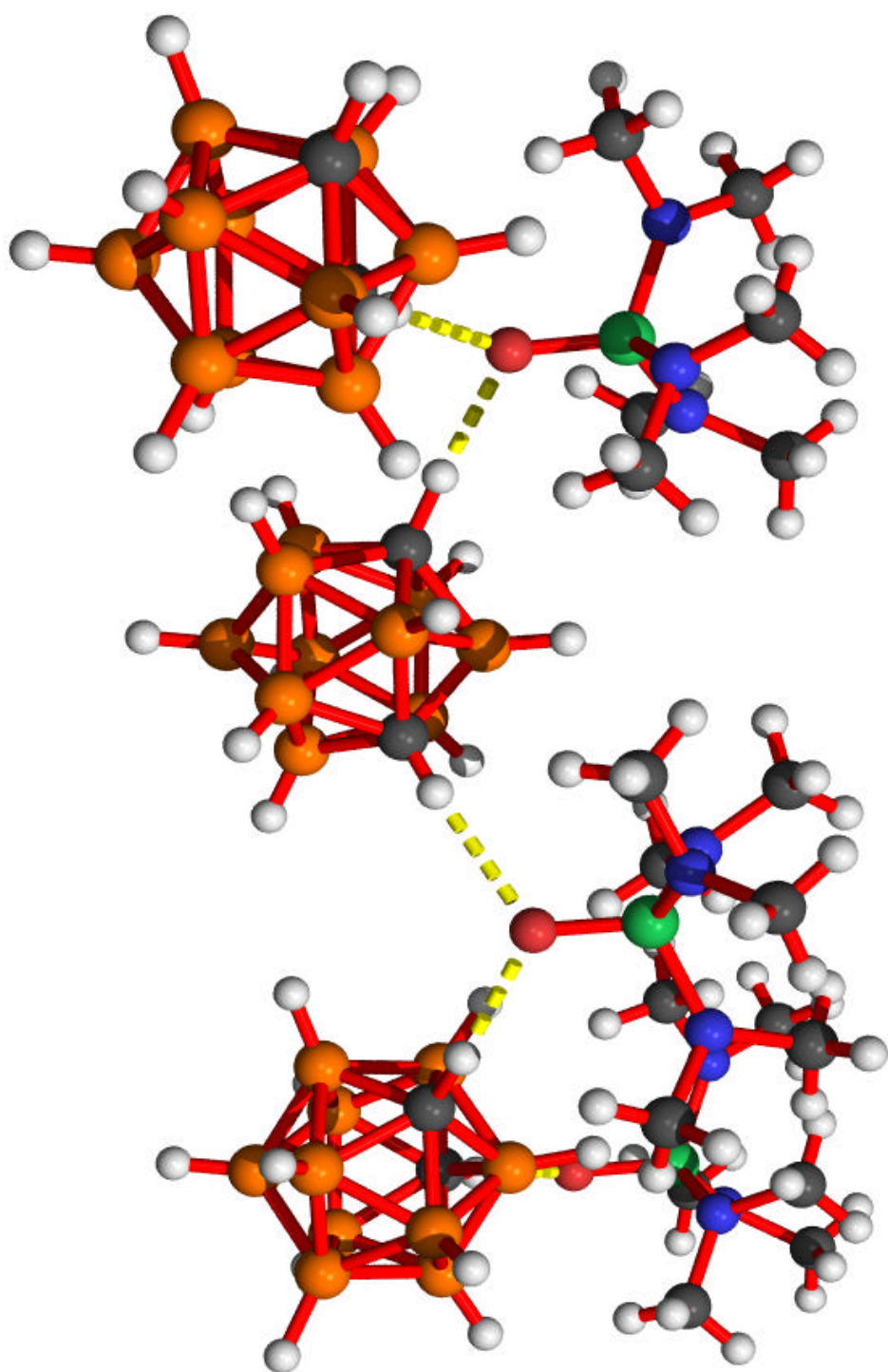
Iminophosphoranes,  $\text{HNPR}_3$ , may be

i) effective deboronating agents

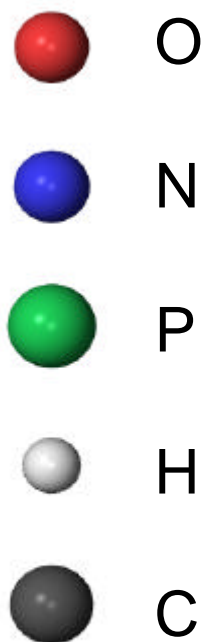
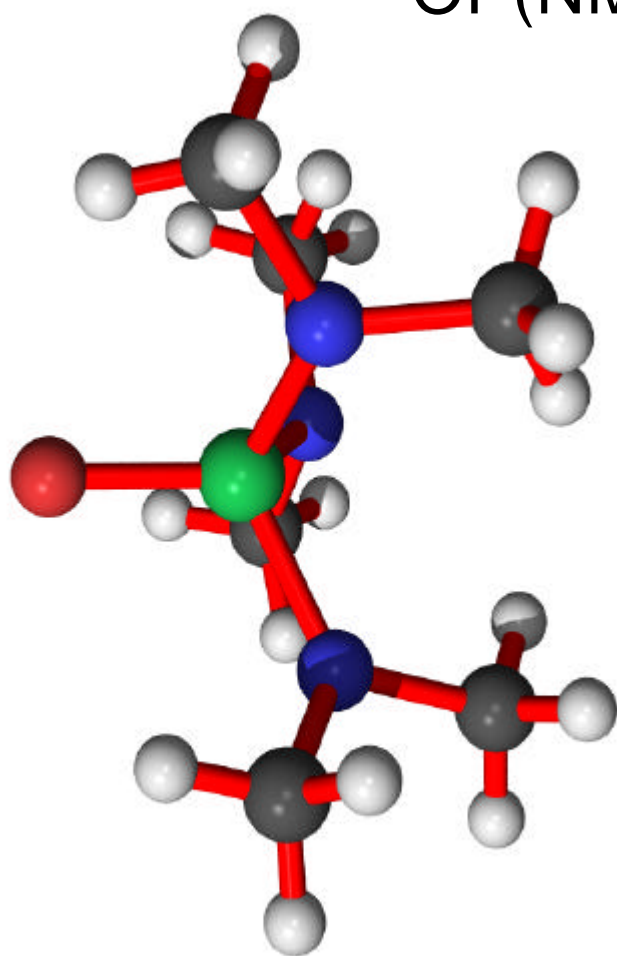
or

ii) good hydrogen bond acceptors.

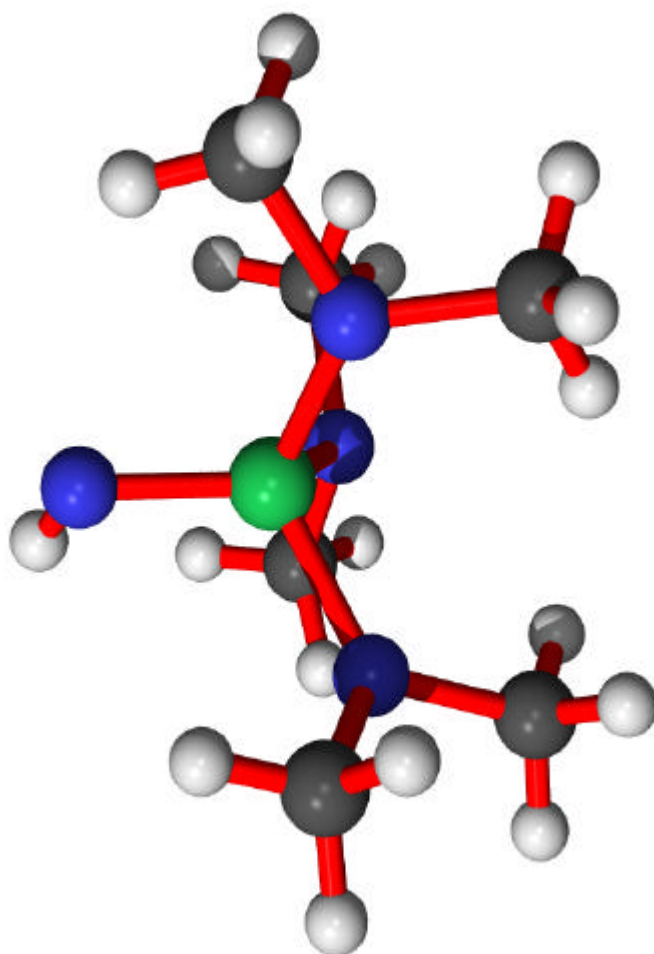
N-Imino-tris(dimethylamino)phosphorane  $\text{HNP}(\text{NMe}_2)_3$  is commercially available and has a similar geometry as HMPA.



