



Universitat Autònoma de Barcelona

**Multifunctional N,O-type Carborane-Based Materials:
from Molecular Complexes
to Three Dimensional Metal-Organic Frameworks**

Min Ying Tsang

TESI DOCTORAL

Programa de Doctorat en Química

Director: Dr. José Giner Planas

Tutor: Prof. Agustí Lledós

Department de Química

Facultat de Ciències

2015

Memòria presentada per aspirar al Grau de Doctor per

Min Ying Tsang

Vist i plau

Dr. José Giner Planas

Prof. Agustí Lledós

Bellaterra, 8 de Julio de 2015



MINISTERIO
DE ECONOMÍA
Y COMPETITIVIDAD



INSTITUT DE CIÈNCIA
DE MATERIALS DE
BARCELONA (ICMAB)

El Doctor JOSÉ GINER PLANAS, Científico Titular del Consejo Superior de Investigaciones Científicas en el Instituto de Ciencia de Materiales de Barcelona (ICMAB),

CERTIFICA:

Que Min Ying Tsang, licenciada en Química, ha realizado bajo su dirección la tesis doctoral titulada “**Multifunctional N,O-type Carborane-Based Materials: from Molecular Complexes to Three Dimensional Metal-Organic Frameworks**” y que se recoge en esta memoria para optar al grado de Doctora en Química por la Universitat Autònoma de Barcelona.

Y para que así conste y tenga los efectos oportunos, firmo este certificado en Bellaterra, a 8 de Junio de 2015.

Dr. José Giner Planas
ICMAB-CSIC

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Este trabajo de investigación, con fecha de defensa el 28 de julio de 2015, tiene como miembros del tribunal a:

Presidenta: Dra Josefina Pons Picart, Profesora Titular del Departamento de Química de la Universitat Autònoma de Barcelona.

Secretaria: Dra Montserrat Rodríguez Pizarro, Profesora Agregada del Departamento de Química de la Universitat de Girona.

Vocal: Dr Óscar Castillo García, Profesor Titular del Departamento de Química Inorgánica de la Universidad del País Vasco.

Como miembros suplentes:

Suplente 1: Dr Jordi García-Antón Aviñó, Profesor Lector del Departamento de Química de la Universitat Autònoma de Barcelona.

Suplente 2: Dra E. Carolina Sañudo Zotes, Profesora Agregada del Departamento de Química Inorgánica e IN2UB de la Universitat de Barcelona.

This thesis is dedicated to my parents

Acknowledgement

Ph.D. is not an individual accomplishment. This thesis would not be possible to be accomplished without the contribution of the following people.

First and foremost, I would like to express sincere thanks to my supervisor and friend, Dr. José Giner Planas. Without his trust and unconditional help and support on research and also on personal issues, I would not be able to complete my study. His patience and enthusiasm has made my stay in Spain a joyful adventure. I would like to thank him especially for his immense knowledge and constant willingness to share which learnt me a lot and widen my horizon. He is always ready to help and his kindness and concern makes me feel secure to study abroad.

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Last but not least, I would like to send my deepest gratitude to my parents and my brother. I am immeasurably appreciate for their patience, acceptance and support for all my decisions not only financially but also spiritually in my life and providing me the best possible conditions for everything. (沒有你哋，就沒有今日嘅我。多謝你哋嘅愛同支持!) Special thanks to my beloved Marcin Węgrzyn for his uncountable support and all the help on many aspects and being the most important person in my life. Also thanks to his parents for their kindness and being supportive. Dziękuję bardzo.

Mucho Gracias por todo y aceptación para permitirme estar en esta gran familia. Seguramente voy a hablar Español un día!

After all, science is essentially international, and it is only through lack of the historical sense that national qualities have been attributed to it.

Marie Curie Skłodowska

Organización de la Tesis

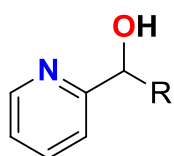
De acuerdo con la normativa vigente, esta Tesis Doctoral se presenta como un compendio de artículos. No obstante, además de incluir los artículos publicados y presentados a la comisión de Doctorado de la UAB en Enero de 2015 (Addendum), con la idea de presentar una Memoria lo más completa posible, también se han incluido los trabajos realizados en el marco de esta Tesis Doctoral y que están en proceso de elaboración (Addendum).

Los trabajos incluidos en esta Memoria y presentados a la Comisión de Doctorado en Enero de 2015 son los siguientes:

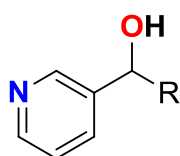
- 1)** “Synthesis and crystallographic studies of disubstituted carboranyl alcohol derivatives: prevailing chiral recognition?”. F. Di Salvo, C. Paterakis, M. Y. Tsang, Y. García, C. Viñas, F. Teixidor, J. G. Planas,* M. E. Light, M. B. Hursthouse, D. Choquesillo-Lazarte, *Cryst Growth Des.* **2013**, *13*, 1473-1484.
- 2)** “Racemic and Enantiopure Unsymmetric Diiron (III) Complex with a Chiral *o*-Carborane-based Pyridylalcohol Ligand: Combined Chiroptical, Magnetic and Non Linear Optical Properties”. F. Di Salvo, M. Y. Tsang, F. Teixidor, C Viñas, J. G. Planas,* J. Crassous, N. Vanthuyne, N. Aliaga-Alcalde, E. Ruiz, G. Coquerel, S. Clevers, V. Dupray, D. Choquesillo-Lazarte, M. E. Light, M. B. Hursthouse, *Chem. Eur. J.* **2014**, *20*, 1081-1090.
- 3)** “Synthesis, Structure and Catalytic Applications for *ortho*- and *meta*-Carboranyl based NBN Pincer-Pd Complexes”. M. Y. Tsang, C Viñas, F. Teixidor, J. G. Planas,* N. Conde, R. SanMartin, M. T. Herrero, E. Domínguez, A. Lledós, P. Vidossich, D. Choquesillo-Lazarte, *Inorg. Chem.* **2014**, *53*, 9284-9295.
- 4)** “Is molecular chirality connected to supramolecular chirality? The particular case of chiral 2-pyridyl alcohols”. M. Y. Tsang, F. Di Salvo, F. Teixidor, C. Viñas, J. G. Planas,* D. Choquesillo-Lazarte, N. Vanthuyne, *Cryst. Growth Des.*, **2015**, *15*, 935-945.

Compound list

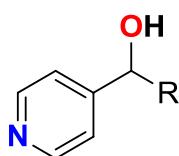
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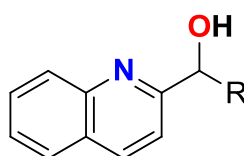
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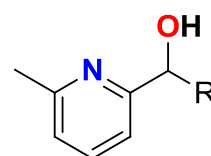
L2



L3

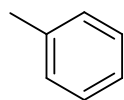


L4

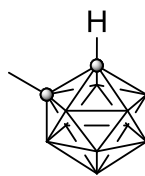


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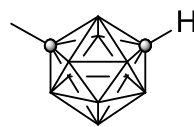
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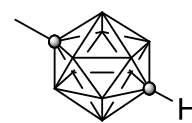
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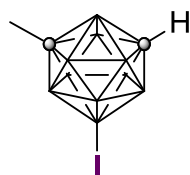
oCB



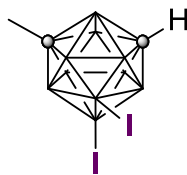
mCB



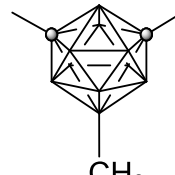
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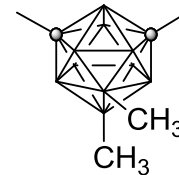
I-mCB



I₂-mCB

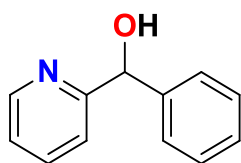


CH₃-mCB

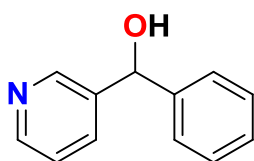


(CH₃)₂-mCB

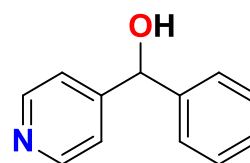
Ligands



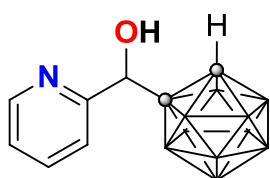
Ph-L1



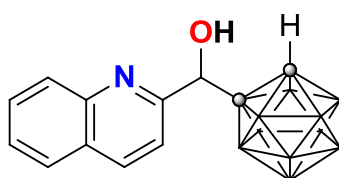
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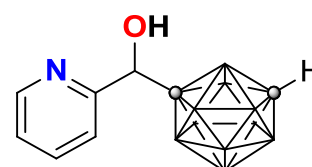
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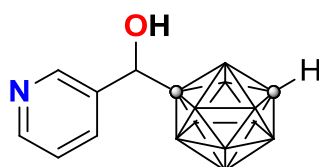
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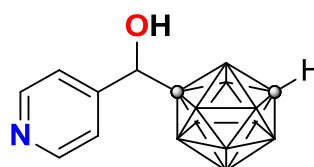
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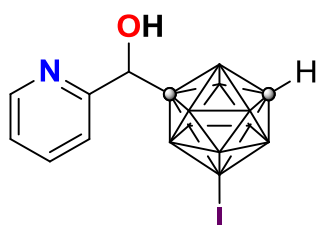
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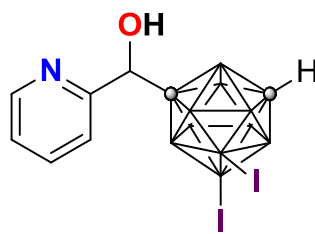
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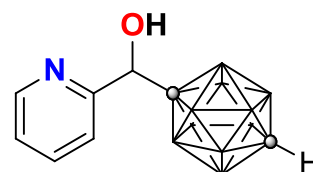
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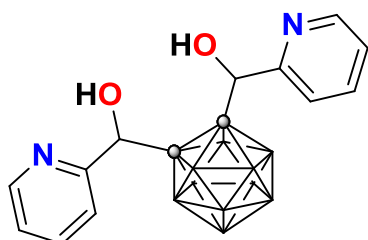
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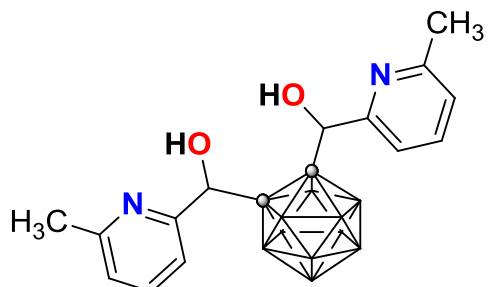
l₂-mCB-L1



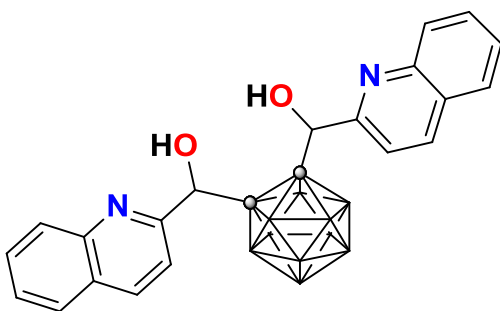
pCB-L1



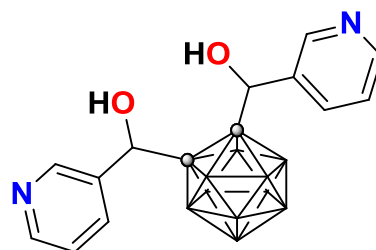
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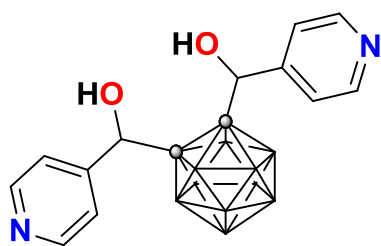
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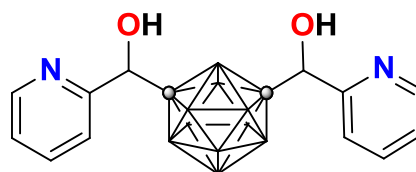
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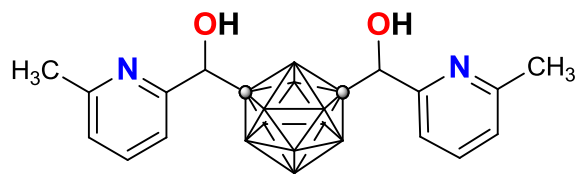
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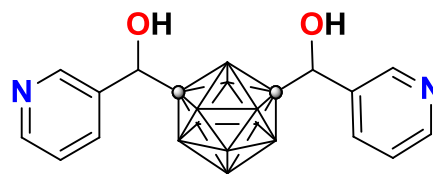
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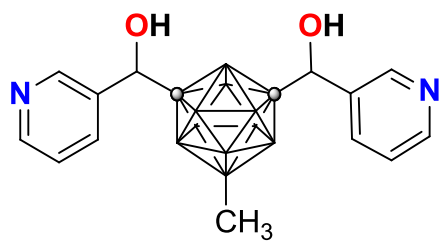
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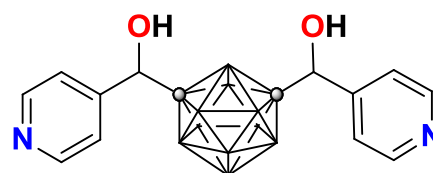
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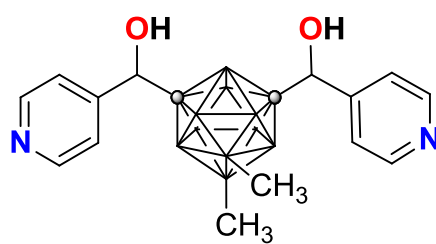
$mCB-(L2)_2$



