

## Microscale Preparation of *closo*- and *nido*- *ortho*-carborane derivatives

### Preparación a microescala de derivados que contienen fragmentos *closo*- y *nido*- *orto*-carborano

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#### Abstract

*Ortho*-carborane derivatives are interesting examples of three center-two electron bonds and are also studied for their potential applications. The work presented here consists of two parts: the first one introduces the bonding, properties and applications of carboranes. The second one is a microscale preparation of the diphosphine 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>. It also includes the synthesis of the *closo* derivative [Ag{1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}(PPh<sub>3</sub>)]SO<sub>3</sub>CF<sub>3</sub> and its conversion to a *nido*-compound [Ag{7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}(PPh<sub>3</sub>)]. The experiment is appropriated in an advanced metalorganic chemistry or transition element course and can also illustrate the carborane or cluster chapter in an inorganic chemistry course.

Keywords: Silver, Carboranes, Metallorganic Chemistry, Laboratory experiment

#### Resumen

Los derivados de *orto*-carboranos constituyen ejemplos interesantes de enlaces de tres centros-dos electrones y son también relevantes debido a sus potenciales aplicaciones. El trabajo presentado consiste en dos partes; en la primera se describe el enlace, propiedades y aplicaciones de los carboranos. La segunda es un experimento que consiste en la preparación de la difosfina 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>. También se incluye la síntesis del *closo*-complejo [Ag{1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}(PPh<sub>3</sub>)]SO<sub>3</sub>CF<sub>3</sub>. y su transformación en el derivado *nido* [Ag{7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}(PPh<sub>3</sub>)]. El experimento está pensado para un curso avanzado de Química Metalorgánica o de Elementos de Transición y puede también ilustrar el capítulo de carboranos o cluster en un curso de Química Inorgánica.

Palabras clave : Plata, Carboranos, Química metalorgánica, Prácticas de laboratorio

Carboranes are considered in almost all Inorganic books. These species exhibit interesting structures and bonding (Grimes, 1970), which illustrate three center-two electron bonds and cluster bonding. Their

potential aromaticity has been suggested and is still being discussed (Wu, 1998 and Hawthorne, 1965). Actually there is a growing interest in *o*-carborane derivatives due to their potential applications (Brown, 1992; Hawthorne, 1988; Barth, 1990 and Hawthorne, 1993) in the synthesis of tumour-seeking drugs for *Boron Neutron Capture Therapy* and in the formation of polymers or homogeneous catalyst. Experimental work is fundamental when teaching chemistry. An experimental session completes the lecture and makes learning easier. The work presented here consists on two parts: the first one is an introduction to carboranes. The second one is an experimental work. It consists on the synthesis of the carborane ligand 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> and its reaction with [Ag(SO<sub>3</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)] to afford a *closo*-compound (twelve vertex) which in a very simple reaction is changed into a *nido*-compound (eleven vertex). The *closo*- and *nido*- nature of the complexes can be proved by I.R. and <sup>1</sup>H N.M.R. techniques. The experiment is appropriate in an advanced metalorganic chemistry or transition element course and can also illustrate the carborane or cluster chapter in an inorganic chemistry course.

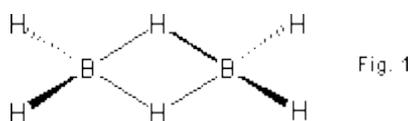
## Introduction to carboranes

The synthesis and properties of dicarba-*closo*-dodecaboranes were first reported at the end of 1963. Their chemistry is one of the most complete in the field of boranes and heteroboranes. The stability of the carborane cage is demonstrated under the many reaction conditions used to prepare a wide range of C- and B-carborane derivatives. Carborane compounds show rather specific properties as they represent distinctive covalent species with a unique molecular architecture, no conventional cluster bonding and unusual chemistry. All these facts make carborane complexes interesting derivatives to be studied in an advanced chemistry course, taking into account the number of topics, which can illustrate.

### ***Bonding and structures: (electron deficient species)***

After hydrocarbons, boranes (boron hydrides) and carboranes (boranes in which some CH vertex substitute BH vertex in the original boron hydride) are the larger class of hydrides with a variety of known structures. These species can also illustrate cluster-bonding theories.

The simplest isolable borane is B<sub>2</sub>H<sub>6</sub>. This species possesses two hydrogen atoms bridging the two boron ones which, exhibit effective tetrahedral geometry. The total number of valence electrons available for bonding in diborane is 12. If each connection in Fig. 1 were a simple two-electron bond, we should require 16 electrons.