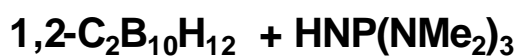
$\text{OP}(\text{NMe}_2)_3$



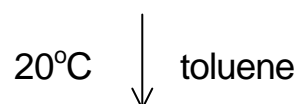
$\text{HNP}(\text{NMe}_2)_3$



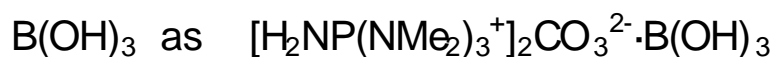
## **Ortho carborane + iminophosphorane**



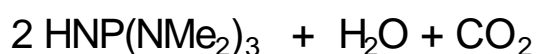
In presence of air – *rapid deboronation*



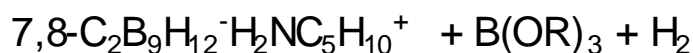
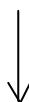
X-ray structures of both boron-containing products obtained.

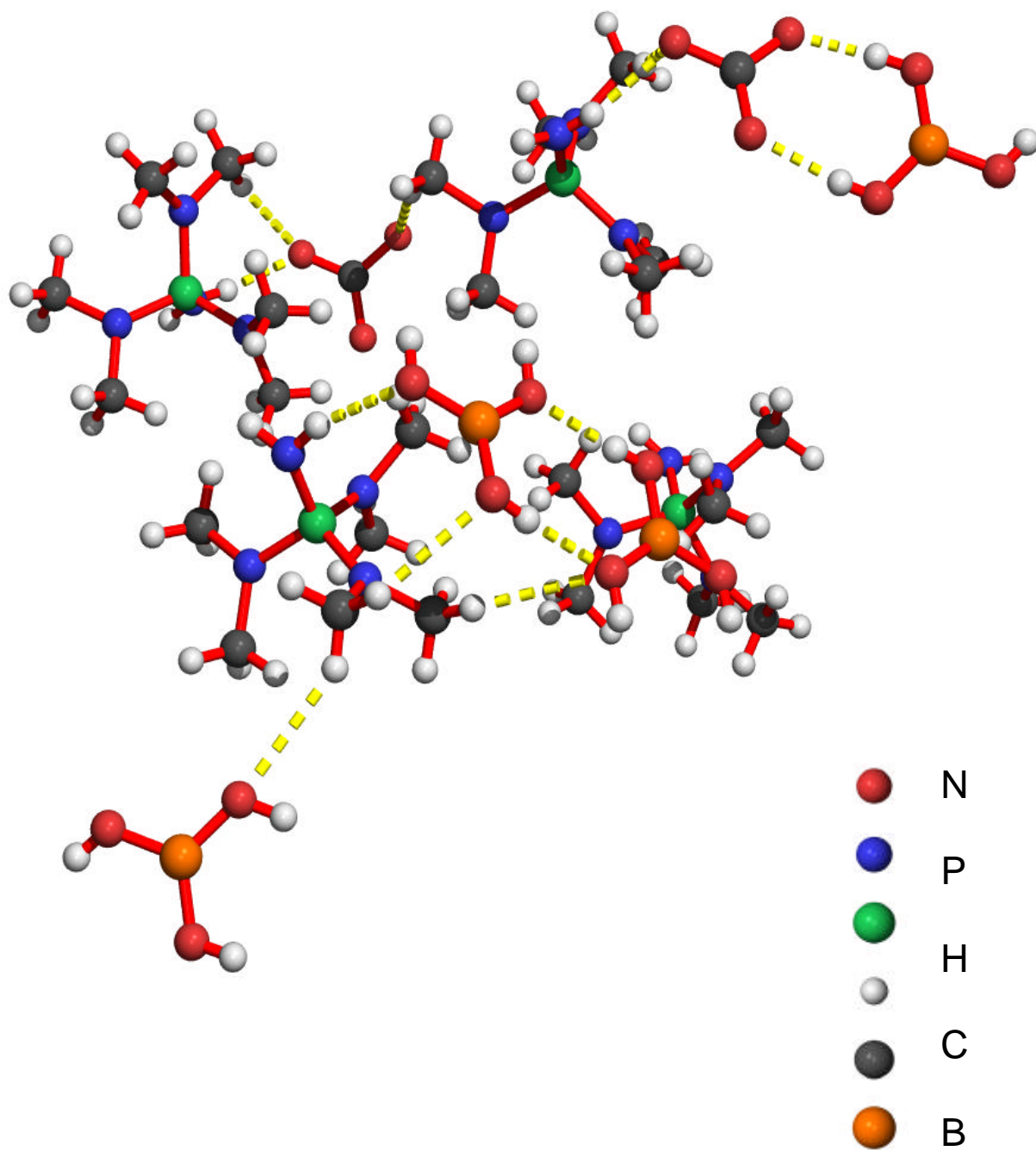


The iminophosphorane absorbs water and carbon dioxide.



Similar to piperidine  $\text{HNC}_5\text{H}_{10}$



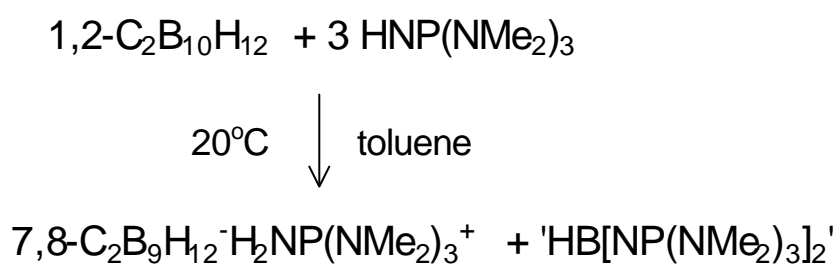


Crystal structure of  $[\text{H}_2\text{NP}(\text{NMe}_2)_3]^+ \text{CO}_3^{2-}$

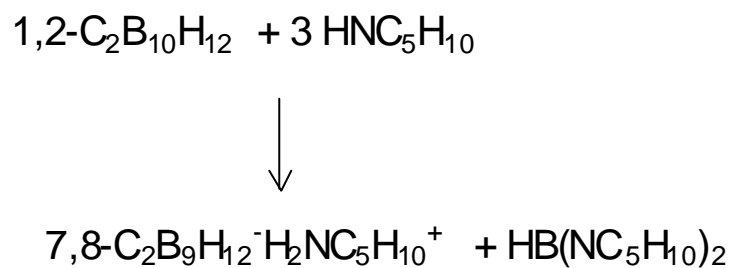
## ***Ortho* carborane + iminophosphorane**

Is water vital for deboronation?