$CH_3-mCB-(L2)_2$

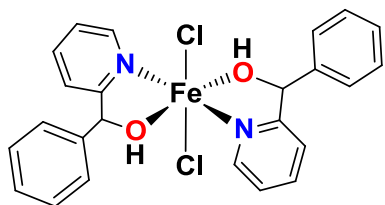


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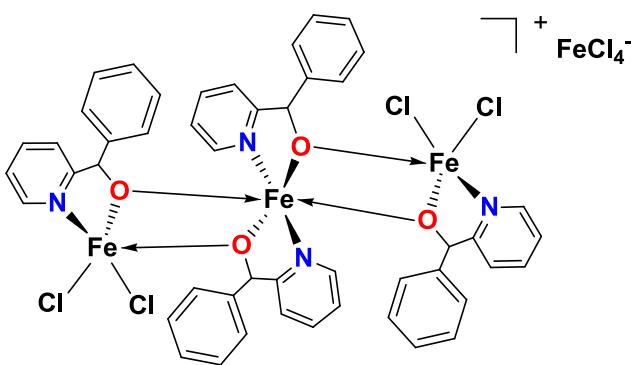


$(CH_3)_2-mCB-(L3)_2$

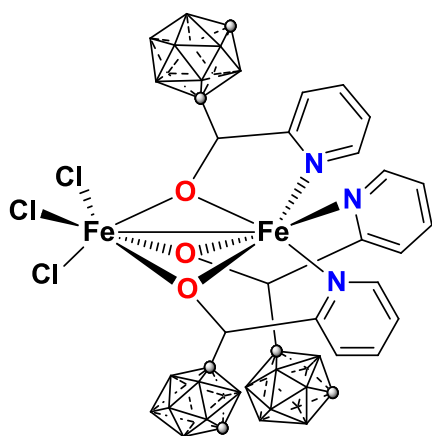
Complexes



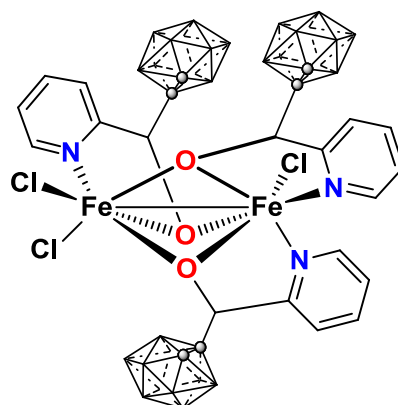
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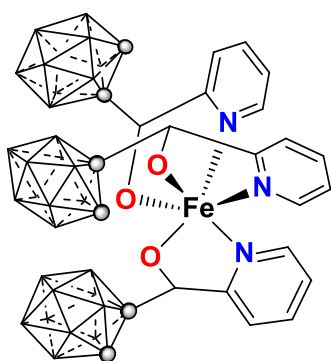
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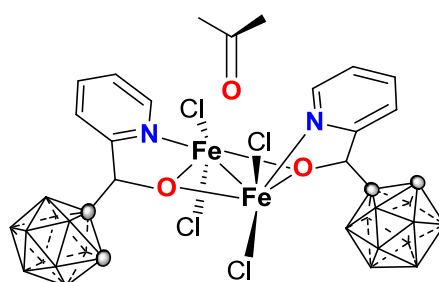
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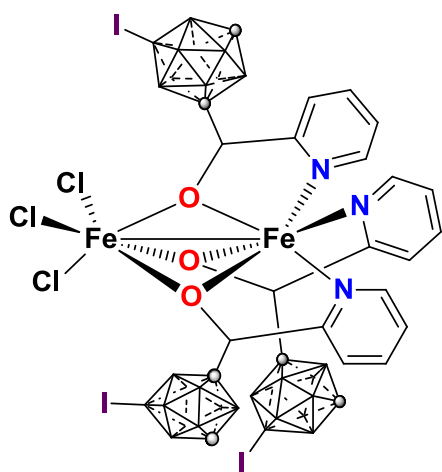
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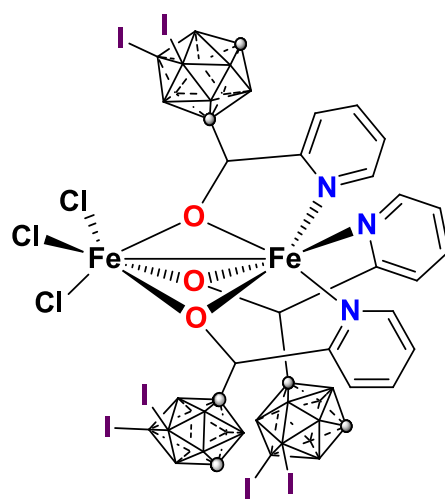
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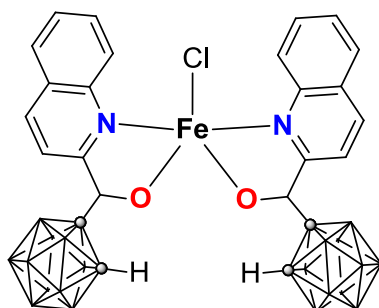
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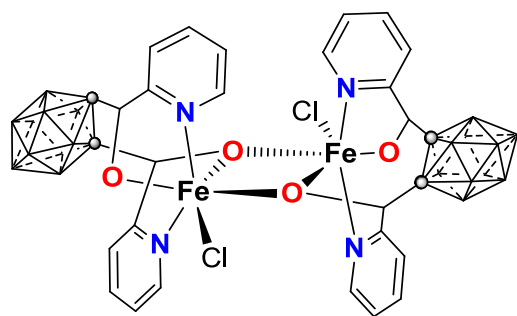
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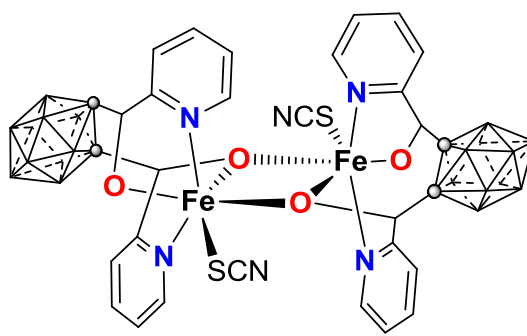
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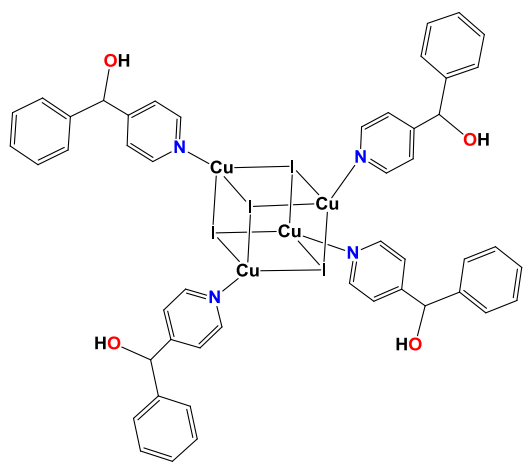
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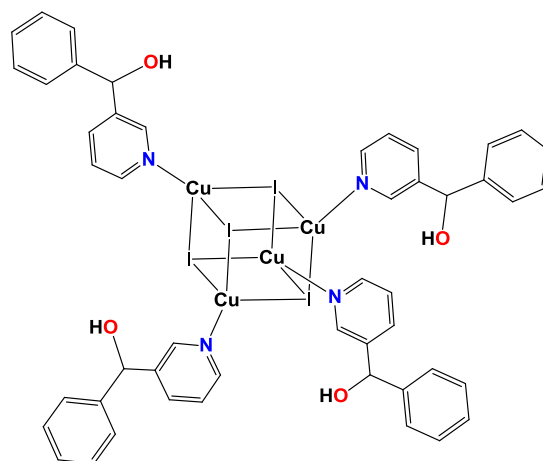
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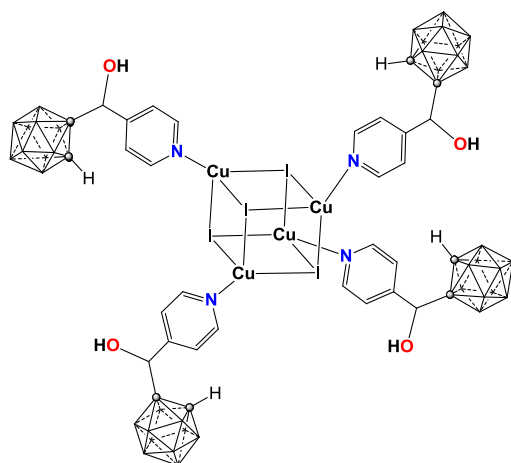
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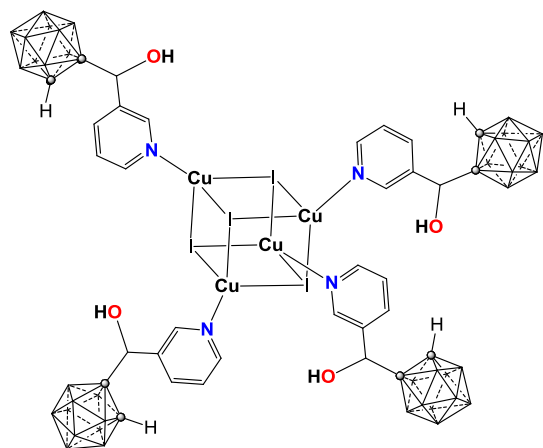
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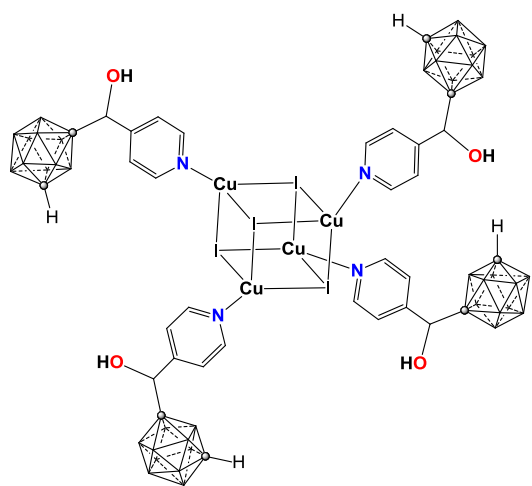
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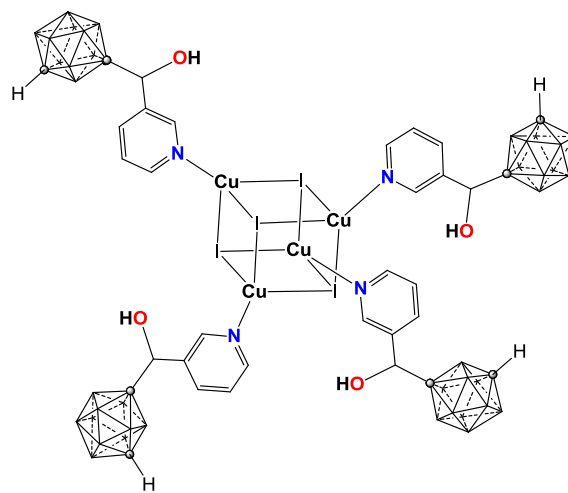
Cu-oCBL3