This apparent shortage of electrons leads to boranes being categorized as "electron-deficient". A

number of approaches have been used to attempt to rationalize the structure of diborane:

i) The most useful description (from Longuet-Higgins) involves three centers, two electron B-H-B bonds. It is assumed that the boron atoms are  $sp^3$  hybridized and form simple two center, two-electron bonds to their terminal hydrogens. The two remaining  $sp^3$  orbitals of each boron and the hydrogen 1s orbitals of the bridging hydrogens can be combined to produce an OM diagram which consists of one bonding one no bonding and one antibonding orbitals. The three-center, two-electron (3c-2e) bond is widely accepted and is not limited to BHB systems, BBB units in higher boranes may also be bonded in this way. In larger boranes, localized bonded descriptions based on 2c-2e and 3c-2e bonds have been extensively developed by Lipscomb (Lipscomb 1963).

ii) An alternative approach has been proposed taking into account the problems possessed by large clusters and *closo*-compounds, particularly the large number of resonance forms that are possible. This approach is called "polyhedral electron skeletal-pair theory, nowadays often referred to as "Wade rules" (Wade 1972, 1975). In this approach the geometries of all the boranes and carboranes are related to a "basis set" of  $n$ -vertex icosahedral *closo*-boranes. These geometries are minimum-energy systems and exhibit triangulate faces

### Synthesis and activity of carboranes

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The reaction of decaborane with acetylenes in the presence of Lewis bases is now a general method for carborane synthesis:  $B_{10}H_{14} + RC\equiv CR' \longrightarrow RCB_{10}H_{10}CR$ . The 1,2-dicarbido-*closo*-decaborane also called *ortho*-carborane ( $1,2-(CH)_2-B_{10}H_{10}$ ), has been the most extensively investigated of all known carboranes. It is stable in the presence of oxidizing agents, alcohols, and strong acids and exhibits phenomenal thermal stability to temperatures up to 400 °C.

i) One of the most important features is its ability to enter into substitution reactions at both the carbon and boron atoms.

-The strong electron-withdrawing character of the *o*-carborane facilitates the reaction of the carborane C-H groups:  $HCB_{10}H_{10}CH + 2 RLi \longrightarrow LiCB_{10}H_{10}CLi + 2 RH$ .

-Direct electrophilic halogenation, alkylation (Grimes, 1970), sulfhydrylation and metalation (Bregadze, 1976; Bregadze, 1985) take place at the boron atom. The introduction of substituents onto the carbon and boron atoms of the carborane cage influences the reactivity of the unsubstituted atoms. The mentioned reactions are typical of aromatic compounds, and for this reason the carborane molecule has been characterized as a "pseudoaromatic" system.

ii) Another important reaction in the carborane chemistry was reported by Wiesboeck and Hawthorne in 1964 (Wiesboeck, 1964). They show that one of the boron atoms nearest to the carbon can be removed by using alcoholic alkali to give the dicarbaundecaborate(-1) ion:

$o\text{-}1,2\text{-(CH)}_2\text{B}_{10}\text{H}_{10} + \text{CH}_3\text{O}^- + 2 \text{BH}_3\text{OH} \longrightarrow o\text{-}7,8\text{-(CH)}_2\text{B}_9\text{H}_{10}]^- + 2 \text{H}_2 + \text{B(OCH}_3)_3$ . This process is known as "partial degradation of the carborane cage" and will be more widely discussed below. In it the closed (*closo*)carborane is changed into an open (*nido*) carborane.

### Potential applications of carborane compounds

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The current claimed applications for boron cluster compounds are based on

i) The unique properties of the molecules.

Extreme acidity of acids conjugated to the polyhedral ions and unique hydrophobicity of these anions. Exceptional stability of the polyhedral species. Virtual three-dimensional "aromaticity". Unexpected ability of nearly all open-cage deltahedral boron hydride derivatives to function as very strong sandwich forming ligands. All of these are properties which provide the development of several polymers (Brown,1992), solvent extraction of radio-nuclides, electrolytes for non-aqueous solvents, and homogeneous catalyst of hydrogenation.

ii) The specific properties of the basic element itself.

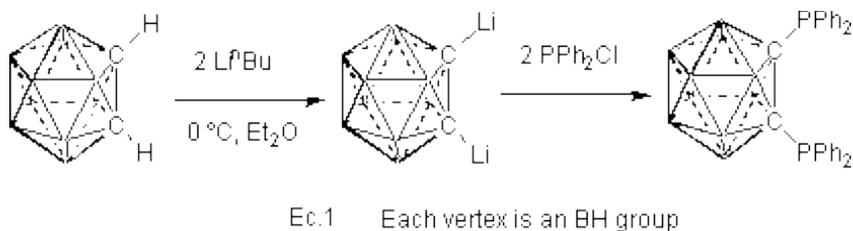
-Applications associated with the properties of boron primarily exploit the unusually high cross section of the  $^{10}\text{B}$  isotope for neutron capture (20% natural abundance). This led to the development of light-weight neutron shields and in particular to the "Boron Neutron Capture Therapy (BNCT) of tumours (Hawthorne, 1991, 1993).