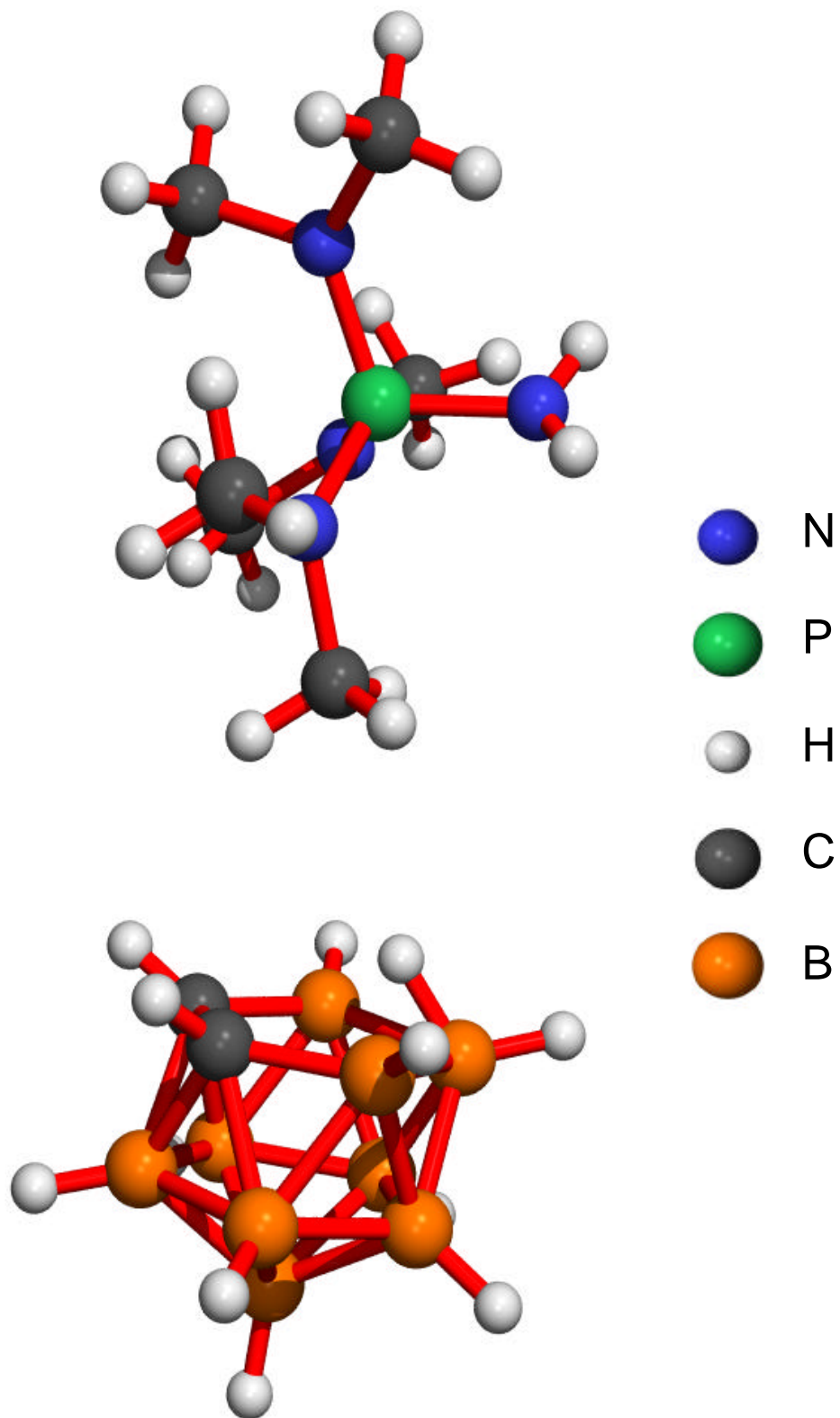
Under nitrogen – *rapid deboronation*



Similar to piperidine  $\text{HNC}_5\text{H}_{10}$





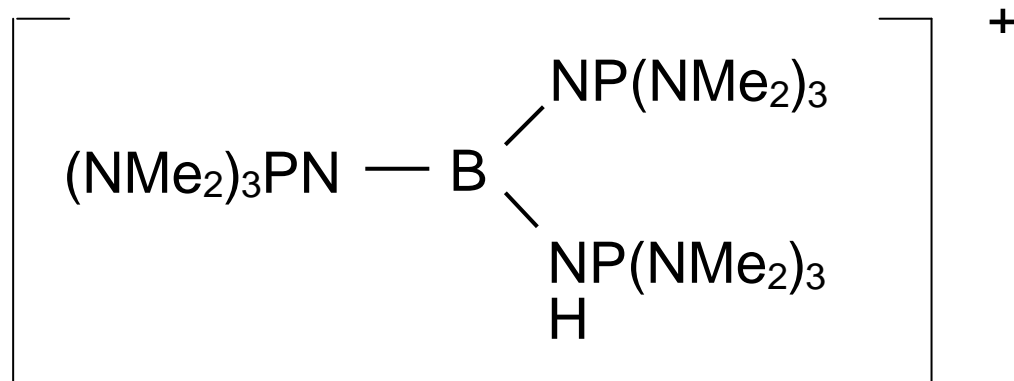


Crystal structure of  $\text{H}_2\text{NP}(\text{NMe}_2)_3^+ \text{C}_2\text{B}_9\text{H}_{12}^-$

*TWO OTHER CARBORANE PRODUCTS WERE  
OBSERVED BY MONITORING THE REACTION  
WITH B-11 and P-31 NMR SPECTROSCOPY*

1. Peaks corresponding to a possible CARBORANE INTERMEDIATE appeared and disappeared rapidly in the first few minutes.

2. Another 7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub><sup>-</sup> salt with a monoboron cation  
(Me<sub>2</sub>N)<sub>3</sub>PNHB[NP(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub><sup>+</sup>

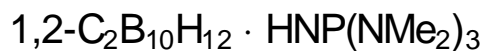
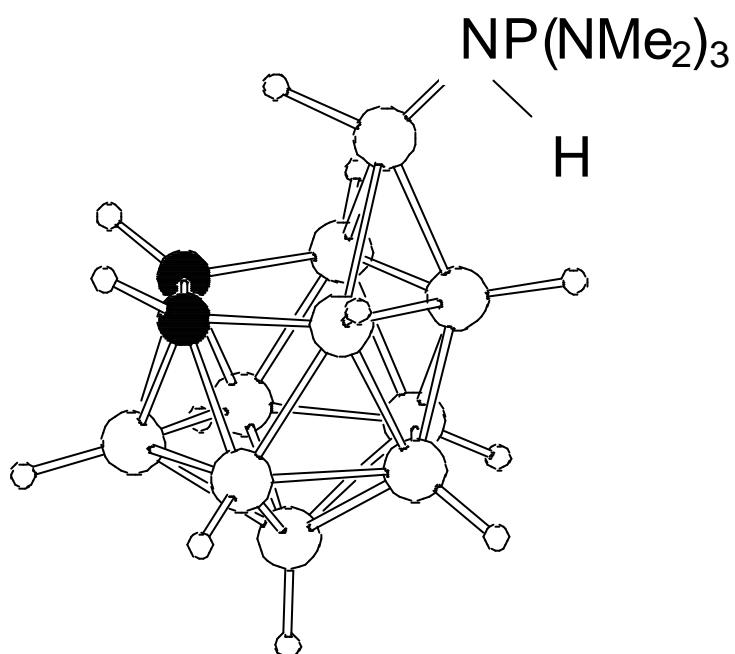


## CARBORANE INTERMEDIATE

A reaction of 1:1  $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$  :  $\text{HNP}(\text{NMe}_2)_3$  in toluene.

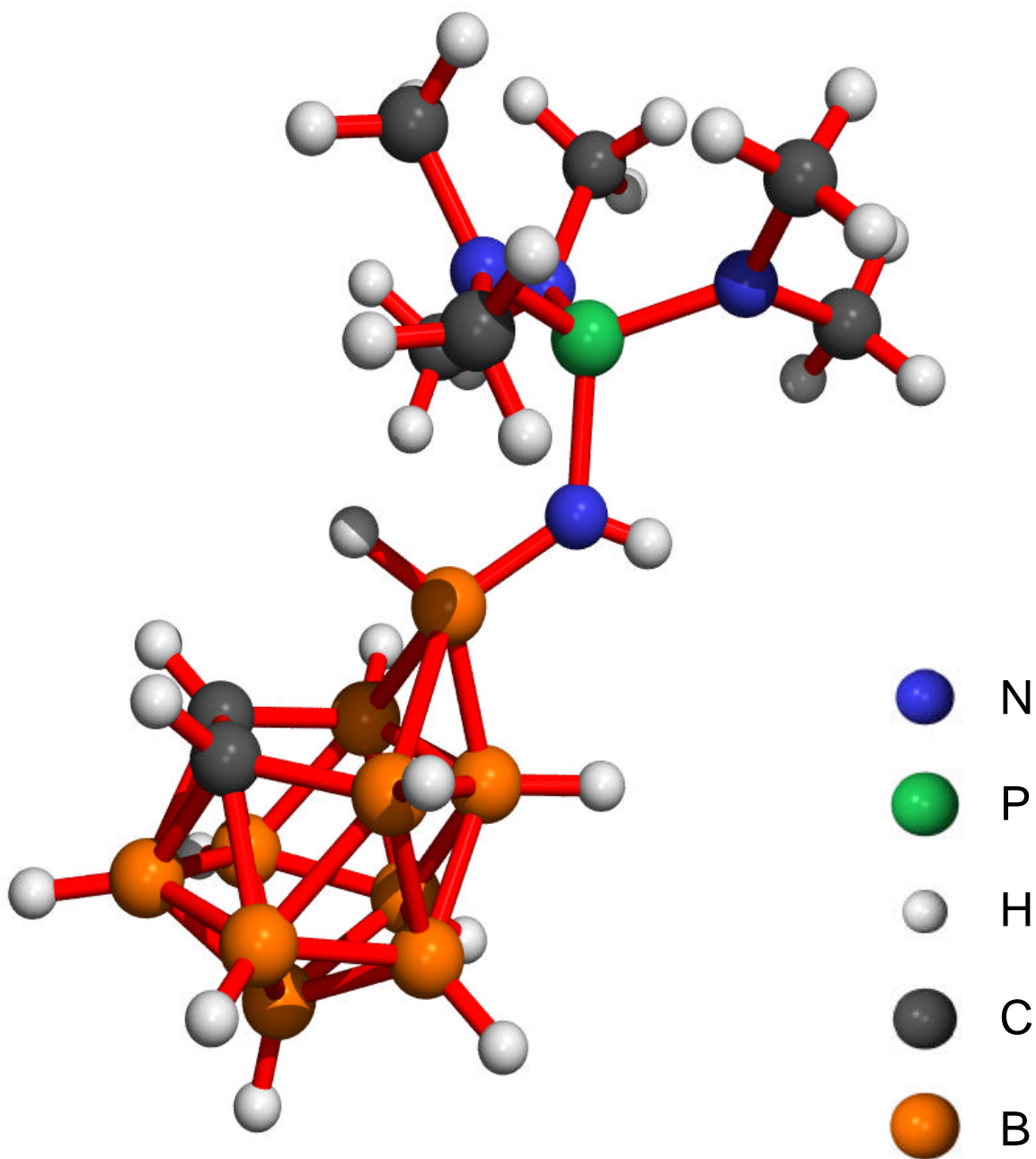
Crystals formed at room temperature.