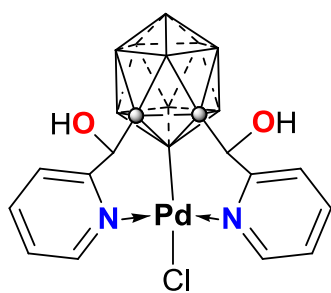
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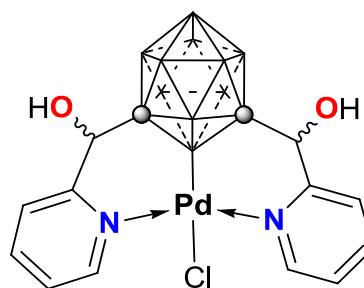
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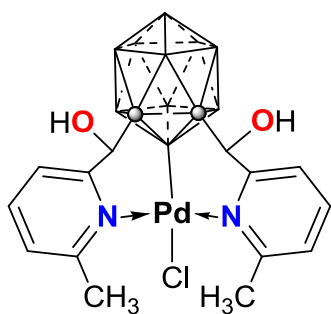
Cu-mCBL2



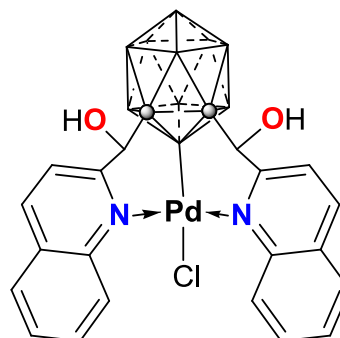
Pd-oCB(L1)₂



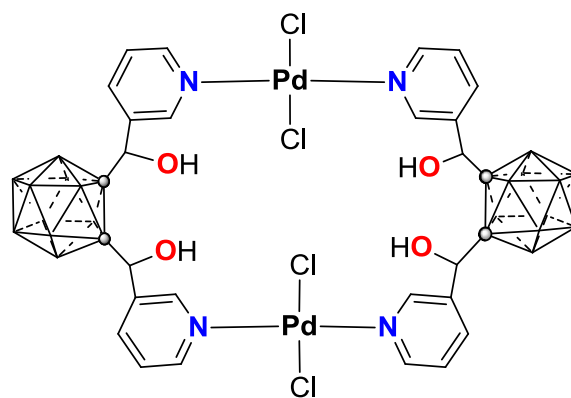
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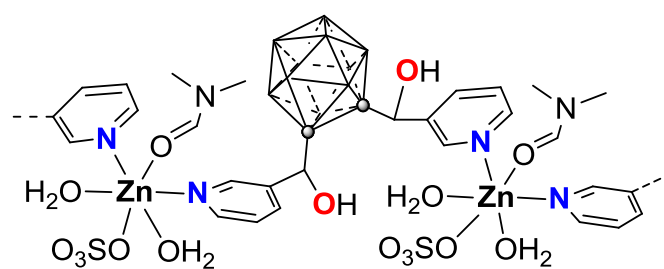
Pd-oCB(L5)₂



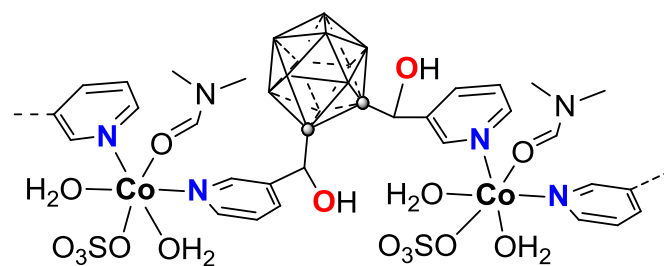
Pd-oCB(L4)₂



Pd₂Cl₂(oCB(L2)₂)₂

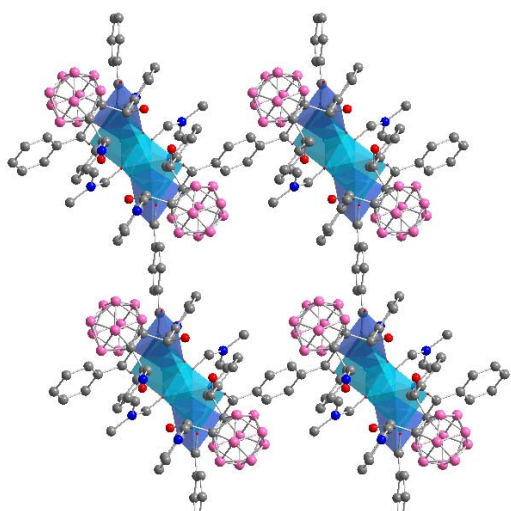


Zn-oCB(L2)₂

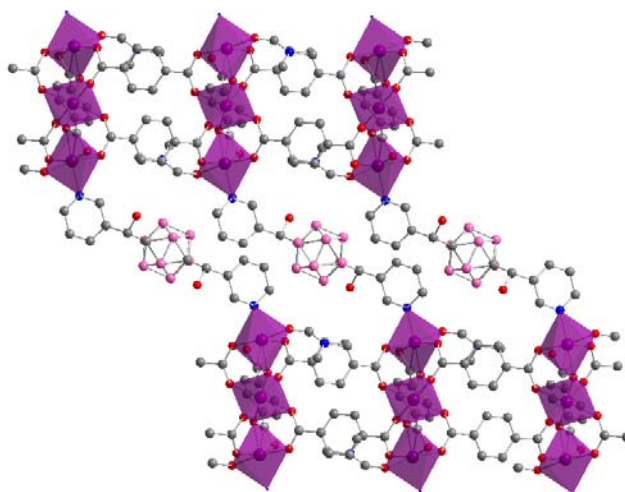


Co-oCB(L2)₂

Metal-Organic Frameworks (MOFs)

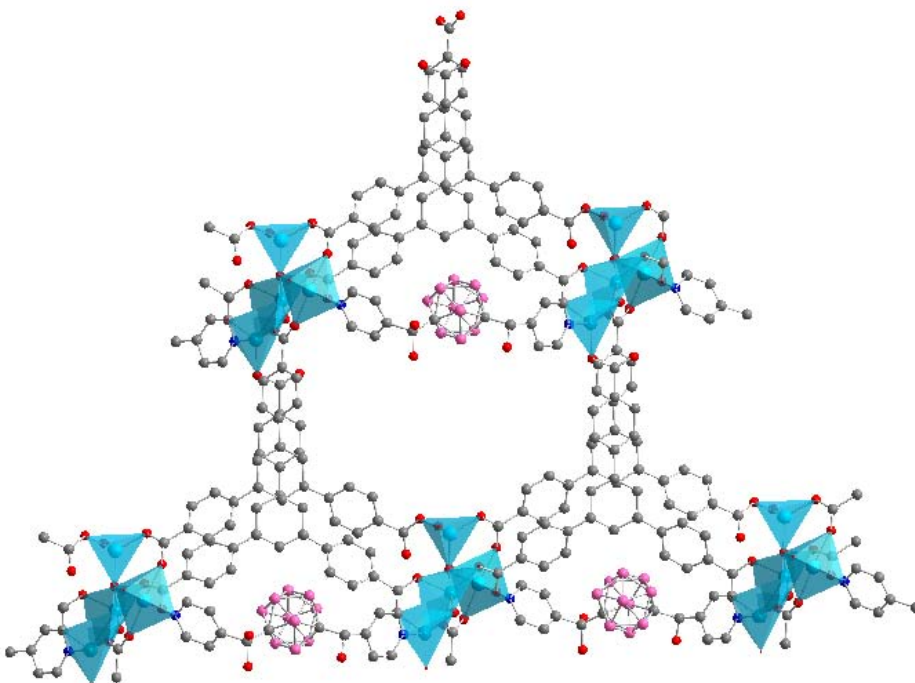


oCB-MOF-1
(Zn + 1,4-BDC + *oCB(L2)*₂)

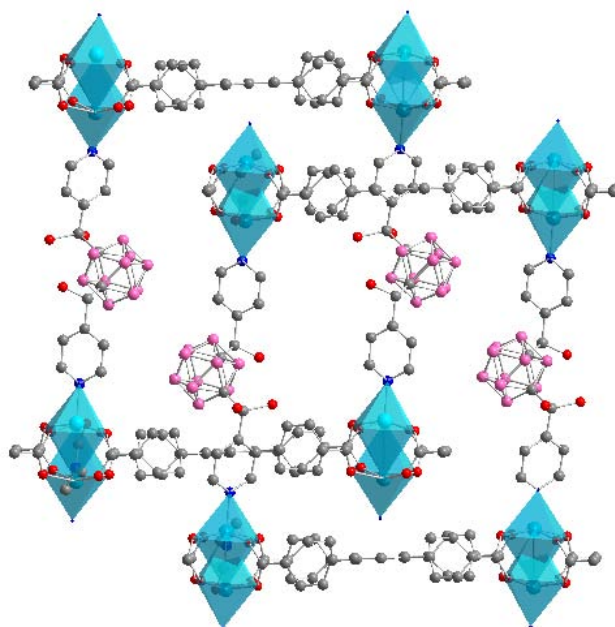


mCB-MOF-2
(Co + 1,4-BDC + *oCB(L2)*₂)

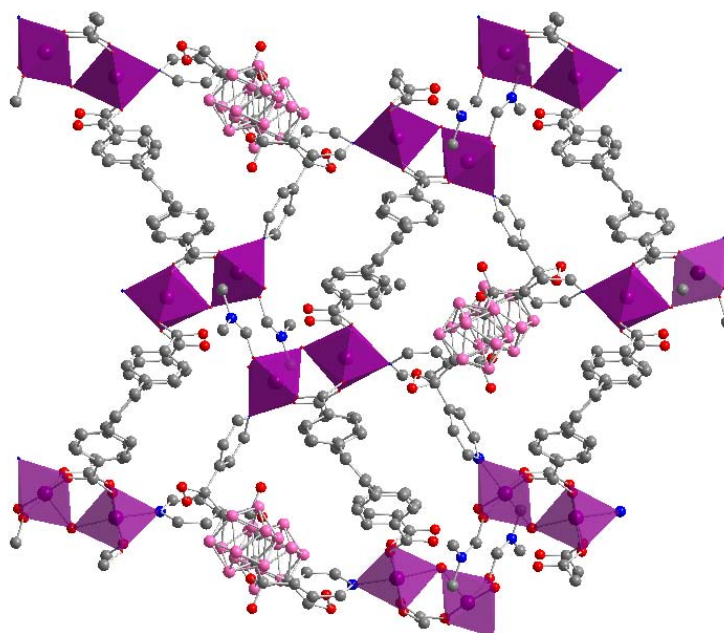
mCB-MOF-2B
(Co + 1,4-BDC + *oCB(L3)*₂)



mCB-MOF-3
(Zn + BTB + *mCB(L3)*₂)



mCB-MOF-4
(Zn + TCPB + *mCB(L3)*₂)



mCB-MOF-5
(Co + TCPB + *mCB(L3)*₂)

Abbreviations

| | | | |
|---------------------|--|---------------------|--|
| 1 or 2 or 3D | 1 or 2 or 3 dimensional | CB | carborane |
| <i>o</i> -carborane | | <i>m</i> -carborane | |
| or oCB | <i>ortho</i> -carborane | or mCB | <i>meta</i> -carborane |
| <i>p</i> -carborane | | STC | supramolecular-tilt-chirality |
| or pCB | <i>para</i> -carborane | MC | molecular chirality |
| Ph | phenyl | SBU | Secondary building unit |
| MOFs | metal-organic frameworks | SMC | supramolecular chirality |
| <i>M</i> | left-handed helix | <i>sc</i> | <i>syn-clinal</i> |
| <i>P</i> | right-handed helix | <i>app</i> | <i>anti-periplanar</i> |
| XLCT* | halide-to-ligand charge transfer excited state | <i>rac</i> - | racemic |
| ³ XLCT | triplet halide-to-ligand charge transfer | <i>Co</i> - | conglomerate |
| CC* | cluster-centered excited state | LE | low energy |
| LMCT | Ligand-to-metal charge transfer | HE | high energy |
| MALDI-TOF-MS | matrix assisted laser desorption ionization-time of flight–mass spectrometry | ³ CC | triplet cluster-centered |
| PXRD | Powder X-ray diffraction | HB | hydrogen bond |
| NMR | nuclear magnetic resonance | ATR-FTIR | attenuated total reflectance fourier transform infrared spectroscopy |
| GC | gas chromatography | XRD | <i>X-ray diffraction</i> |
| SEM | scanning electron microscopy | CD | circular dichroism |
| NPA | natural population analysis | ICP | inductively coupled plasma |
| TGA | thermalgravimetric analysis | NLO | non-linear optic |
| SWV | square wave voltammetry | BET | Brunauer, Emmett and Teller |
| SHG | second harmonic generation | UV-Vis | ultra violet-visible |
| DFT | density functional theory | CV | cyclic voltammetry |
| δ (ppm) | chemical shifts in parts per million | <i>Qst</i> | isosteric heat |
| TCPB | 1,2,4,5-tetrakis(4-carboxyphenyl) benzene | χ_M | Susceptibility |
| BTB | 1,3,5-tris(carboxyphenyl)benzene | θ_c | contact angle |
| KOH | potassium hydroxide | <i>n</i> -BuLi | <i>n</i> -butyl lithium |
| | | <i>Fc</i> | ferrocene |
| | | 2-Hmim | 2-methylimidazole |
| | | NaOH | sodium hydroxide |

| | | | |
|------------|---------------------|----------|-------------------|
| K_2CO_3 | potassium carbonate | HCl | hydrochloric acid |
| K_3PO_4 | potassium phosphate | Et_3N | triethylamine |
| CH_2Cl_2 | dichloromethane | EtOAc | ethyl acetate |
| THF | tetrahydrofuran | $CHCl_3$ | chloroform |
| DMF | dimethylformamide | MeOH | methanol |
| DMSO | dimethyl sulfoxide | EtOH | ethanol |

Abstract

This doctoral thesis describes the syntheses and full characterizations of a whole series of N,O-type mono- and disubstituted carborane-based pyridylalcohol ligands with *ortho*-, *meta*- and/or *para-closo*-carborane cluster as the building backbone. It follows the synthesis of new metal complexes incorporating these ligands and the potential applications for the corresponding materials, ranging from finite molecular complexes to three dimensional frameworks.

