

# A Prebiotic Surface Catalyzed Photochemically Activated Synthesis of Corrin Derivatives: C and D Monomers

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**Abstract:** - Alkynes such as but-2-ynimine, propyne and ethyne form weak charge-transfer,  $\eta^2$ -alkynyl complexes, with surface catalysts such as Mg.porphin in which the alkynyl group is positively charged and the porphin has a negative charge. The enthalpy changes are -0.040, -0.002 and -0.018 h, respectively. However, if the adduct is excited to a higher energy state it may migrate to form a weak charge transfer bond with the nitrogen atom of an adjacent pyrrole unit. If the catalyst, Mg.porphin accepts two adducts they may have opposite charges. The di-adduct complexes may bond leading to high energy products in which the orientation is determined by the exciting radiation. Subsequent reactions with nucleophiles such as cyanoacetylene and methyl cyanide anions may give derivatives of pyrroline that can oligomerize to tetramers that can cyclise to corrin derivatives.

The reactions have been shown to be feasible from the overall enthalpy changes in the ZKE approximation at the HF and MP2 /6-31G\* level.

**Key-Words:** Mg.porphin , but-2-ynimine, propyne, ethyne, corrin derivatives.

## 1 Introduction

Vitamin B12, cobalamin [1]. is a highly conjugated cyclic chromophoric molecule containing the corrin structure [2] chelating a cobalt ion which may be present in oxidation states 1,2 or 3. The cobalt ion may also accept coordination from deoxyadenosyl, cyanide, hydroxide ions, water and dimethylbenzimidazole [3,4]. It is an essential vitamin to prevent pernicious anaemia [5] where it acts as a cofactor to form holoenzymes from the adenosylcobalamin dependent isomerases, the methyl cobalamin dependent methyl transferases and dehalogenases [3]. In the action of the isomerases a hydrogen atom is transferred from the substrate to an adjacent atom site. In the methyl transfer reactions a methyl group coordinated to the cobalt ion is transferred to an acceptor. In anaerobic dehalogenation it facilitates reductive dehalogenation in which a bound chlorine atom forms hydrogen chloride.

The biosynthesis of the active vitamin has been achieved from the amino laevulinic acid [5]. Neither animals or plants can manufacture B12, just microorganisms [5]

From a prebiotic perspective [6] it is desirable if the reactant molecules formed spontaneously from a supposed prebiotic atmosphere to be inevitably

present. It has often been held that the atmosphere of the Earth was originally mildly reducing [5,7] implying the presence of concentrations of carbon monoxide, ammonia, water and hydrogen. It is also supposed that alkynes such as acetylene [8,9] were present as found on Titan, a moon of Saturn. It has also been demonstrated that porphin may act as a catalyst for the formation of sugars [10] and polyenes [11].

This paper proposes a model for the surface catalytic photochemically activated formation of the corrin structure from the gases, propyne, ethyne, hydrogen cyanide and hydrogen with the surface catalyst, magnesium porphin . Experimental gaseous mixture subjected to discharge have been shown to produce biomolecules [12].

## 2 Problem Formulation

The computations tabulated in this paper used the GAUSSIAN98 [13] commercial package. The standard calculations at the HF and MP2 levels including zero-point energy corrections (HF), [14], together with scaling [15], using the same basis set, 6-31G\*. are as previously published [6]. Enthalpy changes at the MP2 level not including scaled zero point energies are designated as  $\Delta H_{(MP2)}$ . The charge

[3]

transfer complexes are less stable when calculated at the Hartree Fock level [14].

If the combined energy of the products is less than the combined energy of the reactants it may show that the reaction is also likely to be spontaneous at higher temperatures. This paper uses the atomic unit of energy, the hartree [13].

$$1h = 627.5095 \text{ kcal.mol}^{-1}$$

$$1h = 4.3597482 \times 10^{-18} \text{ J}$$

### 3 Problem Solution

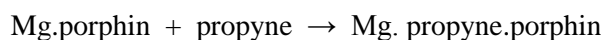
#### 3.1 Total energies (hartrees)

Molecules that are present interstitially and in planets [16] are here taken to be the initial reactant molecules: propyne, ethyne and hydrogen cyanide, where the formation of the but-2-yne nitrile and but-2-ynimine (cis) may be produced by atmospheric free radical or ionic reactions [17].