*Found to be*



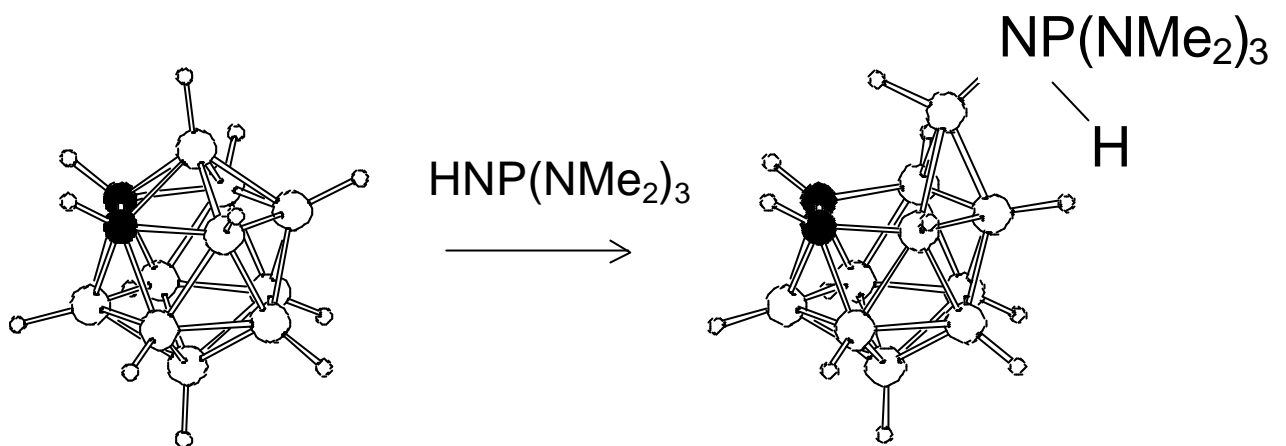
Calculated boron NMR shifts generated from the X-ray geometry show good agreement with the observed boron peaks of the intermediate observed in the NMR-scale reactions.

This suggests it is the first structurally characterized intermediate in the well known conversion of *closo*- $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$  into *nido*- $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$ .

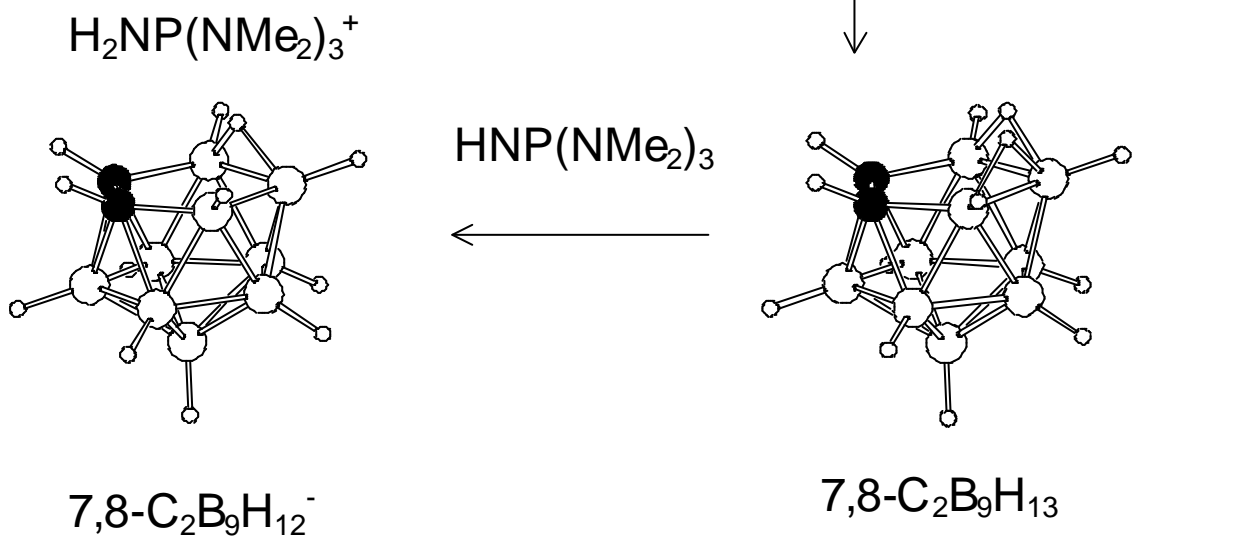


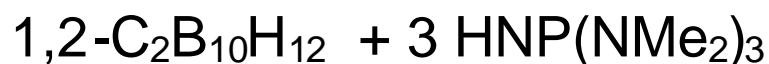
Crystal structure of  $C_2B_{10}H_{12}NHP(NMe_2)_3$

## Possible deboronation pathway



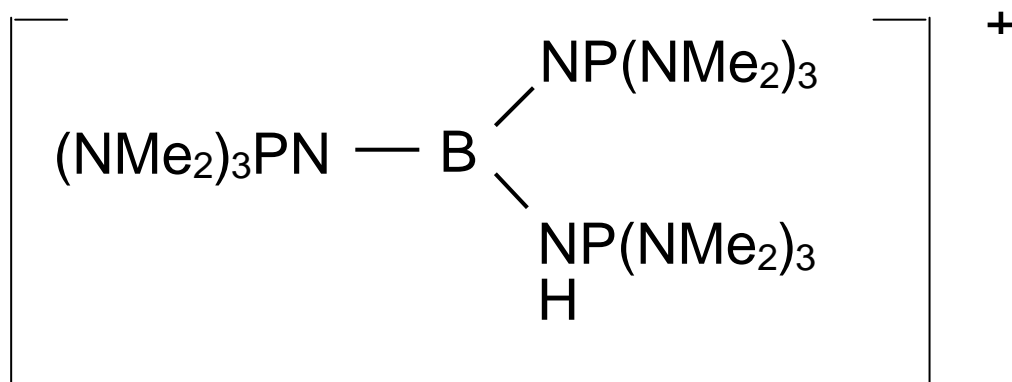
The first step is the attachment of the base to the most positively charged boron atom near the two neighbouring carbon atoms which pivots about B(10), cleaving the two B-C bonds and stretching the two B-B bonds to B(9) and B(11).