Section 3.1 contains the synthesis and characterization of the mono- and disubstituted carborane-based pyridylalcohol ligands (**CB-L** and **CB-(L)₂**, respectively) with *ortho*-, *meta*- and/or *para*-carborane. The compounds were synthesized in one pot by the reaction of mono- or di-lithiated carboranes with pyridyl aldehydes and in high yields. In order to modify the acidity of the ligands, iodination at the boron vertex(es) have been performed to the corresponding monosubstituted *meta*-carborane derivatives. The synthesis of methylated at boron disubstituted *meta*- and *ortho*-carborane derivatives is also described.

For the monosubstituted ligands, ten structurally related racemic and enantiopure 2-pyridylalcohol ligands (**CB-L1**) containing *ortho*-, *meta*- or *para*-carborane core have been studied by single-crystal X-ray crystallography. Most structures show O-H...N hydrogen bonded homochiral 2₁-helical supramolecular networks. A possible expression of the molecular chirality (MC) into the supramolecular chirality (SMC) of 2₁-helical networks is investigated. Finally, the structural analysis of six X-ray structures for the disubstituted ligands shows that the packings of these ligands are dominated by O-H...N and/or O-H...O hydrogen bonds. Further analysis revealed that homochiral self-assembly occurred in the supramolecular constructions of these compounds.

Section 3.2 describes the synthesis of iron (III) and copper (I) complexes with monosubstituted *ortho*-, *meta*-carborane and phenyl based pyridylalcohol ligands and the properties for most of the compounds.

In the first part, the reactivity of the 2-pyridylalcohol ligands **oCB-L1** and **Ph-L1** with FeCl₂ has been compared. It is shown how the introduction of carborane into the 2-(hydroxylmethyl)pyridine (2-hmpH) architecture significantly alters the coordination of the simple phenyl-substituted 2-hmpH. Whereas the carborane-based ligand affords a neutral dinuclear iron (III) complex **Fe₂Cl₃(oCB-L1)₃**, the phenyl derivative gave a cationic tribuclear iron (III) complex **[Fe₃Cl₄(Ph-L1)₄]⁺**. The dinuclear complex has been synthesized in racemic and enantiopure forms and the structural, chiroptical and magnetic properties are reported and discussed. Also, a very rare case of spontaneous resolution of racemic **Fe₂Cl₃(oCB-L1)₃** on precipitation or exposure to solvent vapour is described. Finally, the reactivity of the 2-pyridylalcohol ligands **oCB-L1** and a series of non-iodinated and iodinated *m*-carborane ligands (**mCB-L1**, **I-mCB-L1** and **I₂-mCB-L1**) with FeCl₂ is compared. The resulting iron (III) complexes **Fe₂Cl₃(mCB-L1)₃**, **Fe₂Cl₃(I-mCB-L1)₃** and **Fe₂Cl₃(I₂-mCB-L1)₃** appear to be isomeric structures to that of the **Fe₂Cl₃(oCB-L1)₃** but with a different arrangement of the ligands. The possible

influence of the different acidities and/or bulkiness of the ligands on the final architectures of these molecular complexes is then discussed.

In a second part, the reactivity of the 3- and 4-pyridylalcohol ligands **oCB-L2**, **oCB-L3**, **mCB-L2**, **mCB-L3** and phenyl derivatives (**Ph-L2** and **Ph-L3**) with CuI is compared. Preliminary results show the formation of cubane-liked $\text{Cu}_4\text{I}_4\text{L}_4$ complexes (L = **oCB-L2**, **oCB-L3**, **mCB-L2**, **mCB-L3**, **Ph-L2** and **Ph-L3**) and the crystal structure for one of them has been determined by XRD. Luminescence properties for all these compounds have been studied in the solid state at room temperature. The possible relation between emission bands and the electronic properties of the pyridylalcohol ligands is then discussed.

In **section 3.3**, The reactivity of the disubstituted 2-pyridylalcohol ligands **oCB-(L1)₂**, **mCB(L1)₂** and **oCB-(L5)₂** with palladium and iron is shown. Reactions of the ligands with palladium resulted in a series of palladium (II) NBN pincer type complexes **Pd-(oCB-(L1)₂)**, **Pd-(mCB-(L1)₂)** and **Pd-(oCB-(L5)₂)** through B-H bond activation. The structures revealed exceptionally long Pd-Cl distances due to the strong *trans* influence of the carborane moieties as well as the formation of O-H...Cl intermolecular hydrogen bonds. The latter is analysed by XRD and DFT calculations. Moreover, a localized orbitals approach has been applied to determine the oxidation state of Palladium in these carboranyl pincer complexes and the resulting data suggests palladium (II) is formed instead of palladium (0), as previously suggested in the literature. Since these types of complexes are known to be used for catalytic reactions, the initial catalytic studies have been carried out for the Suzuki coupling reaction. The result shows **Pd-(oCB-(L1)₂)** and **Pd-(mCB-(L1)₂)** are good catalyst precursors in water and with very low amounts of catalyst loadings (10^{-4} mmol%). **Pd-(oCB-(L1)₂)** is also revealed to have very high turn-over-number (TON) ranging from 770000 to 990000.

In the final part of this section, The preliminary results on the reactivity of the two different diastereoisomers, *anti*-**oCB-(L1)₂** or *syn*-**oCB-(L1)₂**, with iron is shown. In the case of *anti*-**oCB-(L1)₂**, a symmetric tetranuclear diiron (III) complex **Fe₂Cl₂(anti-oCB-(L1)₂)₂** is obtained and the magnetic properties are reported and discussed. In the case of *syn*-**oCB-(L1)₂**, degradation of the carborane clusters from *closo*- to *nido*-species is observed in polar solvents, so that complex formation was difficult. Different reactivity of *anti*-**oCB-(L1)₂** and *syn*-**oCB-(L1)₂** is discussed and an diiron (III) complex **Fe₂Cl₃(syn-oCB-(L1)(DMF)(H₂O)** is finally obtained.

Section 3.4 describes the synthesis of palladium (II), cobalt (II) and zinc (II) complexes with disubstituted 3-pyridylalcohol ligands **oCB-(L2)₂**. A macrocyclic Palladium (II) dimer **Pd₂Cl₂(syn-oCB-(L2)₂)₂** is formed by mixing *syn*-**oCB-(L2)₂** and [PdCl₂(MeCN)₂] in DMF under air at ambient temperature. **Pd₂Cl₂(syn-oCB-(L2)₂)₂** can be crystallized with different polar solvents (DMF, DMF/DMSO, DMSO, THF and EtOAc) giving inclusion compounds with an exceptionally high solvent contents. The crystal structures and inclusion behaviours for all the compounds is also discussed.

Differently, complexation with *syn*-**oCB-(L2)₂** with zinc or cobalt result in 1D coordination polymers. This outcome demonstrates the flexibility of the pyridylalcohol side arms give rise to high degrees of biting angle of disubstituted 3-pyridylalcohol ligands *syn*-**oCB-(L2)₂**. Therefore, it is a proof of concept that these disubstituted 3- and 4-pyridylalcohol ligands **oCB-(L2)₂**, **mCB-(L2)₂** and **mCB-(L3)₂** can be used as linkers and potentially extend the coordination compounds from finite molecular levels to infinite three dimensional frameworks.

Section 3.5 contains the synthesis and characterization of five new metal-organic frameworks (MOFs), all incorporating disubstituted 3- or 4-pyridylalcohol ligands **oCB-(L2)₂**, **mCB-(L2)₂** or **mCB-(L3)₂** and various carboxylic acids. Solvothermal reaction of *anti*-**oCB-MOF-1** with Zn(NO₃)₂ and 1,4-benzenedicarboxylate (1,4-BDC) afforded a highly hydrophobic and water stable *anti*-**oCB-MOF-1**. Detail discussion of the gas and water sorption of this MOF is shown, in which *anti*-**oCB-MOF-1** appear to have high affinity to CH₄ and also is hydrophobic. The influence of the different diastereoisomers of **oCB-(L2)₂** in the MOF structure is also investigated. Further study on the formation of *m*-caborane-based MOFs with different metals (zinc and cobalt) and carboxylic acids (1,3,5-tris(carboxylphenyl)benzene (BTB) and 1,2,4,5-tetrakis(4-carboxyphenyl) benzene (TCPB) has been carried out. The resulting MOFs **mCB-MOF-2**, **mCB-MOF-2B**, **mCB-MOF-3**, **mCB-MOF-4** and **mCB-MOF-5** show various architectures and some of them are also stable in water.

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Introduction

1.1 Carboranes

Icosahedral dicarba-*closo*-dodecacarboranes (or carboranes) are clusters of empirical formula $C_2B_{10}H_{12}$. These clusters comprise ten boron atoms and two carbon atoms, being each atom hexacoordinated. In total, 26 skeleton electrons are delocalized over the entire structure of the cluster. Three isomeric forms are known: *ortho*, *meta* and *para*, which are differentiated by the position of the carbons in the cluster (Figure 1-1). The chemistry of these clusters has attracted considerable interest due to their high symmetry and their remarkable stabilities.

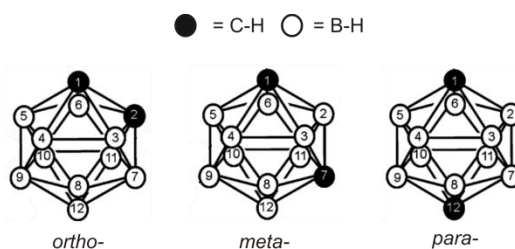


Figure 1-1: Graphical representation of the carborane isomers (*closo*- $C_2B_{10}H_{12}$) with vertex numbering. Solid lines are not to be regarded as classical two-center, two-electron single bonds.

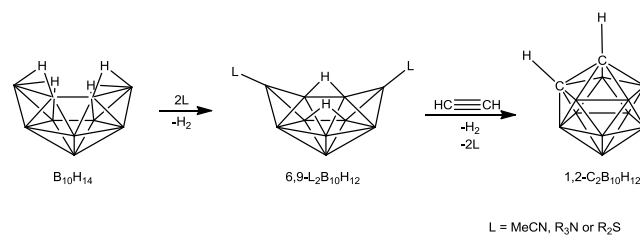
The history of carborane might be traced back to 1923, where carborane derivatives might be present in some of the resulting $C_xB_yH_z$ products from a boron hydride experimental chemist, Alfred Stock. It had been mainly pictured by theoreticians, until an icosahedral $B_{12}H_{12}^{2-}$ salt was isolated by Pitochelli and Hawthorne in 1960^[1] which enlightened the viability of neutral $C_2B_{10}H_{12}$ clusters. The first synthesis of icosahedral $C_2B_{10}H_{12}$ *ortho*-carboranes was published in 1963 in a series of articles from D. Grafstein *et al.*^[2] and R. P. Alexander and H. A. Schroeder *et al.*^[3] The *meta*- and *para*-carborane isomers were then prepared via cage rearrangement of *ortho*-carboranes by heating.^[4]

Carboranes have been traditionally employed in organometallic and coordination chemistry as ligands, in catalysis and in medicine as a source of boron atoms.^[5] More recently, carboranes have found applications in material science, including luminescence materials, coordination polymers, dendrimers, liquid crystals, nanoscience, *etc.*^[6] It follows a brief summary of reactivity and properties of carboranes.