Further reactants are taken to be cyanoacetylene [16] and methyl cyanide [18], also formed atmospherically.

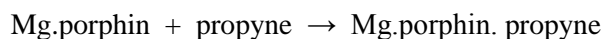
It is also assumed that in the mildly alkaline environment due to the presence of ammonia in the reducing atmosphere, the cyanoacetylene and methyl cyanide anions would exist.

Mg.porphin is a powerful catalyst able to form charge transfer complexes with a number of different kinds of molecules [19]. With propyne the Mg.porphin is positively charged (0.073).



$$\Delta H = -0.00209 \text{ h} \quad [1]$$

However, it is also possible for the propyne to migrate to bond with a pyrrole nitrogen atom to form a high energy complex [11].

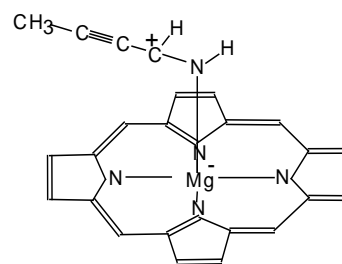
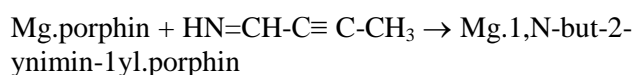


$$\Delta H = 0.01862 \text{ h} \quad [2]$$

Mg.porphin may also form an adduct with acetylene [20],

$$\Delta H_3 = -0.01807 \text{ h}$$

The catalyst also forms a weak charge transfer complex with but-2-ynimine. The ligand is positively charged (0.07) and the porphin has a negative charge.



Mg.1,N-but-2-ynimin-1-yl.porphin (cis) (1)

$$\Delta H = -0.04014 \text{ h}$$

The data for the total energies and zero point energies for the HF and MP2/6-31G\* equilibrium geometries for these molecules and others involved in the synthesis are given in Table.1.

Table 1

MP2 /6-31G\* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	MP2 hartree	ZPE (HF) hartree
Mg.1,N-but-2-ynimin-1-yl.porphin (cis) (1)	-1394.57494	0.37950
3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl $\Delta^1$ - pyrroline <sup>+1</sup> C <sub>11</sub> H <sub>12</sub> N <sub>3</sub> <sup>+</sup>		
Monomer A (2)	-585.94178	0.17352
3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl $\Delta^1$ - pyrroline <sup>+1</sup> C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> <sup>+</sup>		
Monomer B (3)	-625.12035	0.20245
3-cyanoethynyl-4-4'-dimethyl-5-methenyl $\Delta^1$ -pyrroline <sup>+1</sup> (4) Monomer C		
	-493.95240	0.17420
3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl $\Delta^1$ - pyrroline <sup>+1</sup> (5) Monomer D		
	-625.12956	0.20389
Mg.1,N-but-2-ynimin-1-yl.porphin.N-propynyl (6)	-1510.82353	0.43507
Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-propenimin-1-yl.porphin (7).		
	-1510.66357	0.43287
Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin <sup>-1</sup> (8)		
	-1679.40291	0.46707
Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin (9)		
	-1679.90396	0.47850
Mg.1,N-2-cyanoethynyl-3-3'-dimethyl-pent-N4-ynyl.porphin <sup>-1</sup> (10)		
	-1679.99718	0.47454

Mg.1,N-3-cyanoethynyl-4-4'-dimethyl-5-methynyl  
 $\Delta^1$ -NH-pyrrolin-1-yl.porphin.(11)

-1679.93372 0.46910

Mg.1,N-3-cyanoethynyl-4-4'-dimethyl-5-methenyl

$\Delta^1$ -N-pyrrolin-1-yl.porphin (12)