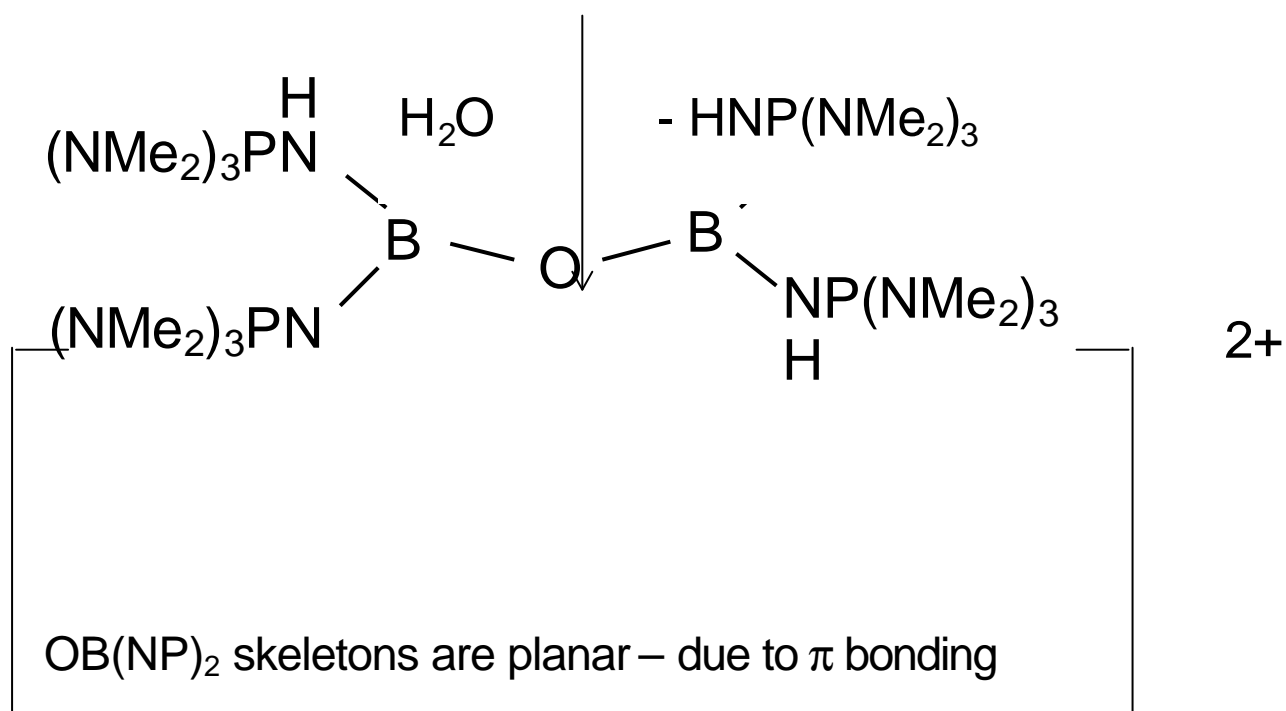
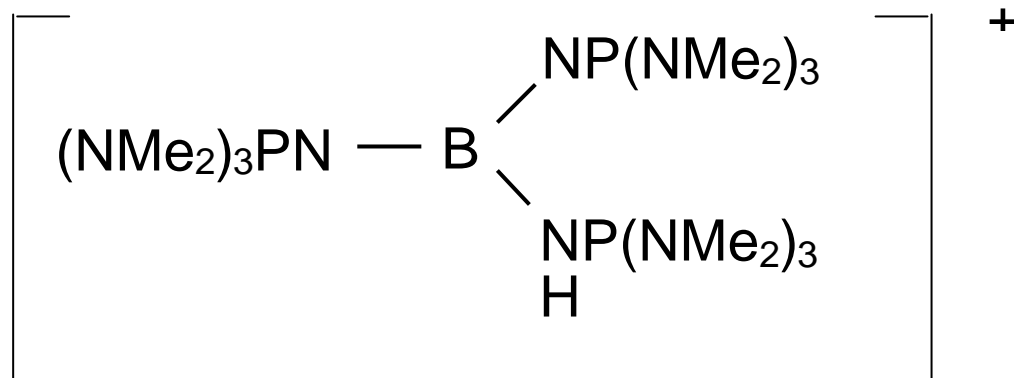
Monoboron products from the deboronation of *ortho* carboranes have previously been obtained as neutral or anionic species.

The monoboron product in this reaction is a cation.

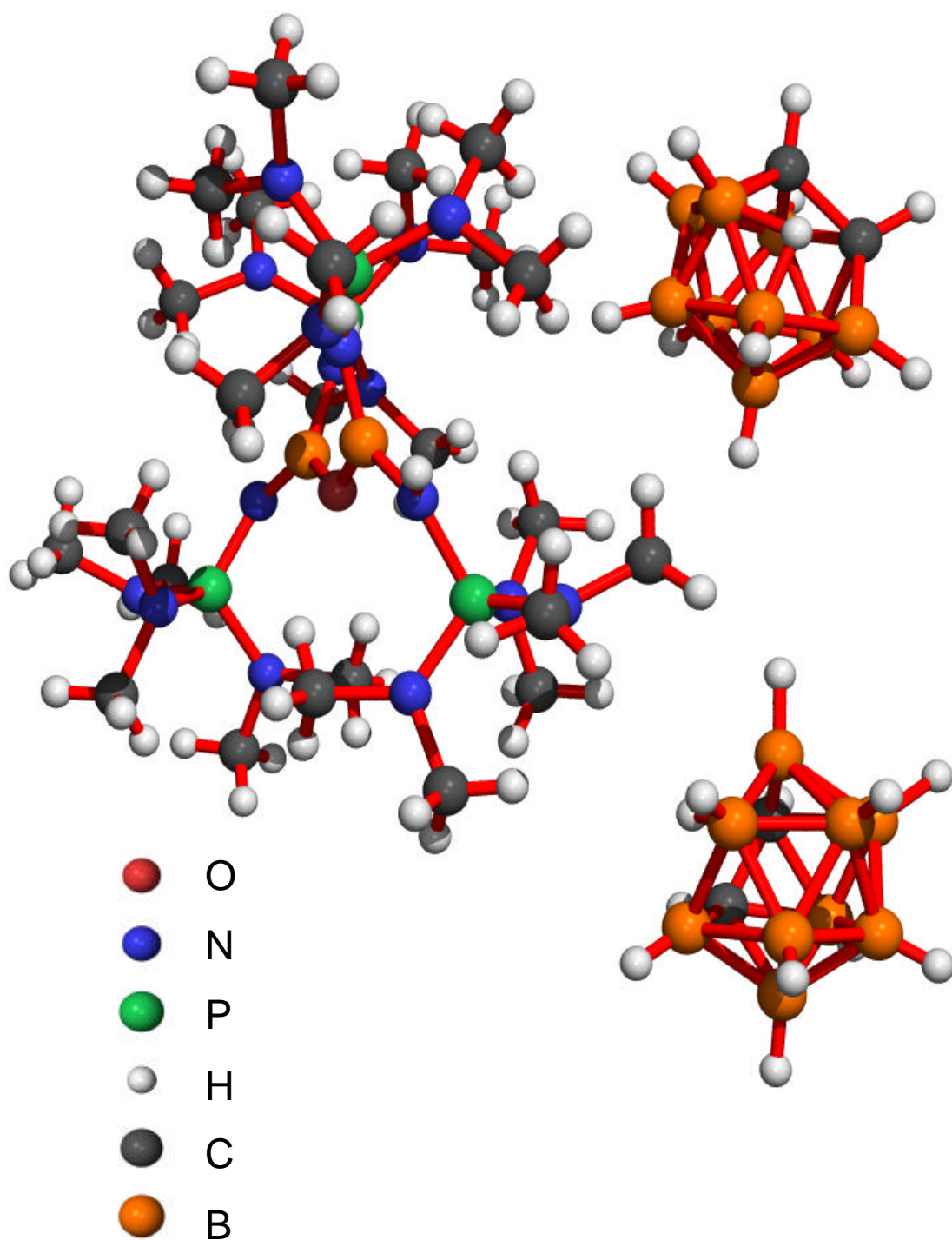


This carborane-phosphoramidate reaction provides a route to cations containing three-coordinate boron of a type previously generated from monoboron species.