1.1.1 Synthesis and Properties

The most common method to synthesize *ortho*-carborane is the reaction of $B_{10}H_{14}$ with acetylenes in the presence of Lewis base (Scheme 1-1), though it is also commercially available nowadays. The *meta*- and *para*- carborane can be obtained from *ortho*-carborane by thermal isomerization at 400 – 500 °C and 600 – 700 °C, respectively under inert conditions.

Scheme1-1: Synthesis of *ortho*-carborane by reaction of $B_{10}H_{14}$ with acetylenes in the presence of Lewis base



Carboranes exist as white solid in ambient temperature and are thermally stable up to 400 °C. Sublimation also occurs at relatively low temperature (60-100 °C) depending on the isomers. Table 1-1 summarized the physical features of *ortho*-, *meta*- and *para*-carboranes.

Table 1-1: Melting point and heat of sublimation of carboranes

| | <i>ortho</i> | <i>meta</i> | <i>Para</i> |
|---|--------------|-------------|-------------|
| Melting point (°C) ^[7] | 295 | 270 | 261 |
| Heat of sublimation (kJ/mol) ^[8] | 71 | 69 | 66 |

The size of carboranes are 148, 143 and 141 Å³ for *ortho*-, *meta*- and *para*-isomers, respectively, in which the rotation volume is around 40 % larger than the phenyl ring (102 Å³) but comparable to adamantane (136 Å³) as illustrate in Figure 1-2.

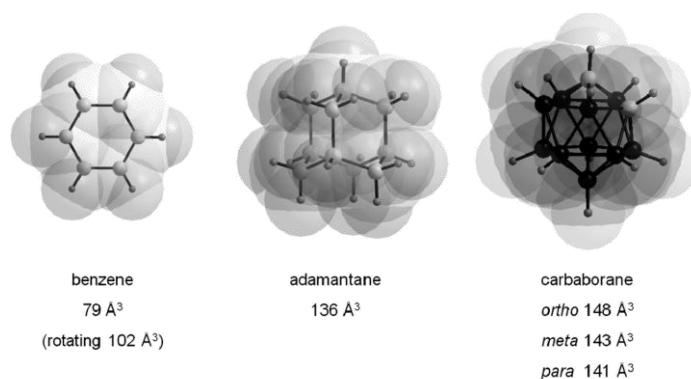


Figure 1-2: Illustration of the van der Waals volumes of benzene, adamantane and carboranes. ^[5c]

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The icosahedral carborane clusters reveal nonclassical bonding interactions giving a very complex overall electronic structure. Thus, for example, carborane clusters are known to exhibit dramatically different electronic effects on the substituents attached to different vertices (see the clusters numbering in Figure 1-1).^[5b] As a consequence of a non-uniform electron distribution and the different electronegativities of boron (2.04) and carbon (2.55), substituents attached to the carbons usually experience an electron-withdrawing effect, whereas substituents at boron atoms furthest from the carbon experience an electron-donating effect. This fundamental property of carboranes was nicely proved by Teixidor and Viñas, who observed that a methyl substituent attached to the boron vertices in these clusters acts as an electron-withdrawing group.^[9] Later, Mirkin and coworkers showed that a phosphine-thioether moiety attached to different vertices of carboranes can

experience either a strongly electron-withdrawing or electron-donating influence.^[10] This effect has been overlooked in the past, resulting in a number of reports incorrectly generalizing the electronic properties of carboranes as “electron withdrawing”.

The spherical feature of the carboranes, with slightly polarized hydrogen atoms and the presence of the hydride-like hydrogens at the B-H vertexes, make the carboranes very hydrophobic.^[11] It has been experimentally demonstrated that *ortho*-carborane is even more hydrophobic than adamantane.^[12] The hydrophobicity reduces with the dipole moments D (*ortho*: 4.53, *meta*: 2.85, *para*: 0), therefore, the hydrophobicity of carboranes increases in the order of *ortho*- to *meta*- to *para*-isomer. This is an important observation as the hydrophobicity of carborane derivatives can be tuned by the choice of the carborane isomer.^[12]

Another consequence of the non-uniform electron distribution and different electronegativity of boron and carbon is the acidity, in which the hydrogen atoms attached to carbon are acidic and those attached to boron are hydridic. This defines the reactivity of carboranes as it will be summarized below. The acidity of the CH vertexes decreases in the order of *ortho*-, *meta*- and *para*-carborane (Table 1-2). Since the pK_a of the CH vertexes correlate strongly with the inductive effects of the isomers, it is tunable depending on the choice of addition substituents and the chosen vertex. For instance, addition of halogen at B (9 or 12) position of *ortho*-carborane increases the acidity, whereas addition of methyl group would decrease the acidity of the CH protons instead.

Table 1-2: pK_a values of CH groups in carboranes

| | <i>ortho</i> | <i>meta</i> | <i>Para</i> |
|--------------|--------------|-------------|-------------|
| pK_a value | 19 - 23 | 24 - 28 | 26 - 30 |

The substitution chemistry of these species occurs either at the acidic CH vertexes (deprotonation and nucleophilic substitution) or at the hydridic BH vertexes (electrophilic substitutions). It follows a summary of the reactivity of these icosahedral carboranes.

1.1.2 Reactivity of Carboranes

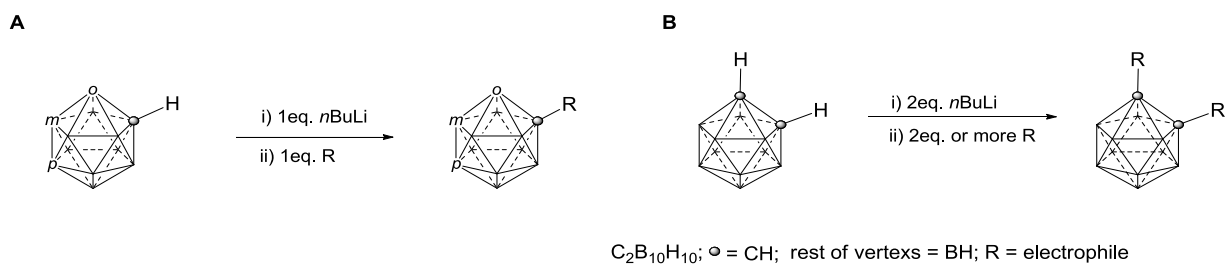
Due to the extended chemistry of carboranes, a complete review of it is out of the scope here. Therefore, only the main functionalization routes are explained and in particular those related to the present thesis.

1.1.2.1 Carbon Substitutions

Nowadays, one of the most used routes for carbon functionalization of carboranes is via nucleophilic substitution reactions as this route is general for all three carborane isomers, and provides products in high yields and relatively mild conditions (Scheme 1-2). As mentioned above, the CH hydrogens are weakly acidic and can be deprotonated with strong bases (e.g. alkyllithium and Grignard reagents).

The negatively charged carbon atoms can then be functionalized with electrophilic reagents such as carbonyl derivatives, alkylhalides, etc.

Scheme 1-2: general synthetic procedure for A: monosubstitution and B: disubstitution

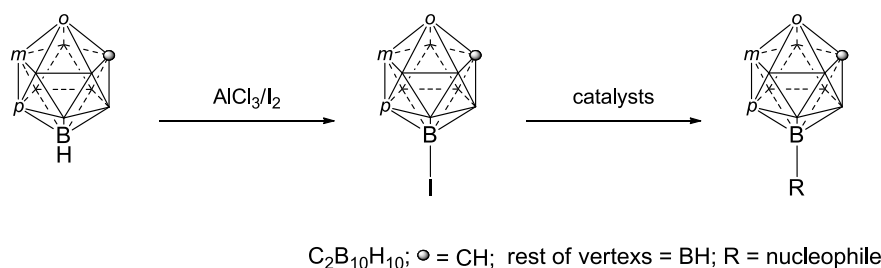


The synthesis of monosubstituted carborane derivatives (Scheme 1-2A) is more delicate compare to disubstitution because the monolithiation of the carborane moiety is complicated by the tendency of the monolithiated carborane to disproportionate to carborane and its dianion. Several strategies have been followed to overcome this problem, such as by using protecting/deprotecting methodologies, using dimethoxyethane as the solvent or by doing the reaction at high dilution.^[13] The best and more simple option is perhaps the conditions reported by Teixidor and Viñas, that consist on carrying the substitution reactions in ethereal solvents and at low temperature (<-70°C).^[14]

1.1.2.2 Boron Substitutions

As mentioned above, due to the hydridic character of the BH vertices of the carboranes, their functionalization is carried out through electrophilic substitution reactions. The boron substitution is however more challenging compared with the carbon substitution, not only because of the lower electronegativity of boron that makes the B-H bonds less polar and consequently less reactive, but also the different electronic features of the BH vertexes give rise to the formation of isomeric products, thus, limiting the functionalization. Boron atoms at positions (9)/(12) are more reactive and easier to substitute than those at positions B(3)/(6), which are the less reactive. Halides are common reactants for boron substitution reactions. Mild electrophilic aromatic substitution reactions using halides and $AlCl_3$ (Scheme 1-3) allows substitutions at selected boron positions. The obtained halogenated carboranes can then be used for further substitutions, for instance, by cross-coupling reactions with a catalyst. A recent review by F. Teixidor *et al.* summarized the synthetic pathways to create different bonds (B-P, B-C, B-N and B-S).^[15]

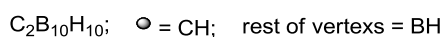
Scheme 1-3: one of the common synthetic procedures of B9-substitution



1.1.2.3 Deboronations

Deboronation reaction is perhaps the most important reaction of carboranes after substitution reactions. As its name indicates, deboronation reaction consists on the removal of a vertex of the closo-carboranes to provide anionic *nido*-carborane derivatives (Scheme 1-4). Such reaction is often needed for further development of water-soluble compounds in biological application or extension to metallocarborane compounds. On the contrary, it is one of the obstacles to develop stable *closo*-carborane-based materials due to the ease of deboronation under basic conditions.

Scheme 1-4: General deboronation reaction by alkoxide to *nido*-species.



Deboronation takes place under basic conditions and with a variety of nucleophiles, for instance, amines, potassium hydroxide or tetrabutylammonium fluoride hydrate (TBAFH).^[16,17,18] These nucleophiles will attack the most electrophilic boron vertexes (*e.g.* B(3)/(6) in *ortho*-carborane and B(2)/(3) in *meta*-carborane). The ease of deboronation decreases in the order of *ortho*- to *meta*- to *para*-carborane.

1.2 Metal Complexes with N- and/or O-Type Ligands

In recent decades, the design of hybrid functional materials has been received special interest because of their potential applications in different areas.^[19] A well-known approach for the preparation of such systems is the synthesis of organic-inorganic frameworks where transition metal ions and nitrogen containing heterocyclic ligands have proven useful for the construction of solid-state architectures and inorganic crystal engineering.^[20] In particular, pyridyl-based ligands have been successfully used for constructing a wide array of architectures with applications ranging from gas storage in porous frameworks to novel luminescence or magnetic materials.^[21] The increasing need for evolved systems and demanding assemblies has led to the emergence of hetero-donating functions,^[21a,f] among which N,O-type ligands such as (2-hydroxymethyl)pyridine (hmpH) are candidates. These simple alcohol pyridines have proven to be successful building blocks for the self-assembly of metallocarborane architectures with exciting physical properties.^[22]

In the following, selected examples of (hydroxymethyl)pyridine (hmp) N,O-type complexes that are related to this PhD thesis will be shown.