-In some new applications the boron cluster species serves as an expensive, but nevertheless very convenient and easily modifiable, source of boron, e.g. for advanced boron-based ceramics (Sneddon, 1991) and for doping the semi-conducting  $\text{E}^{\text{IV}}$  elements where  $\text{B}^{\text{III}}$  behaves as an electron hole.

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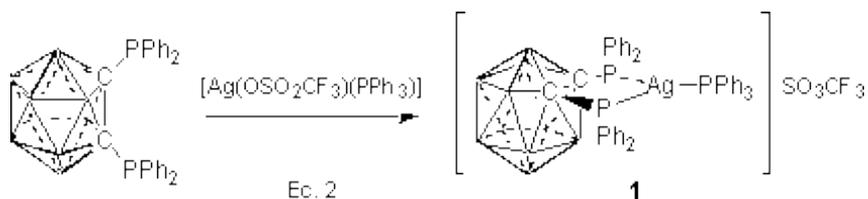
### **Laboratory work**

The synthesis of 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> was reported in 1963 (Alexander, 1963) and here we present some minor modifications in order to obtain a better yield. In this preparation the acidity of the two hydrogen atoms linked to the carbon allows the reaction with carbanionic compounds like Li<sup>n</sup>Bu. The dilithiated derivative is treated with PPh<sub>2</sub>Cl (Ec.1). When preparing small amounts of the diphosphine, the PPh<sub>2</sub>Cl is added to the ‘just prepared’ dilithiated product. The white solid is washed with water and normally no solid remains. The organic solution is dried with MgSO<sub>4</sub> and concentrated. Addition of n-hexane to the concentrate affords the diphosphine ligand. In the described synthesis (1963) the resulting solid from the addition of PPh<sub>2</sub>Cl is hydrolysed with water, filtered and recrystallized using petroleum ether.

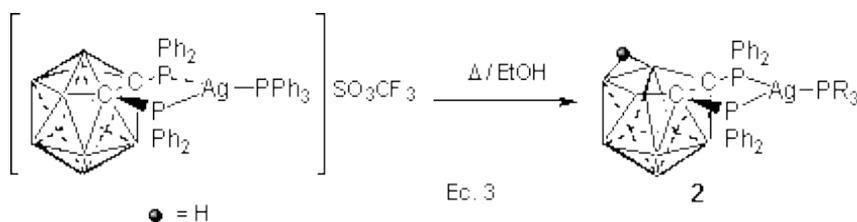


This synthesis can be highly interesting experiment for advanced students, because they learn how to use vacuum techniques or the synthesis.

This diphosphine reacts with complexes which posses labile ligands (as trifluoromethanesulphonate: SO<sub>3</sub>CF<sub>3</sub>). Thus, reaction with [Ag(SO<sub>3</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)] affords the silver complex [Ag{1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>} (PPh<sub>3</sub>)]SO<sub>3</sub>CF<sub>3</sub> (Ec. 2).



The elimination of a boron atom from a *closo*-derivative is called *partial degradation*. In this reaction the boron atom eliminated is always one of those nearest to the carbons and the hydrogen atom of the eliminated vertex is now bridging two of the boron atoms in the open face of the *nido*-derivative. The unsubstituted *o*-carborane is *partially degraded* in refluxing MeOH and excess of KOH (Wiesboeck, 1964.). Organometallic compounds containing the mentioned diphosphine are *partially degraded* by refluxing their ethanolic suspensions. Equation 3 shows the reaction of  $[\text{Ag}\{1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]\text{SO}_3\text{CF}_3$  to afford  $[\text{Ag}\{7,8\text{-}(\text{PPh}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}(\text{PPh}_3)]$



These two compounds are examples of *closo*- and *nido*-derivatives of *ortho*-carborane. The analysis of the I. R. spectra of the complexes confirms their nature because the B-H stretching mode (Marks, 1977.) of the carborane nucleus decreases in energy on going from the *closo*- to the *nido*-derivatives. The partial degradation of the carborane cage is also observed in the  $^1\text{H}$  N.M.R. spectrum of **2** as the bridging hydrogen atom appears as a broad resonance centered at -2 ppm.

The synthesis of these silver compounds can be an independent experiment if more advanced students have synthesized the diphosphine or there is no possibility of its preparation.

### **Procedure:**

#### *Starting materials:*

- Synthesis of  $[\text{Ag}(\text{SO}_3\text{CF}_3)(\text{PPh}_3)]$

To a solution of  $\text{Ag}(\text{SO}_3\text{CF}_3)$  (0.357 g) in diethyl ether a solution of  $\text{PPh}_3$  (0.262g) in diethyl ether was added. The white solid is obtained by filtration after 30 min. of stirring.