-1679.23304 0.47102

but-2-yne nitrile -208.25777 0.05963

but-2-ynimine -209.41044 0.08479

Mg.porphin -1185.12250 0.29262

Mg.OH.porphin<sup>-1</sup> -1260.79369 0.29802

propyne -116.24181 0.06010

ethyne -77.06679 0.02945

H-C  $\equiv$  C-CN -169.07910 0.02976

NC-C  $\equiv$  C<sup>-</sup> -168.49375 0.01711

CH<sub>3</sub>-CN -132.33825 0.04840

NC-CH<sub>2</sub><sup>-</sup> -131.70120 0.03278

H-CN -93.15894 0.01593

CH<sub>4</sub> -40.33255 0.04778

H<sub>2</sub> -1.14414 0.01059

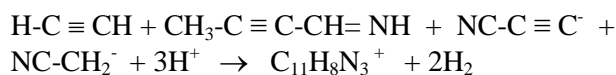
OH<sup>-</sup> -75.51314 0.00885

H<sub>2</sub>O -76.19685 0.02298

### 3.2 The overall stoichiometry for the formation of the four monomers that oligomerize to corrin derivatives.

Although Mg.porphin is here taken as the catalyst for the reaction, the overall stoichiometry for the synthesis of corrin derivatives from but-2-ynimine, propyne, ethyne, methyl cyanide and cyanoacetylene can be represented as follows, where the final hydrogenation and hydrolysis present in the vitamin B12 structure is yet to occur.

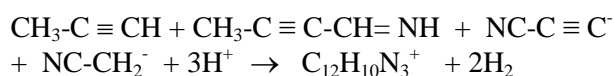
The monomer that forms ring A [2] is formed as follows:



Monomer A (2) Fig.1 [4]

$$\Delta H = -1.53068 \text{ h}$$

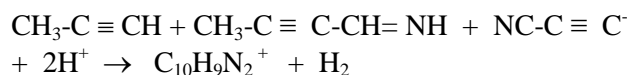
The monomer that forms ring B [2] is formed as follows:



Monomer B (3) Fig.1 [5]

$$\Delta H = -1.54041 \text{ h}$$

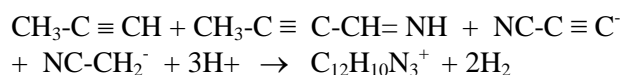
The monomer that forms ring C [2] is formed as follows:



Monomer C (4) Fig.1 [6]

$$\Delta H = -0.93026 \text{ h}$$

The monomer that forms ring D [2] is formed as follows:



Monomer D (5) Fig.1 [7]

$$\Delta H = -1.54369 \text{ h}$$

The enthalpy changes are negative indicating that there may be energetically favourable routes to the formation of each of these monomers from these reactants.

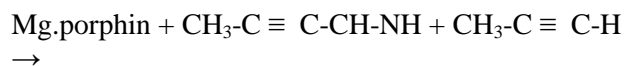
The intermediates by which the stoichiometric reactions may have occurred are as follows:

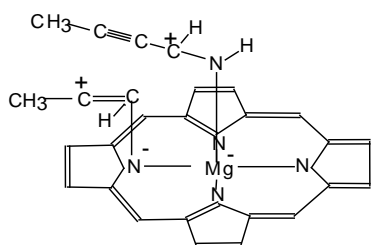
### 3.3 The Formation of monomer C.

#### 3.3.1. The formation of the Mg.1,N-but-2-ynimin-1-yl.porphin.N-propynyl

The sequence of reactions here is initially exactly the same as for the formation of the Monomer B of the corrin structure [17]

Very weak charge transfer complexes may form between but-2-ynimine and the Mg ion of the catalyst Mg.porphin, whilst propyne forms a weak van der Waals adduct centered on a pyrrole nitrogen atom. The charges on the two adducts are different. Whilst the propyne is negative sharing electrons with the pyrrole-N atom with a calculated charge of -0.013, the but-2-ynimine adduct carries a positive charge, calculated as 0.077, giving the catalyst a net positive charge 0.064. When the catalyst is excited with UV radiation an in-plane electronic transition occurs in which the magnetic vector of the radiation is perpendicular to the ring causing rotation of the positively charged adduct [11]. It is postulated that when the magnetic vector is pointing upwards towards the observer this is more effective in causing rotation than when the adduct is forced to the catalyst surface, and a high energy complex is formed, as shown,