1.2.1 Selected Non-Carborane Containing N,O-Type Examples

2-(hydroxymethyl)pyridine (2-hmp) normally coordinate to the metal in a bidentate chelate fashion. G.R. Patzke *et al.* reported a Co (II)-based cubane water oxidation catalyst with 2-hmp ligand, in which the N,O chelate stabilized the cubane Co(II) core for the photosystem II (PSII) biomimetic water oxidation catalysis.^[23] On the other hands, incorporation of paramagnetic metal ions gives rise to series of single molecule magnets (SMM) with interesting magnetic properties. Modification of pyridylalcohol ligands also allows evolving to a wide range of polynuclear metal clusters (Figure 1-3).^[24,25]

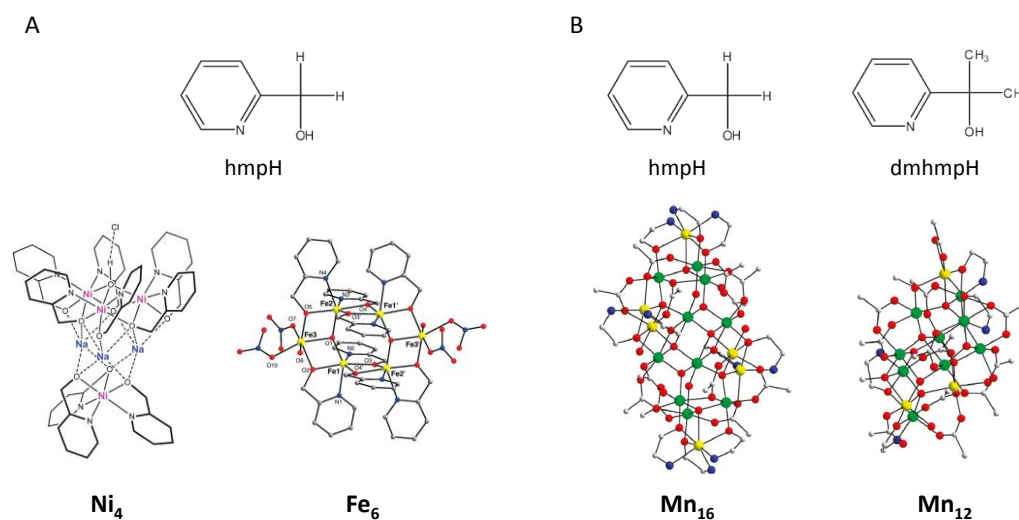


Figure 1-3: reported single molecule magnets by pyridylalcohol ligands. A: Ni₄ cluster^[24] (left) and Fe₆^[25a] cluster with hmpH (right); B: Mn₁₆ cluster with hmpH (left) and Mn₁₂ cluster (right) with dmhmpH^[25b].

3- and 4-(hydroxymethyl)pyridine (3-hmp and 4-hmp) cannot be used as bidentate ligands due to the distance between the nitrogen and oxygen atoms. Instead, they can act as monodentate ligand, usually through the nitrogen, whereas the hydroxymethyl group can be a functional moieties or potential extendable unit for further linkage. G. Christou and A. J. Tasiopoulos *et al.* demonstrated the formation of manganese single molecular magnet (SMM) with 4-hmp, which gives rise to the possibility to functionalize the terminal alcohol group in order to modify the magnetic properties.^[26]

As mentioned above, the position of the pyridine and hydroxyl group will lead to various architectures. Di(pyridyl)diol ligands provide higher number of coordination sites including tetradentate, bidentate or ditopic binding mode. N.P. Raju *et al.* reported an interesting copper (II) and bismuth (III) complexes with the bifunctional ligand di-2-pyridylmethanediol (dpmdH), where it coordinates in a tridentate fashion to form dinuclear complexes showing a ferromagnetic behaviour (Figure 1-4).^[27]

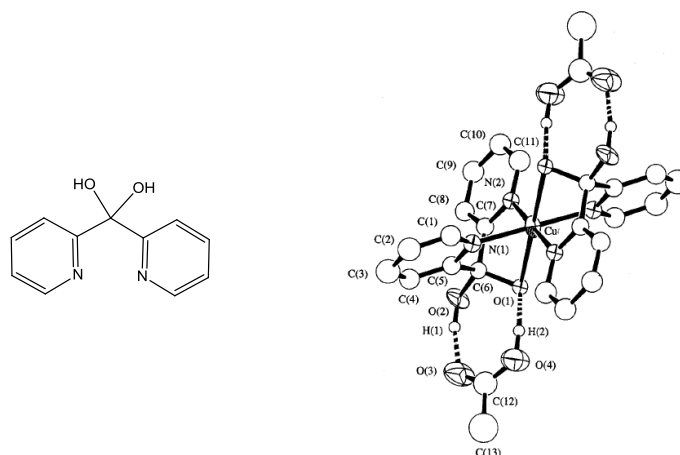


Figure 1-4: di-2-pyridylmethanediol ligand and the corresponding dinuclear copper (II) complex^[27].

Y. Niu *et al.* reported the formation of a one dimensional coordination polymer with 2,3-di(4-pyridyl)-2,3-butanediol (dpbd) with mercury iodide (Figure 1-5A),^[28] whereas R. L. LaDuca and co-worker presented the formation of a two dimensional coordination polymer with 1,2-di(4-pyridyl)ethanediol (dped) ligand and copper (II) bromide (Figure 1-5A).^[29] In these cases the ligands are acting as bridging linkers through the nitrogen and leaving the alcohol groups available, for instance, for further functionalization.

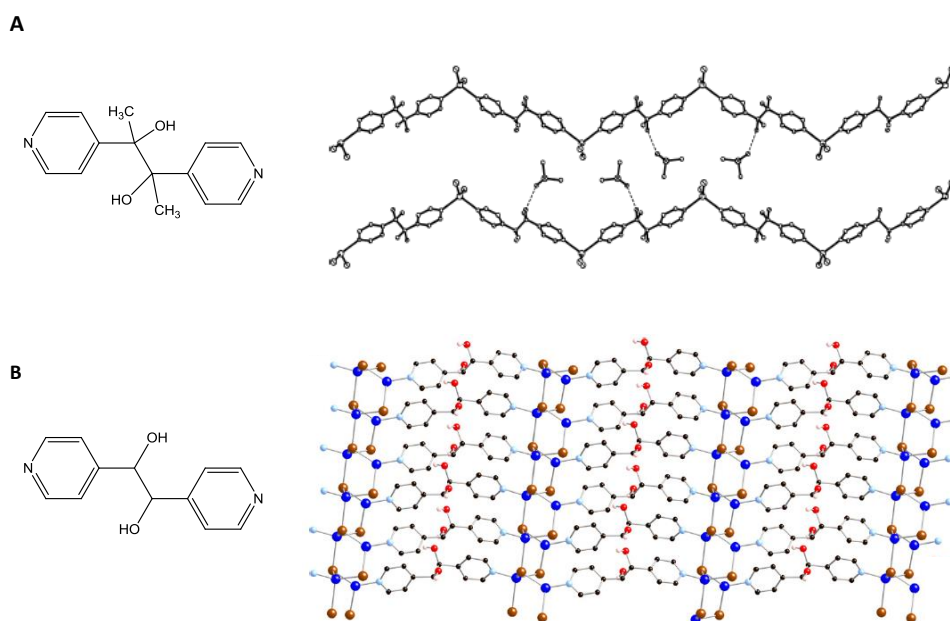


Figure 1-5: A: dpbd ligand and the corresponding Hg(I) 1D coordination polymer^[28]; B: dped ligand and the corresponding Cu (II) 2D layer^[29].

Such dpbd ligand was also introduced for the formation of spin cross-over (SCO) copper (II)^[30] and iron (II)^[31] coordination frameworks by S. Kitagawa *et al.* and C. J. Kepert and co-workers respectively, where the presence of diols can be functional groups and interact with polar solvents. Thus, C. J. Kepert *et al.* applied different polar solvents for the SCO behaviour study, which revealed the SCO

properties are dependent on the introduced guest solvent that modify the Fe···Fe distance and the pore dimensions (Figure 1-6).^[32]

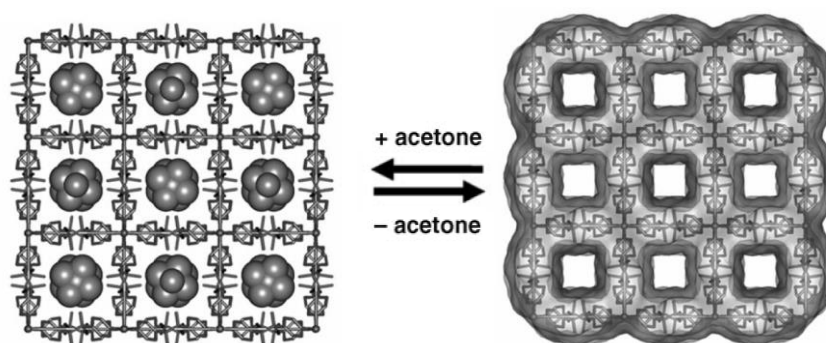


Figure 1-6: Iron (II) SCO coordination framework^[32]

1.2.2 Carborane Containing Examples

Carborane containing N,O-type ligands that have been used for the synthesis of metal complexes are scarce. Only a few examples are known in the literature and those include one example reported by the Inorganic Synthesis and Catalysis Laboratory.^[33]

Coordination of carboranyl-phenylpyridine ligand with platinum (II) results in a highly luminescent complex.^[34] The high luminescence quantum yield (82%) could be a potential candidate for optoelectronic materials (Figure 1-7A). The introduction of carborane cluster in such system can benefit from the bulkiness of the cluster that minimize the metal-metal contact and therefore can prevent emission quenching.

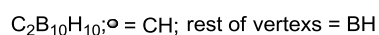
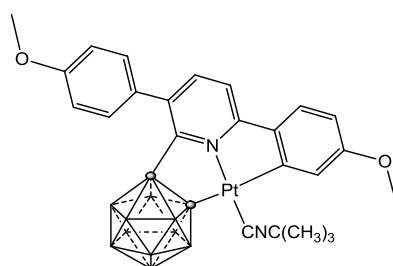


Figure 1-7: luminescent Pt (II) complex^[34]

Another example is that for nickel (II), palladium (II) and rhodium (III) chiral pincer complexes (Figure 1-8).^[35] It was found for example that the rhodium (III) pincer complexes act as catalysts precursors for the enantioselective reduction of α,β -unsaturated esters as well as for the aldol reduction reaction of *tert*-butyl acrylate and benzaldehyde. High enantioselectivities were observed and explained by the electron-withdrawing property of the carborane cluster.

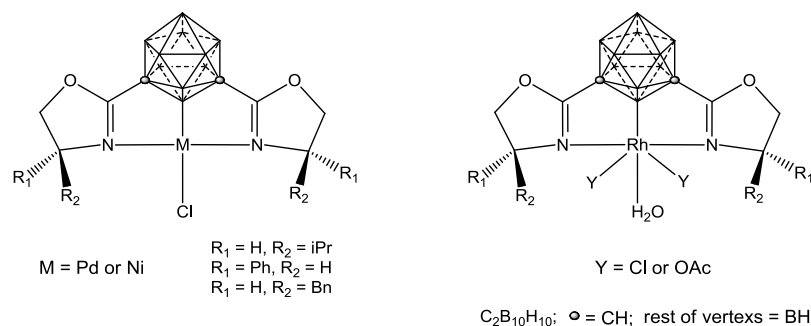


Figure 1-8: meta-carborane-based pincer catalysts.^[35]

Moreover, a series of *ortho*-carborane-based cobalt (II) complexes have been reported and showed interesting porosity and magnetic properties in the supramolecular array by intermolecular hydrogen bonding (Figure 1-9A).^[33] Besides, a family of carborane-based 3- or 4-pyridylalcohol based platinum (II) complexes have been reported as a complete study on the molecular recognition of β -cyclodextrin (β -CD) and the carborane-containing platinum complexes (Figure 1-9B).^[36]

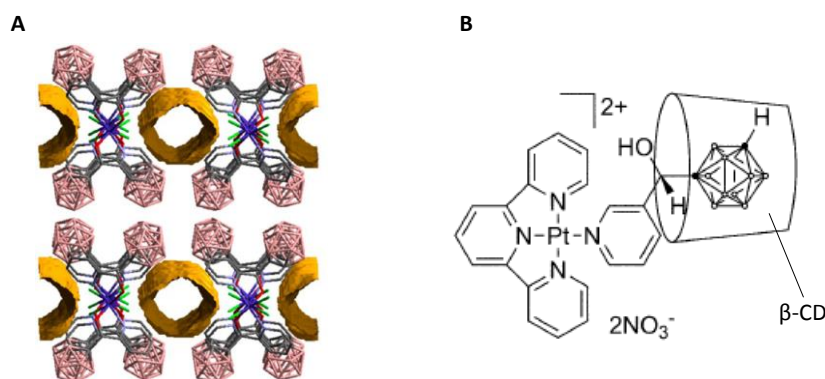


Figure 1-9: Carborane-based pyridylalcohol complexes: A: selected supramolecular array by cobalt (II) complex and illustration of cavities (yellow channel)^[33] and B: selected platinum (II) complex^[36]

1.3 Metal-Organic Frameworks

Metal organic frameworks (MOFs) are crystalline materials that consist of transition metal ions and multidentate organic linkers to form three dimensional porous networks. IUPAC (The International Union for Pure and Applied Chemistry) recently recommended the definition of MOF as “a coordination network with organic ligands containing potential voids”.^[37] The story of MOF materials began in the mid-20th century.^[38] These materials have been intensively studied over two decades due to the high scientific and industrial impacts. Research on such materials is growing exponentially every year and has reached to remarkable achievements.^[39] The interest of such materials is related to their extraordinary intrinsic properties, large porosity, easy chemical functionalization and structural diversity. Nowadays, the development on synthetic techniques is mature. Hence, most studies are focused on size and morphologies control and post-synthesis to enhance the functionalities, as well as the applicable features such as gas separation and catalysis. Moreover,

scale-up syntheses and innovation on new types of MOFs are also on-going despite of different needs for real-life applications.^[40]