- Synthesis of the *o*-carborane ligand  $1,2\text{-}(\text{PPh}_2)\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$

To a 100 ml three-neck flask fitted with a magnetic stirrer, a nitrogen inlet and outlet, and an addition funnel *ortho*-carborane (0.288 g) and ether (60 ml) are charged and the solution cooled to  $0^\circ\text{C}$ . A solution of butyl-lithium (2.5 ml, 1.6M) in diethyl ether (10 ml) is added. The solution is stirred at  $0^\circ\text{C}$  for 30 min.

and  $\text{PPh}_2\text{Cl}$  (0.78 ml) is added. After stirring an additional 30 min. the solution is refluxed for another 30 min. The suspension is warmed to room temperature and washed with water. The resulting organic solution\* is dried with  $\text{MgSO}_4$ . The suspension is filtered and the solution is concentrated to ca. 5 ml. Addition of n-hexane affords a white solid.

\*The possible remaining solid is filtered off and dissolved in  $\text{CH}_2\text{Cl}_2$ , washed with water and dried with  $\text{MgSO}_4$ . Concentration of the solution (ca. 5 ml) and addition of n-hexane yields the white product.

### ***Silver compounds:***

- Synthesis of  $[\text{Ag}\{1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]\text{SO}_3\text{CF}_3$

To a solution of 1,2-( $\text{PPh}_2$ )<sub>2</sub>-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (0.078 g) in dichloromethane (20 ml)  $[\text{Ag}(\text{SO}_3\text{CF}_3)(\text{PPh}_3)]$  (0.077 g) is added. The solution is stirred for thirty min. and concentrated to ca. 5 ml. Addition of n-hexane affords a white solid. I. R. spectrum:  $\nu(\text{BH})$  2633  $\text{cm}^{-1}$ .

- Synthesis of  $[\text{Ag}\{7,8-(\text{PPh}_2)_2-7,8-\text{C}_2\text{B}_9\text{H}_{10}\}(\text{PPh}_3)]$

A suspension of  $[\text{Ag}\{1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]\text{SO}_3\text{CF}_3$  (0.098 g) in ethanol (30 ml) is refluxed for 30 min. The suspension is filtered off and the solid dried with n-hexane. I. R. spectrum:  $\nu(\text{BH})$  2575  $\text{cm}^{-1}$ .  $^1\text{H N.M.R.}$  spectrum: -2 ppm. (s, br).

### **Questions for the students:**

- Give a definition for: Carborane, cluster, metal-organic compound .

- Which is the meaning of “electron deficient”.

- Explain the O.M. diagram for the  $\text{B}_2\text{H}_6$  (make suggestions and compare information with literature data).

- For advanced: students: Explain the high reactivity of  $^n\text{BuLi}$ .

- Explain the numbering of the boron vertex in the *closo*- and *nido*-carborane clusters commented in the experimental part.

- The partial degradation of the carborane is afforded by reaction in refluxing ethanol. Explain the differences between *closo* and *nido-ortho*-carboranes and look in the literature for different partial

degrading conditions.

-The syntheses of the silver derivatives are substitution reactions of labile ligands. Look for other labile ligand used in metal-organic chemistry.

- Explain the broad signal at  $-2$  ppm in the  $^1\text{H N.M.R.}$  spectrum of  $[\text{Ag}\{7,8\text{-}(\text{PPh}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}(\text{PPh}_3)]$

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Notes:

<sup>1</sup>Rules for nomenclature and numeration of the vertex in *ortho*- or *nido*-carborane derivatives are shown in: Adams, R. M. *Pure and Applied Chem.*, **30**, 683, 1972

<sup>2</sup>*Ortho*-carborane was Dexil Corporation,  $\text{PPh}_3\cdot\text{Ag}(\text{SO}_3\text{CF}_3)$  and  $\text{PPh}_2\text{Cl}$  were Aldrich and Butyllithium was SDS. All were used as given

<sup>3</sup>Distilled and anhydrous ether was used in the preparation of the diphosphine.

<sup>4</sup>The synthesis of the diphosphine must be only worked up only by advanced students and always helped by the teacher.  $\text{Li}^n\text{Bu}$  must be carefully handed, always under argon or nitrogen atmosphere.

<sup>5</sup>Infrared spectra were recorded in the range  $4000\text{-}200\text{cm}^{-1}$  on a Perkin-Elmer 883 spectrophotometer using Nujolmulls between polyethylene sheets.  $^1\text{H N.M.R.}$  spectra were recorded on a Varian Unity 300 spectrophotometer in  $\text{CDCl}_3$ . Chemical shifts are cited relative to  $\text{SiMe}_4$  ( $^1\text{H}$ , external).

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