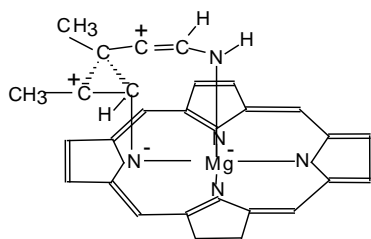




Mg.1,N-but-2-ynimin-1-yl.porphin.N-propynyl (6)  
[8]

$$\Delta H = -0.05094 \text{ h}$$

which subsequently bonds,



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-propenimin-1-yl.porphin (7).

$$\Delta H = 0.15780 \text{ h}$$

As the enthalpy change is appreciable and positive it is postulated that this occurs by electromagnetic excitation where the first excitation of these very weak complexes requires about 0.21 h.

The high energy complex is then susceptible to nucleophilic attack by numerous molecules in various sequences of reactions. Here the reactions given are those that lead to the stereospecificity for ring C depicted in Fig.1 for a corrin derivative with similar stereochemistry to that found in Vitamin B12 [2]

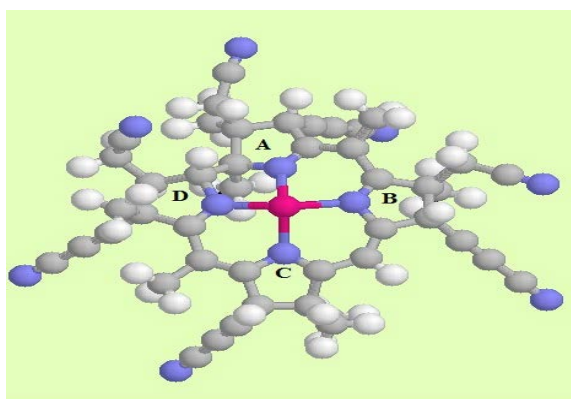
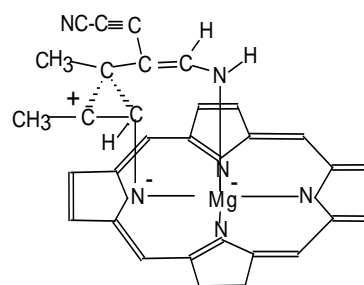
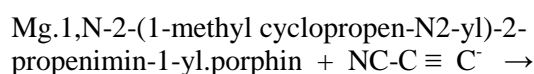


Fig.1. The designation of the corrin rings as recommended by IUPAC [2].

### 3.3.2. The formation of Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin.

The high energy complex is subject to nucleophilic reaction with the anion from cyanoacetylene,



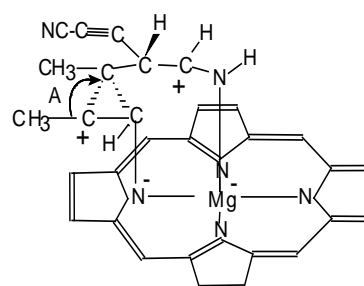
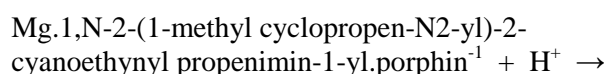
Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin<sup>-1</sup> (8)  
[9]

No activation energy is recorded for this addition.

$$\Delta H = -0.23039 \text{ h}$$

### 3.3.3. The formation of Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin.

The negatively charged adduct may easily react with a proton in an energetic reaction where it is assumed that it preferentially attacks from above the adduct surface,



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin (9)  
[10]

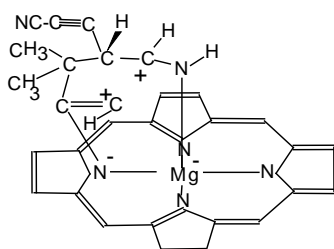
$$\Delta H = -0.49088 \text{ h}$$

No activation energy was recorded for this proton addition.