Attempts to obtain a crystal structure of

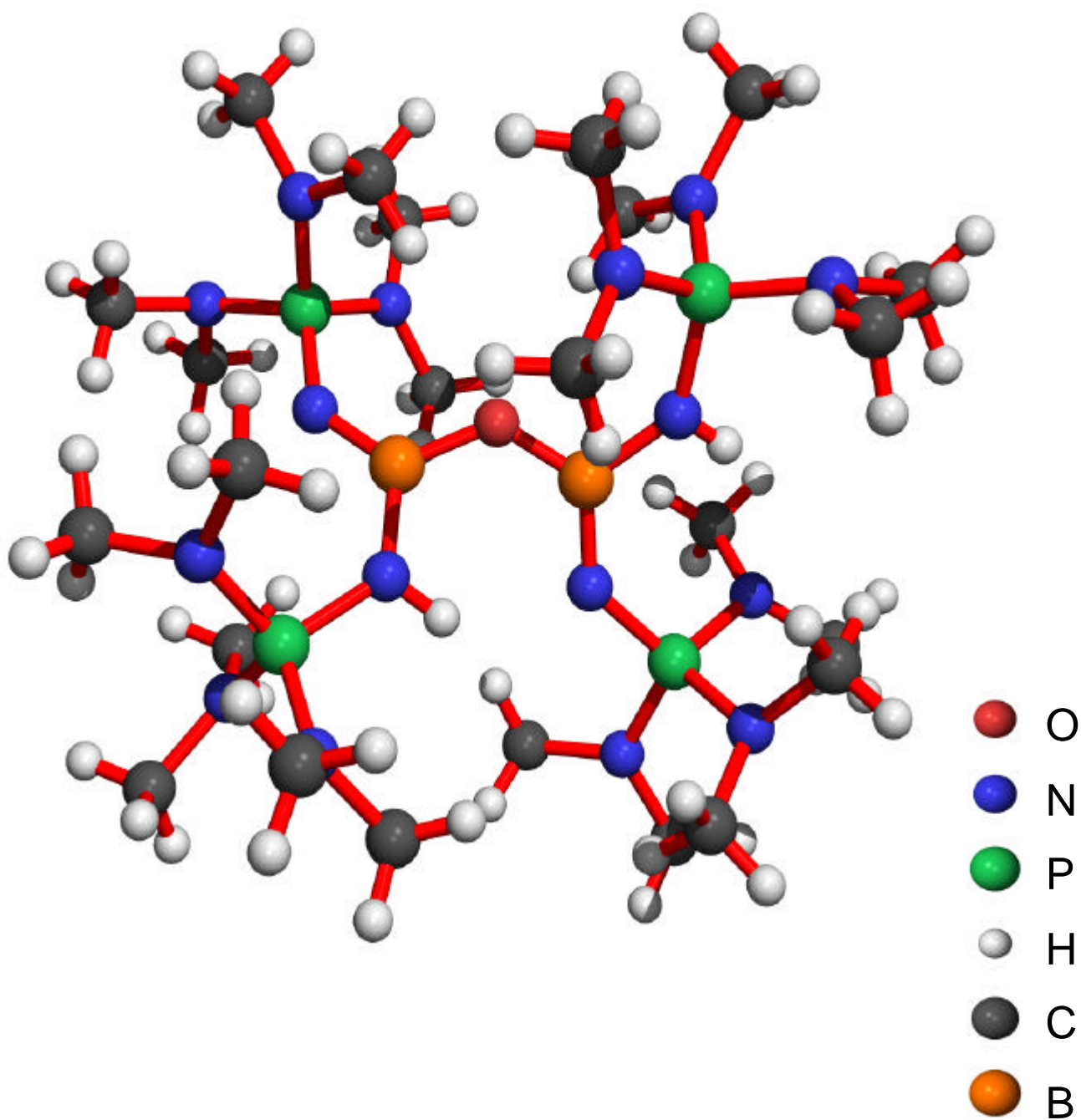


Crystal structure of  
 $[(\text{Me}_2\text{N})_3\text{PNHBNP}(\text{NMe}_2)_3]_2\text{O}^{2+}(\text{C}_2\text{B}_{10}\text{H}_{12})_2$

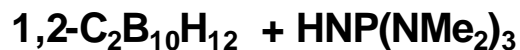




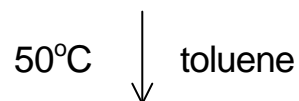
Crystal structure of  
 $[(\text{Me}_2\text{N})_3\text{PNHBNP}(\text{NMe}_2)_3]_2\text{O}^{2+}$



## ***Meta* carborane + iminophosphorane**

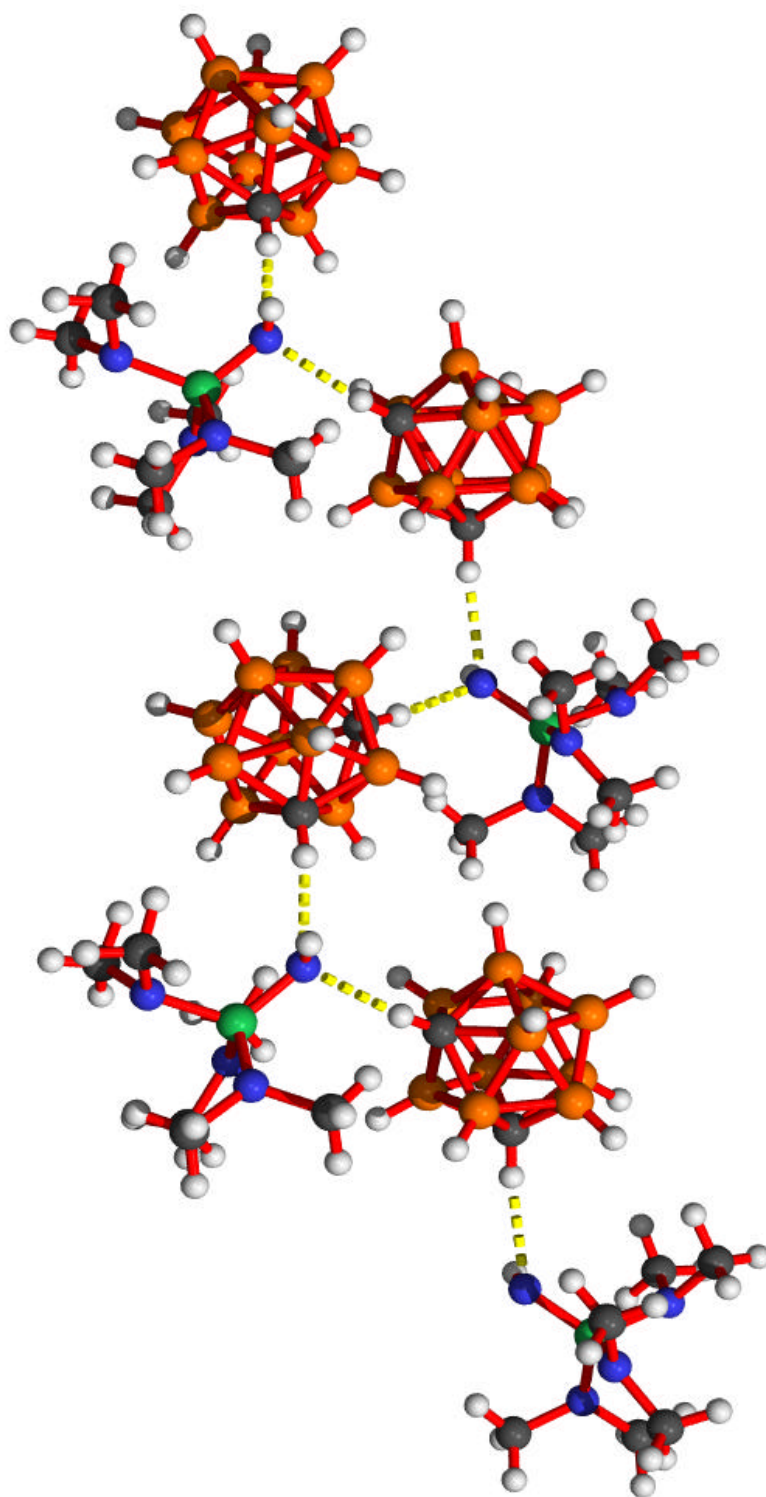


In presence of air – *deboronation at 50°C*



The salt is air-sensitive in the solid state – general characteristic for derivatives of  $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$

The base is a more effective deboronating agent than alkoxides and fluorides for *meta* carboranes.