1.3.1 Synthetic Methodologies

MOF syntheses methodologies have been extensively reviewed.^[41] The most commonly used method for MOFs syntheses is by solvothermal reaction, in which the reaction mixture is in a closed system (*e.g.* autoclave) under relatively high vapour pressure and temperature (<250°C). This method has almost no restriction and therefore optimized conditions for different MOFs can be tuned by altering various parameters such as reaction temperature, time, solvent, precursor, *etc.* However, the solvothermal method normally requires long reaction time. Thus, other methods have been developed such as microwave-assisted heating, electrochemical, sonochemical or mechanochemical methods. Among these, the more popular method is the microwave-assisted synthesis since high temperature output and direct radiation transfer to the reactants can be achieved in short period of time (less than 1 h). Whereas electrochemical methods allow the controlled formation of films, mechanochemical method provides an alternative to perform solvent free synthesis, and sonochemical methods aim to produce MOFs in high efficiency, although limited amount of MOFs are reported by this method (Figure 1-10).^[41]

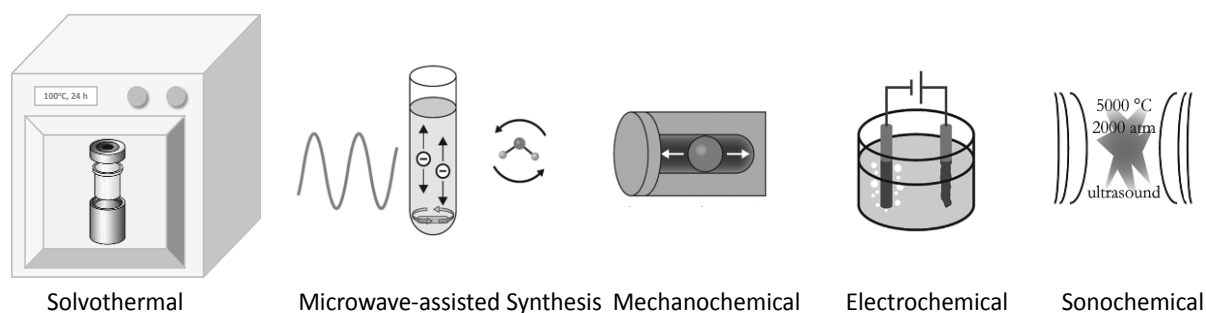


Figure 1-10: summary of synthetic methodologies for MOFs formation.^[41]

Size and morphology control is crucial for achieving the maximum functionality of MOFs. Some studies have been done on size control by introducing modulators in order to interfere the nucleation.^[42] or controlling the morphology by shaping or crystal growth.^[43] Currently, spray drying strategy is also introduced to generate nanoscale MOFs.^[44a] Also, scaled up synthesis of ZIF-8 up to 4 kg⁻¹ by mechanochemical method with screw extrusion is reported by S. L James and co-workers.^[44b]

As inorganic-organic hybrid materials, the primary choice of the organic part has been polycarboxylates (Figure 1-11A) and polypyridines.^[45] Organic ligands that possess both carboxylate groups and N donors are also investigated in MOFs.^[46] Thus, the chemistry of MOFs has been dominated by these ligands. Sometimes, the above mentioned ligands are simultaneously used to generate mixed ligand MOFs. The mixed-component MOFs are basically formed by transition metal ions and multidentate carboxylic acid to form 2D layers, whereas the so called pillar ligands (normally

pyridyl-based) connect the 2D layers to form 3D network (Figure 1-11B). This approach can allow larger modification flexibility in terms of pore size and introduction of functional groups.^[47]

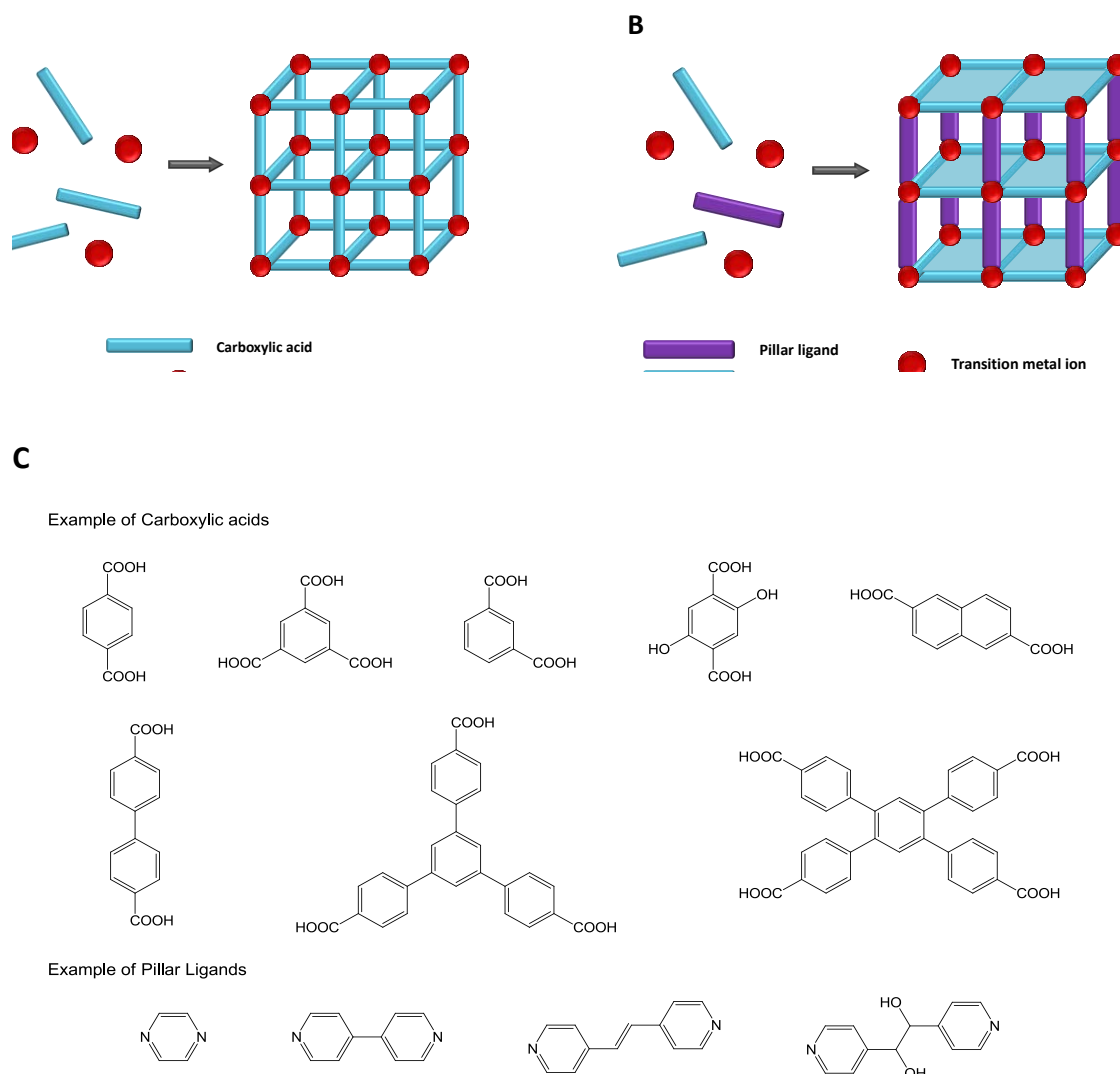


Figure 1-11: MOFs types: A: carboxylate-based, B: mixed-component MOFs. C: examples of carboxylic acids and pyridyl-based pillar ligands

Porosity is essential for application, however, almost all of the MOFs are microporous (diameter < 2 nm), only limited amount of MOFs are reported as mesoporous (diameter 2 – 50 nm) due to the catenation or structural stability. The simplest way to determine the accessible porosity is by Brunauer, Emmett and Teller (BET) surface area measurement by N₂ at 77 K and analysis of the curve pattern (Figure 1-12).^[48]

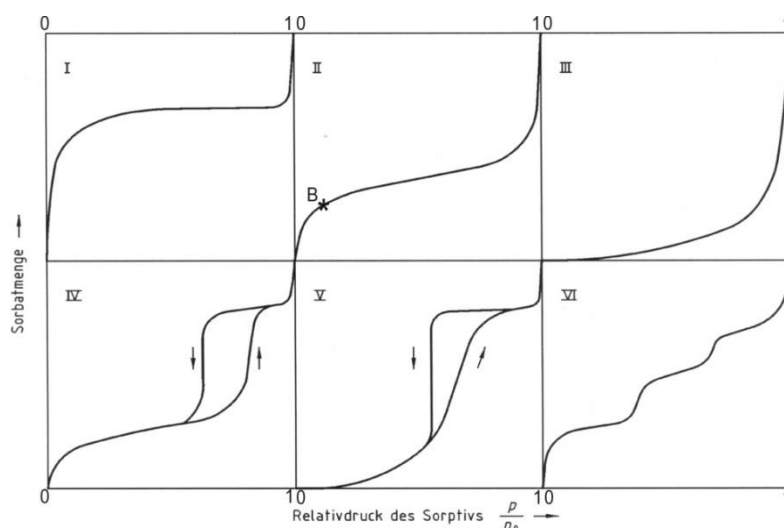


Figure 1-12: Sorption isotherms: I: microporous. II: non-porous, III: weak adsorbate-adsorbant interaction non-porous/microporous, IV: mesoporous, V: weak adsorbate-adsorbant interaction microporous/mesoporous, VI: multilayer adsorption on non-porous surface.^[48]

1.3.2. Applications and Recent Concerns

One of the main applications for MOF materials is for gas storage or selective gas separation due to the changeable intrinsic pore features and the high surface areas. Most of the focus has been on H_2 ^[49] or CH_4 ^[50] storage in order to enhance the storing capacity and environmental friendly purpose for energy application. CO_2 ^[51] sorption is also another main concern due to the critical emission level to the atmosphere. Gases separation from mixtures has also drawn high attention for purification purpose^[52]. Some selected examples for high gas sorption ability or selectivity are listed in Table 1-3.

Table 1-3: examples for MOFs consist of high gas sorption or selectivity.

| High gas sorption | | |
|---|--|--|
| H_2 storage (1 bar, 77 K) ^[49] | CH_4 storage (35 bar, 298 K) ^[50] | CO_2 sorption (1 bar, 298 K) ^[51] |
| MIL-101, PCN-9, Cu-BTT, MOF-505, PCN12 | PCN-14, MOF-74, NU-140, HKUST-1, NOTT-101a, UTSA-20 | MOF-74, HKUST-1, PCN-6, SNU-50, en-Mg2(dobpdc) |
| Gas selectivity | | |
| CO_2/N_2 | CO_2/CH_4 | CH_4/N_2 |
| CAU-1 ^[53a] , [Cu(bcppm)H ₂ O] ^[50b] | NJFU-2 ^[54a] , [Cu ₃ (TDPAH)(H ₂ O) ₃] ^[54b] | [Cu(Me-4py-trz-ia)] ^[55] |

Another area of interest is on catalysis which basically relies on the various possibilities to encapsulate the metal catalysts, modify the pore as active sites, or as platform to attach certain substrates in order to selectively control the reaction process.^[56] Many other applications such as magnetic spin crossover materials,^[57] drug deliveries,^[58] contrast agents^[59] and sensors^[60] etc. are under investigation as well by incorporating the corresponding metals or functional organic building blocks.

Although thousands of MOFs with fascinating properties have been discovered, only limited amount of them can be introduced into the industrial area due to the obstacles on scale-up syntheses, energy efficiency, environmental concerns as well as the final production cost. In addition, the chemical stability is also another concern such as water vapour resistance for application especially for industrial usage, since many of the MOFs cannot resist and eventually collapse under humid condition due to the displacement of water to the organic ligands (Figure 1-13).^[61] Recent reviews summarized the key point on justifying the water stability and adsorption in MOFs.^[62] It concluded that the strength of metal-ligand bond over metal-water interaction, hydrophobicity of the interior and the steric factors to protect of the metal clusters from the attack of water molecules are the important criteria to achieve water stable MOFs.