### 3.3.4. The formation of Mg.1,N-2-cyanoethynyl-3-3'-dimethyl-pent-N4-ynyl.porphin

It is postulated that a methyl transfer reaction occurs under excitation where the angle, A, structure (9), is decreased and the three membered ring is relaxed, to produce an isomer, as shown,

Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin  $\rightarrow$



Mg.1,N-2-cyanoethynyl-3,3'-dimethyl-pent-N4-nyl.porphin (10)

[11]

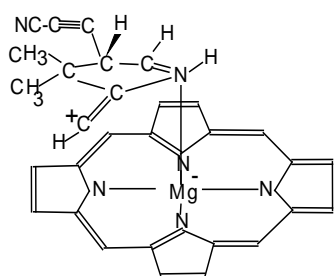
$$\Delta H = -0.09674 \text{ h}$$

The activation energy for the transfer was calculated as 0.137 h, with the reverse reaction having an activation energy of 0.221 h.

### 3.3.5. The formation of Mg.1,N-2-cyanoethynyl-3,3'-dimethyl-4-methynyl $\Delta^1$ -NH-pyrrolin-1-yl.porphin [1]

The Mg.1,N-2-cyanoethynyl-3,3'-dimethyl-pent-N4-nyl.porphin may easily cyclize,

Mg.1,N-2-cyanoethynyl-3,3'-dimethyl-pent-N4-nyl.porphin  $\rightarrow$



Mg.1,N-2-cyanoethynyl-3,3'-dimethyl-4-methynyl  $\Delta^1$ -NH-pyrrolin-1-yl.porphin (11)

[12]

The activation energy was calculated as 0.047 h, with the reverse requiring 0.017 h.

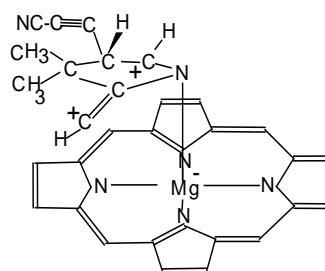
$$\Delta H = 0.05861 \text{ h}$$

### 3.3.6 The formation of Mg.1,N-2-cyanoethynyl-3,3'-dimethyl-4-methynyl $\Delta^1$ -N-pyrrolin-1-yl.porphin

The addition of a proton with Mg.1,N-2-cyanoethynyl-3,3'-dimethyl-4-methynyl  $\Delta^1$ -NH-

pyrrolin-1-yl.porphin results in the elimination of hydrogen gas in an energetically favourable reaction,

Mg.1,N-2-cyanoethynyl-3,3'-dimethyl-4-methynyl  $\Delta^1$ -NH-pyrrolin-1-yl.porphin +  $H^+ \rightarrow H_2 +$



Mg.1,N-3-cyanoethynyl-4-4'-dimethyl-5-methenyl  $\Delta^1$ -N-pyrrolin-1-yl.porphin<sup>+</sup> (12)

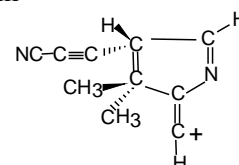
[13]

$$\Delta H = -0.43232 \text{ h}$$

### 3.3.7 The formation of 3-cyanoethynyl-4,4'-dimethyl-5-methenyl $\Delta^1$ -pyrroline<sup>+</sup>

The complex containing a weak charge transfer bond may easily dissociate to give Monomer C and the catalyst in the mildly alkaline medium.

Mg.1,N-3-cyanoethynyl-4-4'-dimethyl-5-methenyl  $\Delta^1$ -N-pyrrolin-1-yl.porphin  
 $\rightarrow$  Mg.porphin +



3-cyanoethynyl-4-4'-dimethyl-5-methenyl  $\Delta^1$ -pyrroline<sup>+</sup> (4)

[14]

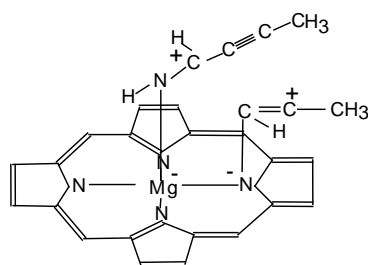
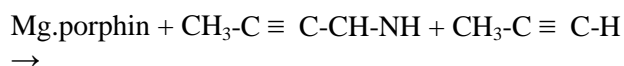
$$\Delta H = 0.15441 \text{ h}$$