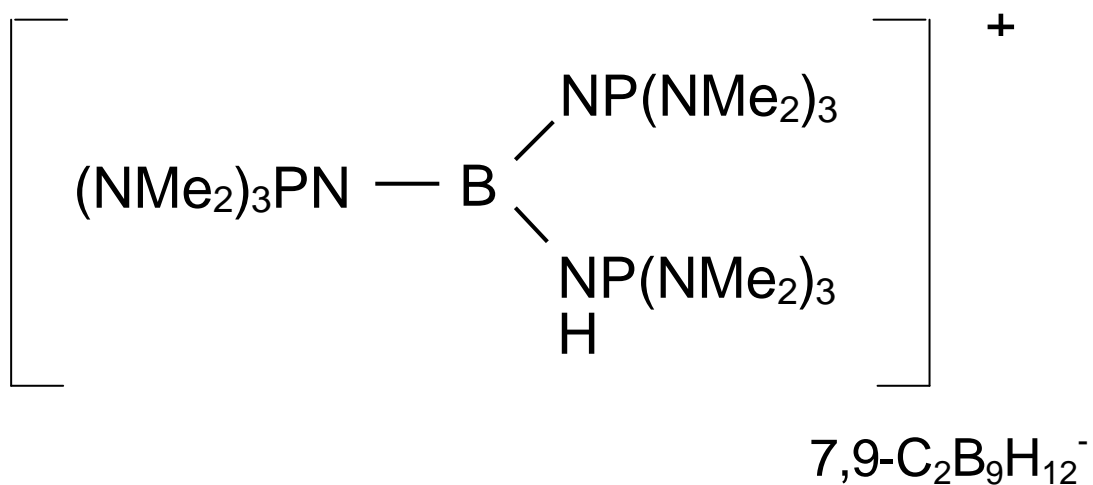
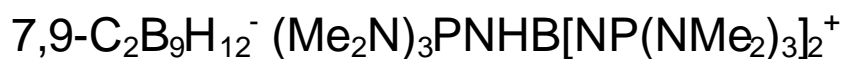
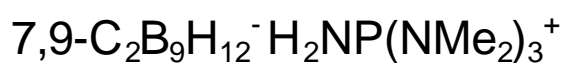


Crystal structure of  
 $1,7\text{-}[\text{C}_2\text{B}_{10}\text{H}_{12}\cdot\text{HNP}(\text{NMe}_2)_3]_8$

## ***Meta* carborane + iminophosphorane**

Under nitrogen

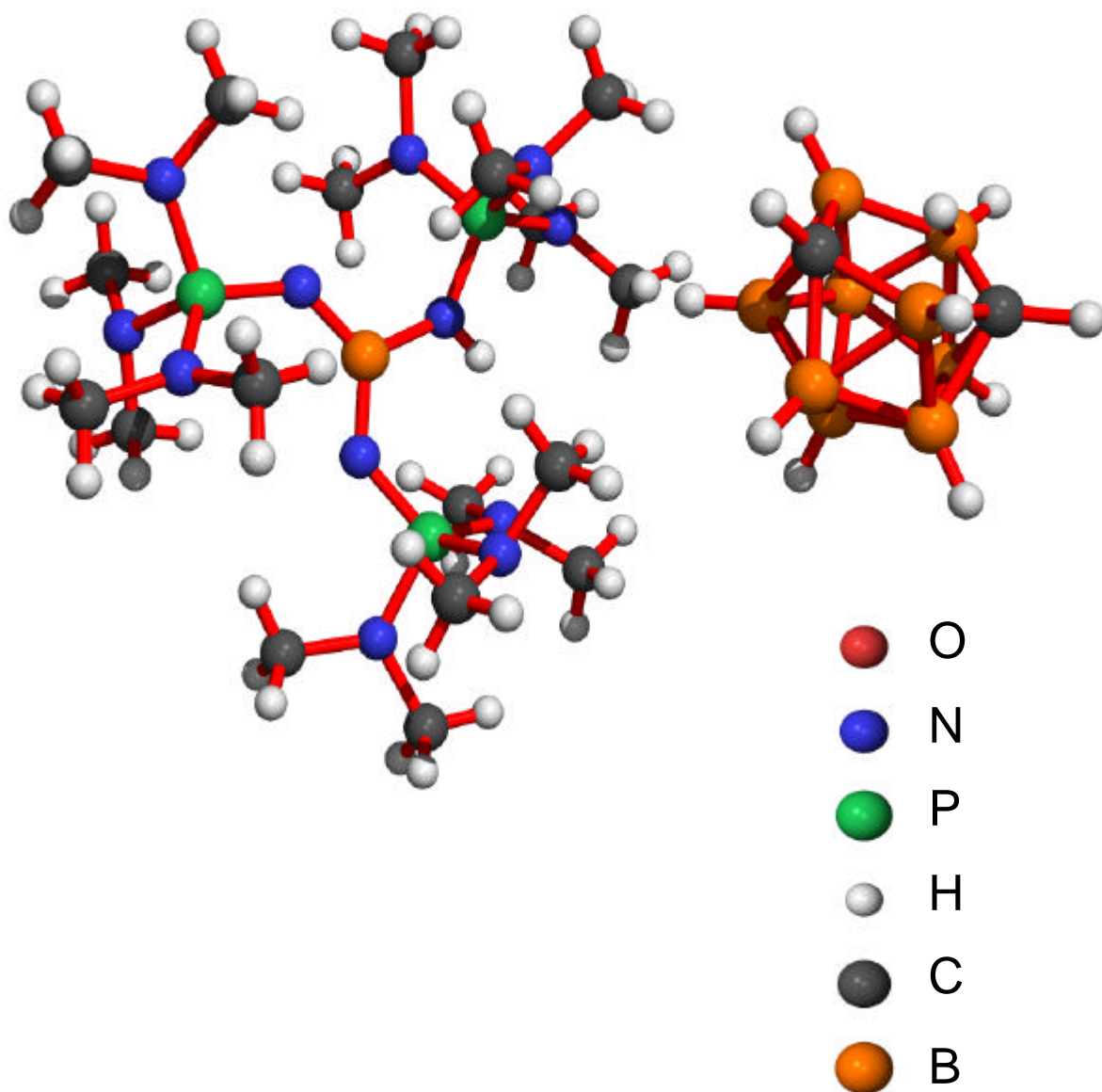
Similar salts as for the *ortho* carborane reaction



Crystal structure for the *nido* anion  $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$  is obtained for the first time

$\text{B}(\text{NP})_3$  skeleton is planar – due to  $\pi$  bonding

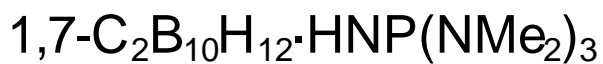
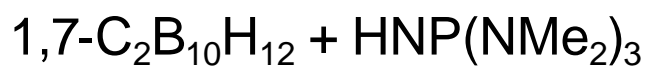
Crystal structure of  
 $[(\text{Me}_2\text{N})_3\text{PNHB}[\text{NP}(\text{NMe}_2)_3]_2]^+ 7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$



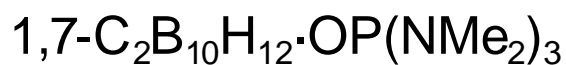
## ***Meta* carborane + iminophosphorane**

Under nitrogen

At  $-20^{\circ}\text{C}$  a 1:1 ratio mixture in toluene gives crystals of the hydrogen-bond adduct



Different pattern to the HMPA adduct



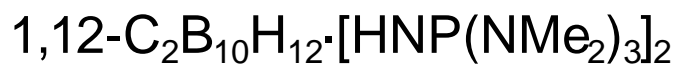
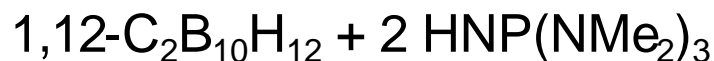
## ***Para* carborane + iminophosphorane**

Deboronation of *para* carborane could not be achieved with the iminophosphorane (even in large excess and elevated temperatures) in the presence or absence of air