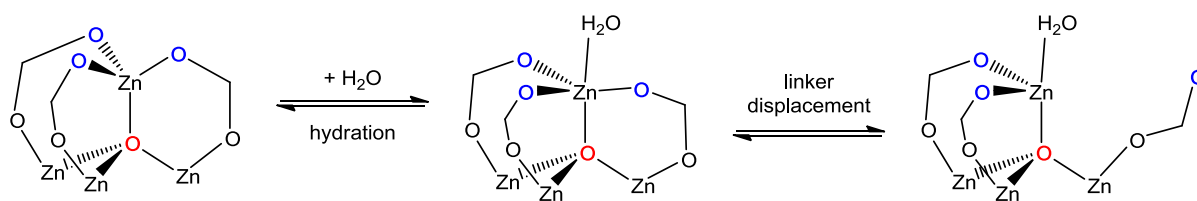


Figure 1-13: Illustration of water displacement to the organic linkers in metal cluster.^[61]

In order to increase the water stability in MOFs, different strategies have been applied such as post-synthesis to introduce hydrophobic functional group in the pore,^[63] external surface modification,^[64] fabrication of hydrophobic hybrid materials or composites^[65] as well as ligand designs.^[66] (Figure 1-14)

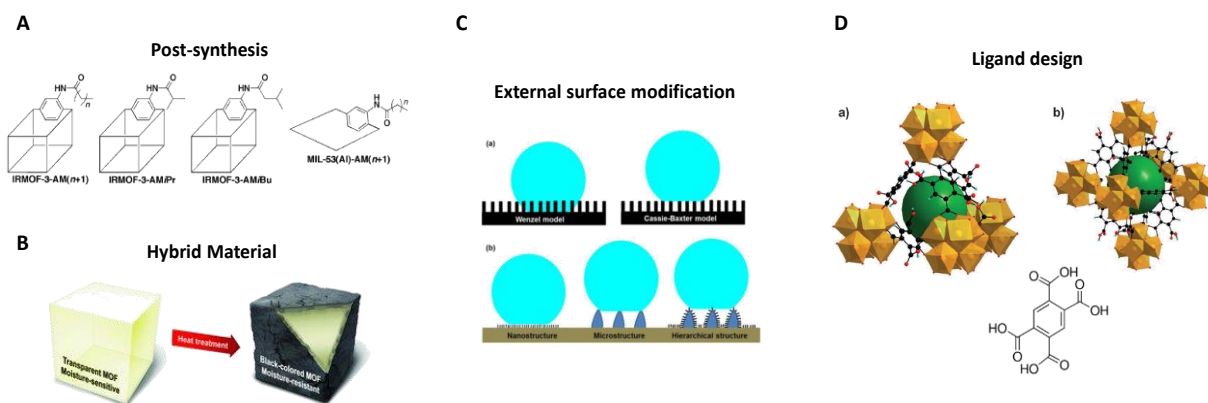


Figure 1-14: Strategies for enhancement of water stability. Example: A: post-synthesis,^[63] B: hybrid material^[64], C: external surface modification^[65], D: ligand design^[66].

Up to now, there are only several MOFs exhibiting water stable features, for instance, MIL-53(Cr) and ZIF-8. Therefore, development of water stable MOFs is undoubtedly crucial for further application.

1.3.3. Carboranes in Metal-Organic Frameworks

Among the large variety of MOFs reported,^[67] carborane-based MOFs are also found but only account for less than 20 reports (including two reviews)^[68] in the last 10 years. There are two main types of carborane-based ligands for MOFs: anionic carboranes or metallocarboranes (lead by Hardies' group)^[69] and neutral carboranes or metallocarboranes (lead by Mirkin and Hupp's group).^[70] Gas adsorption studies have only been carried out in the neutral carborane-based MOFs and basically all studies are devoted to the dicarboxylic acid of the *para*-carborane as linker (Figure 1-15). MOFs containing the latter *p*-carborane ligand exhibit unprecedented stabilities with respect to thermal degradation, inherited from the carborane ligand. The bulky (and three dimensional) nature of the carborane also serves in protecting unsaturated metal centres, that are important for CO₂ adsorption selectivity. Most importantly, some of the MOFs including this carborane-based ligand show gas uptake properties and excellent selectivities for CO₂/CH₄ mixtures.^[70] No sorption or stability experiments toward H₂O have been carried out in these types of MOFs. Figure 1-15 summarizes some of the ligands employed by these two groups.

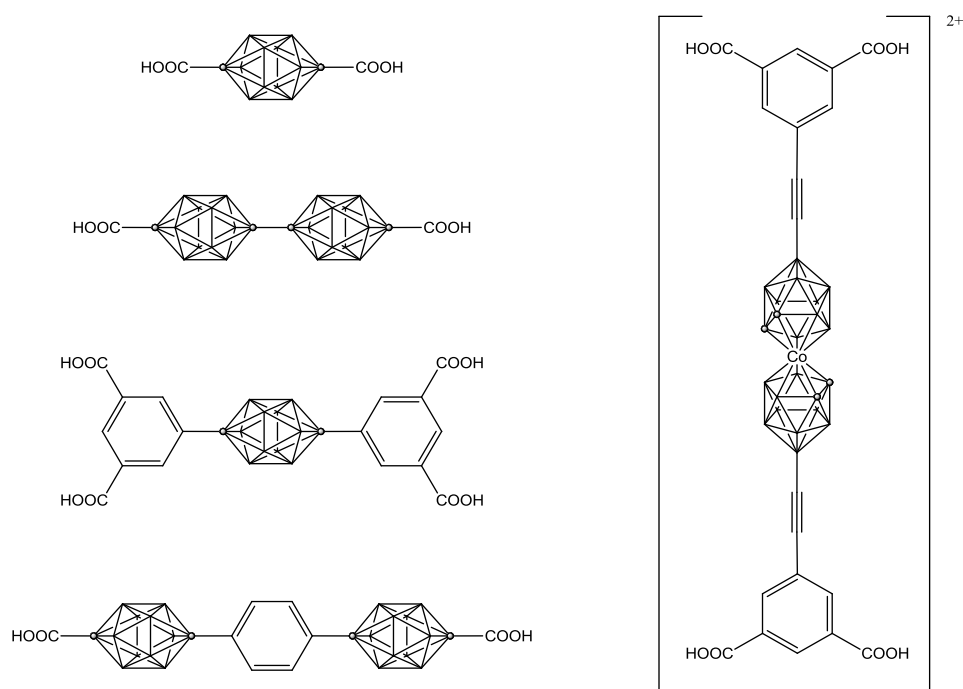


Figure 1-15: Summary of the carboxylic acid based carborane ligands that employed for MOFs synthesis by Mirkin and Hupp's group.^[70]

The very first *para*-carborane-based MOF has been reported in 2007 by Mirkin *et al.* The idea was to fabricate an isostructural MOF by 1,12-dihydroxycarbonyl-1,12-*para-closo*-carborane (*p*-CDC) to that of the well-known phenyl based MOF-5, [Zn₄O(1,4-BDC)₃]_n, in order to decrease the pore size and result in higher H₂ uptake (Figure 1-16). Although it was obtained a MOF with more complicated architecture [Zn₃(OH)(*p*-CDC)_{2.5}DEF₄]_n, H₂ uptake was significantly higher.^[71] Since then, their group has intensively developed *p*-carborane-based MOFs with various carboxylic acid derivatives.^[70,72]

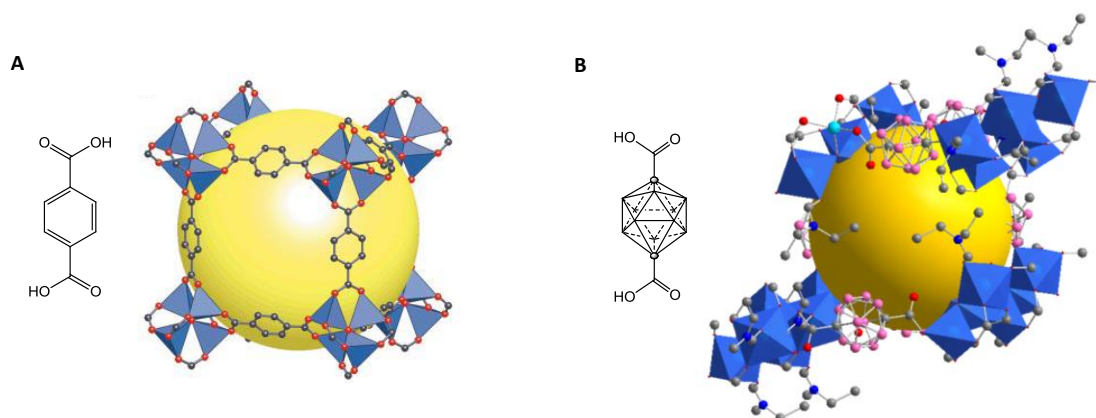


Figure 1-16: A: 1,4-BDC (top) and MOF-5 $[\text{Zn}_4\text{O}(1,4\text{-BDC})_3]_n$ (bottom); B: *p*-CDC (top) and *para*-carborane-based MOF $[\text{Zn}_3(\text{OH})(p\text{-CDC})_{2.5}\text{DEF}_4]_n$ (bottom)^[71]

Most recently, an isostructural framework to that of MOF-143 has been synthesized by using a tritopic *para*-carborane-based ligand has been synthesized (NU-700) (Figure 1-17). The result showed that incorporating carborane in the skeleton can stabilize the structure after activation, where the conventional MOF-143 would result in structural collapse.^[73]

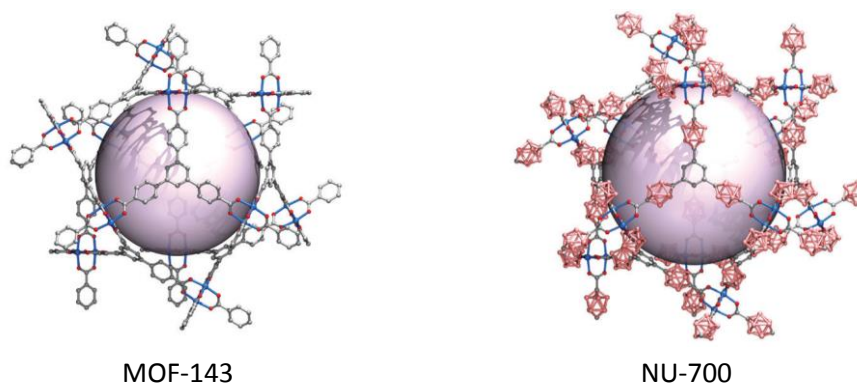


Figure 1-17: structure of conventional MOF-143 (left) and carborane-based MOF NU-700 (right)^[73]

It is remarkable that all of the above mentioned carborane-based MOFs include the *p*-carborane isomer, as this is certainly the most expensive of all isomers (Price for 1 g (Katchem Ltd.): *o*-carborane: 68 EUR; *m*-carborane: 76, *p*-carborane: 476 EUR). There is only one reported by Jin *et al.* where a dicarboxylic acid-functionalized *meta*-carborane-based MOF 1,7-dihydroxycarbonyl-1,7-*meta*-closo-carborane (*m*-CDC) has been synthesized and showed good selectivity for CO₂ sorption over N₂ and CH₄.^[74]

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Objectives

As described in the introduction, ligands that contain N,O-donor atoms are successful candidates as building blocks for coordination compounds with various attractive properties. The inclusion of carboranes into such architectures is basically unknown, as well as the possible effect of the carborane clusters in the coordination chemistry of such ligands. The high thermal and chemical stability, hydrophobicity, acceptor character, ease of functionalization and three-dimensional nature of the icosahedral carborane clusters make these new molecules valuable ligands in coordination chemistry and development of functional materials. Thus, the main objective of the present thesis is the synthesis of new metal complexes incorporating N,O-type carborane-based ligands and the study of their properties.

The first objective of the present thesis was to complete the synthesis and characterization of series of a series of mono- and disubstituted pyridylalcohol ligands with *ortho*-, *meta*- and/or *para*-carborane (**oCB**, **mCB** and/or **pCB**, respectively). Apart from this, due to the possible formation of hydrogen bonds by the presence of alcohol (-OH) and pyridine moieties as well as the chirality of these compounds, additional studies on the crystallographic structures of these compounds were planned. It was particularly interesting to investigate the possible influence of their chirality in the supramolecular structures.

The second objective was to synthesize metal complexes with the above mentioned ligands and with different transition metals (M = Fe, Co, Pd, Cu and Zn). It was planned to follow conventional coordination chemistry synthetic routes to prepare the new complexes and study the coordination modes of N,O-type carborane-based ligands. The variety of coordination modes of these ligands, ranging from monodentate to multidentate or as bridging ligands give rise to new opportunities to develop potential multifunctional materials ranging from finite zero dimensional molecular complexes to infinite three dimensional structures.

The third and final objective of the present work was to study the properties of the synthesized materials and the potential applications.