## 3.4 The Formation of monomer D.

### 3.4.1. The formation of the Mg.1,N-but-2-ynimin-1-yl.porphin.N-propynyl.

Initially this follows exactly the formation of the Monomer C. A weak charge transfer complex may form between but-2-ynimine and the Mg ion of the catalyst Mg.porphin, whilst the propyne forms a weak van der Waals adduct centered on a pyrrole nitrogen atom. The charges on the two adducts are different. Whilst the propyne is marginally negative sharing electrons with the pyrrole-N atom with a calculated charge of -0.01, the but-2-ynimine adduct carries a positive charge, calculated as 0.08, giving

the catalyst a net positive charge 0.07. When the catalyst is excited with UV radiation an in-plane electronic transition occurs in which the magnetic vector of the radiation is perpendicular to the ring causing rotation of the positively charged adduct [11]. It is postulated that when the magnetic vector is pointing upwards towards the observer this is more effective in causing rotation than when the adduct is forced to the catalyst surface, and a high energy complex is formed, as shown,

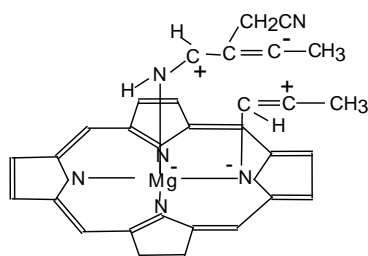
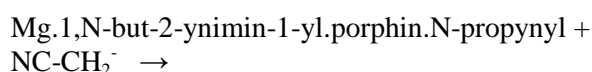


Mg.1,N-but-2-ynimin-1-yl.porphin.N-propynyl (6)  
[15]

$$\Delta H = 0.05094 \text{ h}$$

### 3.4.2. The formation of Mg.1,N-2-cyanomethanyl 2-propen-1-yl.porphin.N-propynyl<sup>-1</sup>.

The high energy di-adduct is subject to nucleophilic reaction with the anion from cyanomethane,

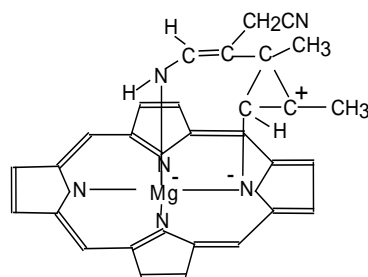


Mg.1,N-2-cyanomethanyl 2-propenimin-1-yl.porphin.N-propynyl<sup>-1</sup> (13) [16]

$$\Delta H = -0.05451 \text{ h}$$

The di-adduct then carries a negative charge, calculated as -0.845, with the N-2-cyanomethanyl 2-propenimine adduct carrying a charge of -0.818 and the propyne adduct carrying a charge of -0.027 and should rotate clockwise in the radiation

magnetic field pointing upwards when viewed from above. Subsequently it may bond, as shown,



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanomethanyl propenimin-1-yl.porphin<sup>-1</sup> (14)

$$\Delta H = 0.00789 \text{ h}$$

No activation energy is recorded for this addition. As the enthalpy change is only marginal and positive it is postulated that this occurs by electromagnetic excitation where the first excitation of these very weak complexes requires about 0.21 h. The high energy complex is then susceptible to nucleophilic attack by numerous molecules in various sequences of reactions. Here the reactions given are those that lead to the stereospecificity for ring D depicted in Fig.1 for a corrin derivative with similar stereochemistry to that found in Vitamin B12 [2]

The data for the total energies and zero point energies for the HF and MP2/6-31G\* equilibrium geometries for these molecules and others involved in the synthesis are given in Table.2.

Table 2  
MP2/6-31G\* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	MP2 hartree	ZPE (HF) hartree
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Mg.1,N-2-cyanomethanyl 2-propen-1-yl.porphin.N-propynyl<sup>-1</sup>. (13)

$$-1642.58485 \quad 0.47417$$

Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanomethanyl propenimin-1-yl.porphin<sup>-1</sup> (14)

$$-1642.57910 \quad 0.47658$$

Mg.1,N-2-(1-methyl cyclopropenyl)-2-cyanomethanyl propanimin-1-yl.porphin (15)

$$-1643.15431 \quad 0.49378$$

Mg.1,N-2-cyanoethynyl-3-cyanomethanyl-3-methyl-pent-N4-ethynyl.porphin<sup>-1</sup> (16)