*In presence of air*

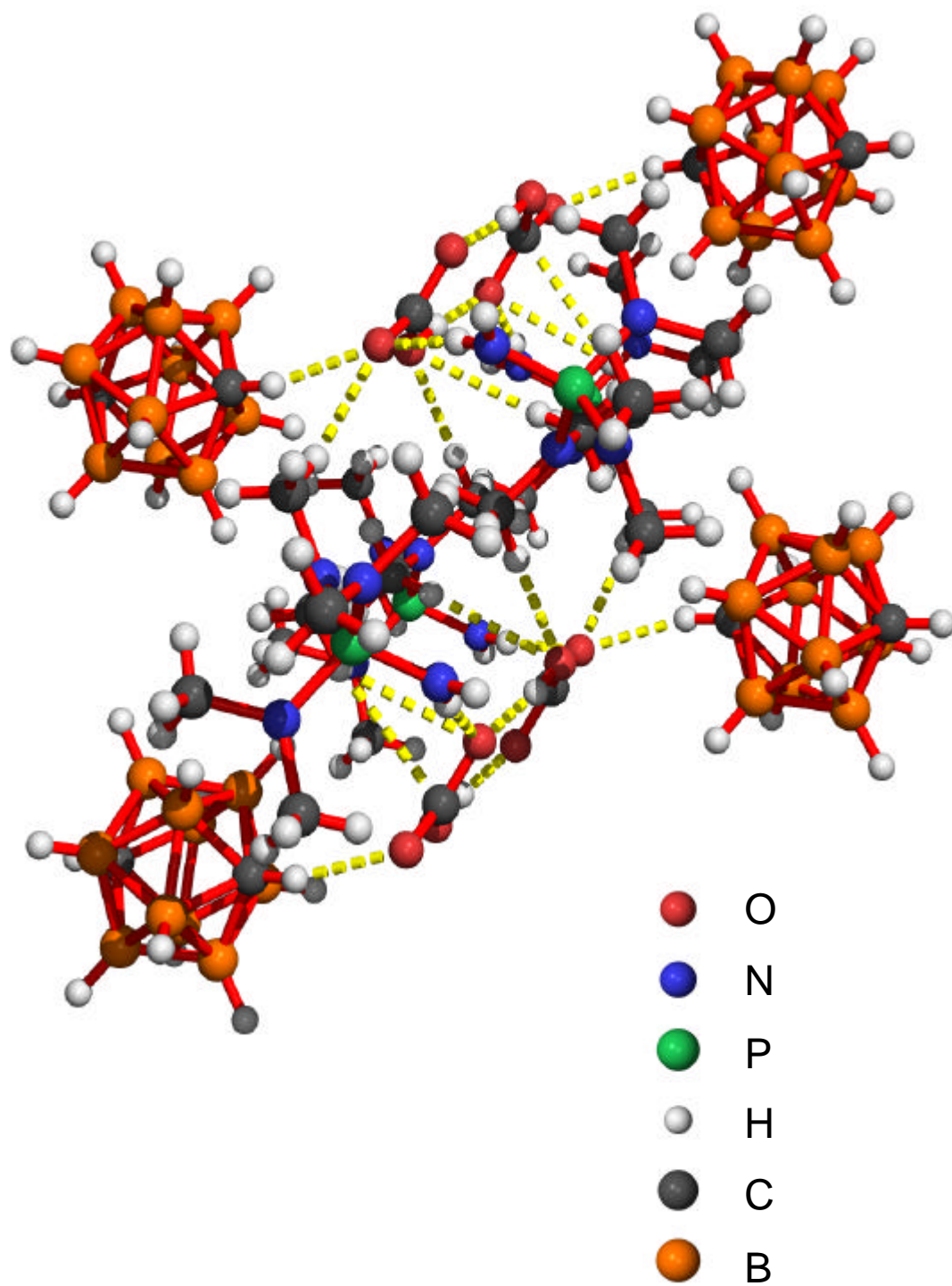


*Under nitrogen*



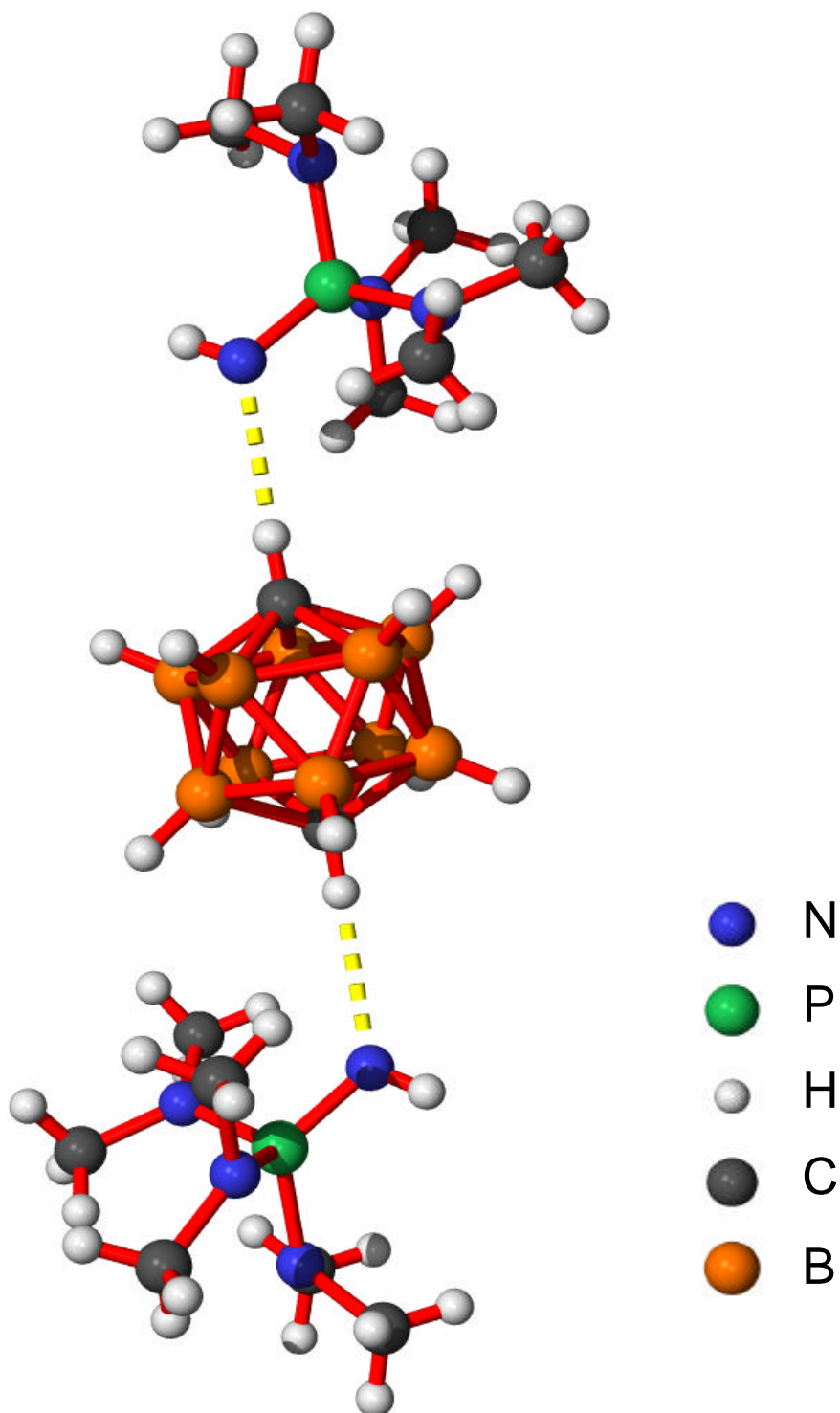
A 1:2 adduct

Crystal structure of  
 $2 \text{H}_2\text{NP}(\text{NMe}_2)_3^+ \text{HCO}_3^- \cdot 1,12\text{-C}_{20}\text{B}_{10}\text{H}_{12}$





Crystal structure of  
 $2 \text{ HNP}(\text{NMe}_2)_3 \cdot 1,12\text{-C}_2\text{B}_{10}\text{H}_{12}$



## CONCLUSIONS

The iminophosphorane is a good deboronating agent for *ortho* and *meta* carboranes (but not for *para* carborane).

These deboronations provide novel routes to three coordinate monoboron cations.

A carborane intermediate (as  $C_2B_{10}H_{12} \cdot HNP(NMe_2)_3$ ) is structurally characterized for the first time in the icosahedral carborane *closo-nido* conversions.

The iminophosphorane is a good hydrogen-bond acceptor for *meta* and *para* carboranes.

# **Acknowledgements**

## ***EPSRC***

### ***Durham Crystallography Service***

Judith A. K. Howard

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Royston C. B. Copley

Angus Mackinnon

Ivan S. Neretin

### ***Related Carborane Projects***

Andrew K. Hughes

Andrew L. Johnson

Aileen M. Martin

John M. Malget