-1811.65786 0.51104  
Mg.1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethynyl  $\Delta^1$ -NH-pyrrolin-1-yl.porphin<sup>-1</sup>  
(17) -1811.18208 0.51035

Mg.1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl  $\Delta^1$ -NH-pyrrolin-1-yl.porphin  
(18) -1810.80784 0.49787

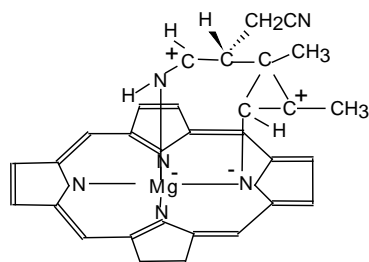
Mg.1,N-3-(2-cyanoethynyl)-4-(cyanomethanyl)-4-methyl-5-ethenyl  $\Delta^1$ -N-pyrrolin-1-yl.porphin<sup>+1</sup>  
(19) -1810.11756 0.49031

3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl  $\Delta^1$ -pyrroline<sup>+1</sup> (5)  
-625.12956 0.20389

### 3.4.3. The formation of Mg.1,N-2-(1-methyl cyclopropenyl)-2-cyanoethynyl propanimin-1-yl.porphin

The negatively charged adduct may easily react with a proton in an energetic reaction where it is assumed that it preferentially attacks from above the adduct surface,

Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin<sup>-1</sup> + H<sup>+</sup> →



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanomethanyl propanimin-1-yl.porphin (15)  
[17]

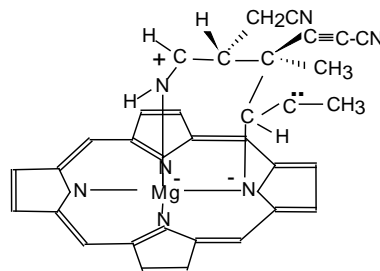
$$\Delta H = -0.55989 \text{ h}$$

No activation energy was recorded for this proton addition.

### 3.4.4. The formation of Mg.1,N-2-cyanoethynyl-3-cyanomethanyl-3-methyl-pent-N4-ethynyl.porphin

The strong nucleophile, cyanoacetylene anion can open up the complex to form the adduct, Mg.1,N-2--cyanoethynyl-3-cyanomethanyl-3-methyl-pent-N4-ynyl.porphin.

Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin + NC-C≡C<sup>-</sup> →

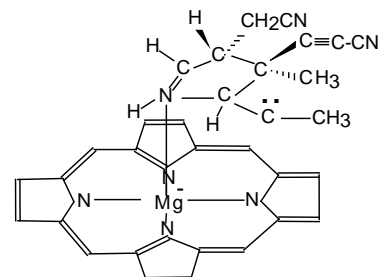


Mg.1,N-2-cyanomethanyl-3-cyanoethynyl-3-methyl-pent-N4-ethynyl.porphin<sup>-1</sup> (16)  
[18]

$$\Delta H = -0.01005 \text{ h}$$

### 3.4.5. The formation of Mg.1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethynyl $\Delta^1$ -NH-pyrrolin-1-yl.porphin.

The Mg.1,N-2-cyanomethanyl-3-cyanoethynyl-3-methyl-pent-N4-ethynyl.porphin<sup>-1</sup> may easily cyclize,



Mg.1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethynyl  $\Delta^1$ -NH-pyrrolin-1-yl.porphin<sup>-1</sup>  
(17) [19]

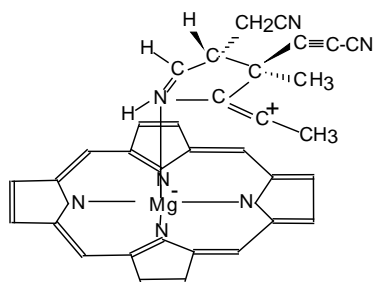
The activation energy was calculated as 0.204 h, with the ring dissociation requiring an activation of 0.195 h.

$$\Delta H = 0.00680 \text{ h}$$

### 3.4.6 The formation of Mg.1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl $\Delta^1$ -NH-pyrrolin-1-yl.porphin.

With the Mg.1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethynyl  $\Delta^1$ -NH-pyrrolin-1-yl.porphin<sup>-1</sup> the addition of a proton results in the elimination of hydrogen gas in an energetically favourable reaction,

Mg.1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl  $\Delta^1$ -NH-pyrrolin-1-yl.porphin<sup>-1</sup> + H<sup>+</sup> → H<sub>2</sub> +



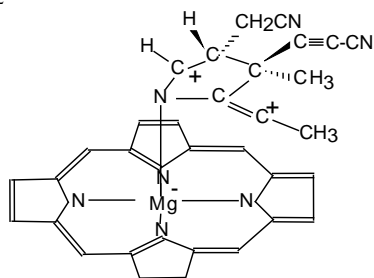
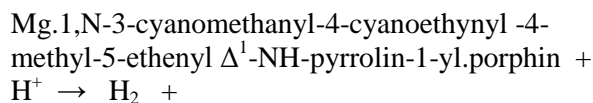
Mg,1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl  $\Delta^1$ -NH-pyrrolin-1-yl.porphin (18)

[20]

$$\Delta H = -0.30284 \text{ h}$$

### 3.4.7 The formation of Mg,1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl $\Delta^1$ -N-pyrrolin-1-yl.porphin<sup>+1</sup>

Further reaction with a proton in an energetically favourable reaction gives a stable pyrroline structure,



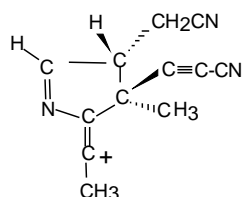
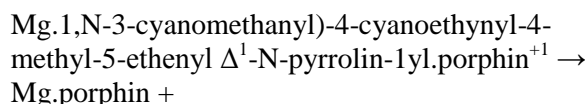
Mg,1,N-3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl  $\Delta^1$ -N-pyrrolin-1-yl.porphin<sup>+1</sup> (19)

[21]

$$\Delta H = -0.45116 \text{ h}$$

### 3.4.8 The formation of 3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl $\Delta^1$ - pyrroline<sup>+1</sup>

The complex containing a weak charge transfer bond may easily dissociate to give Monomer D and the catalyst.



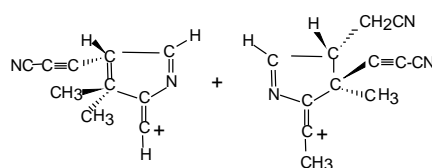
3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl  $\Delta^1$ - pyrroline<sup>+1</sup> (5)

$$\Delta H = -0.12898 \text{ h} \quad [22]$$

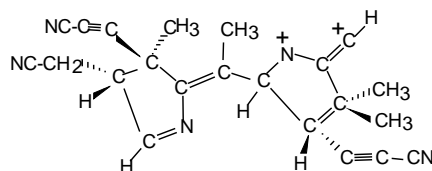
It cleaves from the catalyst in the mildly alkaline environment with the formation of Mg.OH.porphin<sup>-1</sup>.

### 4. Conclusion

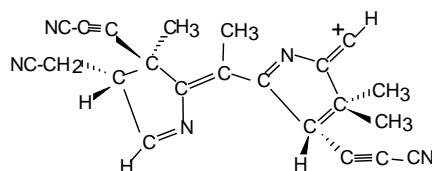
The synthesis of Monomers C and D as depicted here is predicated on the formation of weak complexes calculated as charge transfer and van der Waals, which may be orientated to form stereospecific di-adducts by the magnetic field of exciting radiation. The monomers C and D are highly reactive and may easily engage in dimerization with an activation energy of 0.065 h, as shown,



$\rightarrow$



and the formation of a dimer in the mildly alkaline solution, as shown,



1-(3-cyanoethynyl-4-4'-dimethyl-5-methenyl  $\Delta^1$ -pyrroline-2yl)-1'-(3-cyanomethanyl-4-cyanoethynyl-4-methyl- $\Delta^1$ - pyrrolin-5yl) ) -1-methyl methene<sup>+</sup>

The enthalpy change was calculated as -0.537 h. The dimer is further stabilized with ions such as  $Mg^{++}$ , as a prerequisite for the formation of corrin derivatives.

Further work at a higher accuracy may alter the values given here.



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